Monday Morning, April 23, 2018

Plenary Lecture
Room Town & Country - Session PL

Plenary Lecture

8:00am **PL-1 Predictive Synthesis and Characterization of Oxide Films with Metastable Structures***, **Gregory Rohrer**,* Carnegie Mellon University, USA
INVITED

Directed synthesis methods that access specific crystalline polymorphs are of great interest in crystal growth, materials design, and the production of useful coatings. This talk will describe how a new method, called combinatorial substrate epitaxy (CSE), can be used to understand the preferred epitaxial orientations of a wide range of heteroepitaxial structures and to fabricate various novel metastable materials. In this approach, the target compound is deposited on polished polycrystalline substrates, rather than commercial single crystals or buffer layers. It has been demonstrated that each surface grain in the polycrystalline substrate can be treated as the equivalent of a single-crystal surface in a traditional film growth experiment, therefore providing every combination of substrate orientation in a single experiment. The method has the unique advantage of not being restricted to the use of commercially available single crystals. The local structures of the growth products are analyzed using electron backscatter diffraction (EBSD). In this talk, the CSE method will be described in detail as will the analysis of EBSD data from thin film polymorphs. Examples of how the method has been used to grow metastable polymorphs will be described and a prognosis for the use of CSE for the development of new coatings will be discussed.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B5-1

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Helmut Riedl, TU Wien, Institute of Materials Science and Technology

10:00am **B5-1-1 Effect of Boron on the Mechanical Properties, especially Fracture Toughness, of TiN**, ***Rainer Hahn***, CDL-AOS at TU Wien, Austria; *M Bartosik, A Tymoszuk,* TU Wien, Austria; *P Polcik,* Plansee Composite Materials GmbH, Germany; *M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Mayrhofer,* TU Wien, Austria

Titanium Nitride (TiN) thin films pioneered the application of ceramic hard coatings on tool materials for improving the wear resistance and consequently tool lifetime. The enhancement in wear resistance strongly depends on the mechanical properties of the coating, which can be further increased by alloying strategies. Here, we present the effect of boron alloying to TiN hard coatings on their mechanical properties, with a focus on the fracture toughness (K_{IC}).

Thin films with different boron contents, ranging from 0.5 to 25 at%, were deposited using reactive, as well as non-reactive, unbalanced magnetron sputtering. The boron content and bonding characteristics (different types of B-bonds) were analysed by X-ray photoelectron spectroscopy and complemented by X-ray diffraction experiments to gather information on the structure of our hard coatings. The experiments unveil a clear increase in B-N-typed bonds with increasing boron content, resulting in a transition from fine-grained single-phase Ti(B)N (up to a B content of around 5 at%) to nanocrystalline two-phase Ti(B)N-BN structures (for contents >5 at%).

Micromechanical experiments ----------—conventional nanoindentation as well as fracture experiments— reveal hardnesses of up to 32 GPa and fracture toughness values of up to 11 MPa√m (both values include the influence of pronounced residual stresses in the coatings on Si (100) substrates) for boron contents of up to 5 at%. Higher boron contents resulted in a decrease in fracture toughness, hardness, and indentation modulus. We envision a soft, X-ray amorphous BN phase surrounding nanocrystalline TiN grains, to be responsible for this behaviour.

Based on our results we can conclude that B alloying has the potential to boost the mechanical properties of nitride based hard coating materials but only when softer BN phases are avoided, which can be controlled by carefully adapting the deposition parameters.

10:20am **B5-1-2 Evolution of Structure, Residual Stresses and Wear Resistance of Multi-layered AlTiSiN-AlCrN Coatings upon Thermal Loading Revealed by Cross-sectional X-ray Diffraction and Tribological Testing**, ***Stefan Klima***, *N Jäger, M Meindlhumer,* Montanuniversität Leoben, Austria; *H Hruby,* eifeler-Vacotec GmbH, Germany; *C Mitterer, J Keckes, R Daniel,* Montanuniversität Leoben, Austria

Multilayered nanocrystalline coatings typically differ in terms of microstructure (phase, texture, size and shape of grains), residual stresses and mechanical properties with respect to their monolithic counterparts due to specific size restrictions, altered growth conditions and effect of the interfaces. This allows an application-relevant optimization of microstructure-dependent coating properties by a specific coating architecture prepared under optimized deposition conditions. In order to understand the complex structure-stress-property relations in hierarchical nanostructured coatings, a multi-layered multi-phase AlN-based coating system was developed and studied by cross-sectional position-resolved synchrotron X-ray nanodiffraction in transmission geometry, nanoindentation and tribological testing. The specially designed coating architecture was analyzed in the as-deposited state and after thermal treatment, with a special focus on the thermo-mechanical properties and oxidation resistance. In this system, AlTiSiN and AlCrN layers were combined with a specific focus on the role of structure confinement by the multi-layered architecture for varied thicknesses of individual layer components. This approach allowed studying the effect of inherent structure (phase, texture, size and shape of grains), number of interfaces and residual stress distribution over the coating thickness on the mechanical properties and wear. Moreover, the effect of the combination of the metastable AlTiSiN, composed of cubic, hexagonal and amorphous phases, and the stable hexagonal structure of AlCrN on the development of structure, stress state and properties was studied in detail, revealing complex depth-evolutions of phases, texture, grain size and residual stresses. Furthermore, the particular coating structures of the complex multi-layered system were individually tested under various tribological conditions such as counterpart materials, annealing conditions and temperatures. The results document pronounced changes in the mechanical properties, thermal stability, residual stresses and wear resistance in the dependence of the coating architecture, which contributes to a general understanding of the structure-stress relationships in multi-layered films with various architectures and material combinations.

10:40am **B5-1-3 Plasma Tailoring for Controlled Compositional and Microstructural Evolution of TiB_2 Coatings from Magnetron Sputtering Techniques and DC Vacuum Arc**, ***Johanna Rosen***, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *N Nedfors, I Zhirkov,* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

Titanium diboride (TiB_2) is a versatile (hard) material of high potential for various thin film applications due to its combination of, e.g., high strength, high melting temperature, and high conductivity. This presentation will show paths for controlled synthesis of TiB_2 through choice of synthesis technique and drastically different (inherent) plasma properties. Starting with magnetron sputtering of TiB_x films from a TiB_2 target, it often result in highly overstoichiometric films due to differences in kinetic energy, ejection angle, and gas-phase scattering of sputtered Ti and B species. We show that the B/Ti atomic ratio can be reduced from 2.7 to 2.1 by increasing the Ar pressure from 5 mTorr to 20 mTorr, while also changing to stronger magnets in the magnetron to retain dense films of high crystal quality. High power impulse magnetron sputtering (HiPIMS) have a higher fraction of ionized sputtered species compared to regular dc magnetron sputtering, and it is possible to control the flux of ionized species by varying the pulse frequency, and hence duty cycle. This allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant. We show that the additional energy supplied during film growth in the HiPIMS process results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to ≥ 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Applying a pulsed bias in synchronous with the HiPIMS pulse, the relative fractions of B^+, Ti^+ and Ar^+ within the flux of bombarding ions can be varied. This makes it possible to tune and lower the residual stress compared to coatings deposited under bombardment of mainly Ar^+ ions. Finally, we also present results from TiB_2 synthesis based on DC vacuum arc, and a new design of cathode - anode assembly allowing a stable, reproducible, and close to fully ionized plasma flux of Ti and B. The arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

11:20am **B5-1-5 Development of Novel Gradient C-CrAlSiN Based Cathodic Arc PVD Coatings for High Speed/dry Machining Applications**, ***Puneet Chandran***, *V Krishna,* International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), India; *A VenuGopal,* NIT Warangal, India

High speed dry machining is gaining interest by the day especially with the increasing employment of difficult-to-machine materials in niche areas. The advantages associated with this process (high productivity, superior work quality) fall short during the machining of difficult materials due to the high wear rate and low thermal stability associated with conventional tools/coatings. Nanocomposite coatings have been employed in such cases in view of their multiple advantages such as enhanced hardness along with high thermal stability and excellent oxidation resistance. Although these coatings are considered to perform better than the conventional coatings, their functionality is reduced during high speed dry machining owing to the higher coefficient of friction. A lubricating (low coefficient of friction) layer/coating to overcome the high friction in between the mating surfaces is essential. A probable solution is the application of diamond like carbon coatings which are characterized by high hardness along with a low coefficient of friction. However, these films are plagued by extremely high compressive stresses, low thermal stability and poor substrate-coating adhesion. Thus, carbon doped nanocomposite coatings have been conceptualized to overcome the area where the diamond like carbon coatings have failed, rendering an advanced coating for high speed dry machining applications.

Optimized CrAlSiN nanocomposite coating and carbon incorporated CrAlSiN coating were deposited separately using the cylindrical cathodic arc PVD technique. The as deposited films were comprehensively analyzed to determine their adhesion strength, phase composition, friction coefficient, hardness and sliding wear properties. Preliminary observations revealed

that although the films did not show evidence of DLC formation (from Raman analysis) there was a considerable decrease in the coefficient of friction with carbon content. Further, an increase in the incorporation of carbon into the optimized CrAlSiN coatings led to a steep decrease in the hardness values. This result persuaded a study on developing a novel carbon based gradient coating which would retain the properties of a nanocomposite whilst supporting the nanocomposite under-layer by reducing the coefficient of friction. The performance of the coating was evaluated based on real time machining behavior during drilling and milling on EN 24 work piece. A detailed discussion on the physical, mechanical and tribological properties of the gradient carbon based CrAlSiN coatings in relation to their wear behavior during drilling and milling will be presented in the conference.

Coatings for Biomedical and Healthcare Applications
Room California - Session D1-1

Surface Coatings and Surface Modifications in Biological Environments

Moderators: Kerstin Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

10:00am **D1-1-1 Highly Porous Scaffolds on TNZT Alloys for Bone Implant Applications**, ***Samir Aouadi***, *E Blackert, S Murguia, M Kramer, S Bakkar, M Young,* University of North Texas, USA

TNZT alloys with compositions of Ti-35Nb-7Zr-5Ta are materials that are more biocompatible than the more widely used Ti-6Al-4V alloy since each of its constituent elements is biocompatible. In addition, it has the lowest Young's modulus of all the titanium-based alloys created so far (50-60 GPa). This property allows for a greater transfer of functional loads, which ultimately leads to bone growth stimulation. TNZT alloys were produced by arc melting of pure elements and were forged into rods. Oxide nano-scaffolds were grown on TNZT using the hydrothermal method to investgate the potential of these nanostructured surfaces to improve osseointegration. The alloys with and without nano-scaffolds were characterized using top-view and cross-sectional scanning electron microscopy equipped with an energy dispersive x-ray spetrometer to investigate the structure, morphology and chemistry of the resulting nanostructures. Finally, the formation of hydroxyapatitite on the modified surfaces was investigated upon immersion in simulated body fluid (SBF).

10:20am **D1-1-2 Improving Cellular Proliferation on the Ti-6Al-4V Alloy by the Formation of Crystalline Nanotubes of Titanium Oxide**, ***ItzelPamela Torres-Avila***, Instituto Politecnico Nacional-Upibi, Mexico*; E Hernández-Sánchez, J Castrejón-Flores,* Instituto politécnico Nacional-UPIBI, Mexico*; J Velazqez,* Instituto Politécnico Nacional-ESIQIE, Mexico*; R Carrera-Espinoza,* Universidad de las Américas Puebla, Mexico*; U Figueroa-López,* Tecnologico de Monterrey, Campus Estado de México, Mexico

This work is about the formation of crystalline nanotubes of titanium oxide at the surface of the Ti-6Al-4V alloy and the evaluation of their effect on the cellular proliferation. The formation of nanotubes was performed by the anodic oxidation technique. The work potential was established in 60 V. The anodizing process was performed at times of 10, 20, 30, 40 50 and 60 min, in order to evaluate the effect of treatment time on the characteristics of the nanotubes and thus, on the cellular proliferation. A mixture of ethylene glycol, water and ammonium fluoride was used as electrolytic fluid. Scanning electron microscopy (SEM) and X ray diffraction (XRD) were applied to determine the morphology and the crystalline nature of the nanotubes. SEM examination showed a well-defined matrix of nanotubes of titanium oxide with crystalline structure and diameter in the range of 60 to 80 nm. The XRD patterns showed more and more defined picks as the treatment time was increased. The results also revealed a clear influence of the treatment time on the structure of the titanium oxide nanotubes, especially on the adherence to the substrate, where the best adherence was observed with 60 min of treatment. The cellular assays showed that the cells attach to the nanotubes and proliferated.

10:40am **D1-1-3 Effects of Nb and Ti on the Corrosion and Biocompatibility Behavior of Zr-based and Fe-based Thin Film Metallic Glasses**, ***Jhong-Bo Wang***, *Y Yang,* National Taipei University of Technology, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Recently, thin film metallic glasses (TFMGs) have drawn lots of attention from researchers due to their potential applications in the biomedical fields. In this work, a series of Zr-based and Fe-based TFMGs were prepared by a pulsed DC and RF magnetron co-sputtering system. TFMGs were deposited on 316L stainless steel and P-type (100) Si wafers. For the Zr-based and Fe-based TFMG, Nb and Ti elements were added, respectively. The amorphous structures of coatings were determined by a glancing angle X-ray diffractometer. The surface and cross sectional morphologies of thin films were examined by a scanning electron microscopy (SEM). The surface roughness of thin films was explored by an atomic force microscopy (AFM). A nanoindenter, HRC-DB adhesion test were used to evaluate the hardness and adhesion properties of thin films, respectively. The bio-corrosion properties were tested by an electrochemical polarization measurements. The biocompatibility of TFMGs was examined using MG63 cell and the MTS assay. Effects of Nb and Ti addition on the corrosion resistance and biocompatibility behavior of TFMGs were discussed.

11:00am **D1-1-4 Tribological Behavior of Nanotubes Grown on Ti-35Nb Alloy by Anodization**, *A Luz,* UFPR, Brazil*;* ***Carlos Lepienski***, Universidade Tecnológica Federal do Paraná, Brazil*; C Siqueira,* Universidade Federal do Paraná, Brazil*; G Souza,* Universidade Estadual de Ponta Grossa, Brazil*; N Kuromoto,* Universidade Federal do Paraná, Brazil

β-type titanium alloys have been proposed to replace the Ti–6Al–4V alloy due to the V and Al toxicity for long term use. Such β alloys with Nb, Mo, Zr, Sn or Ta additions are considered nontoxic, presenting lower elastic modulus than other conventional biomaterials. However, the tribological behavior of Ti and its alloys are unsatisfactory, featured by high wear rates and friction coefficients that limit applications in the biomedical area. Surface treatments can be employed to improve the surface properties while maintaining the bulk properties. Nanotubes can be produced through anodization, composed of oxides with elements from the substrate, such as TiO_2. Structure and morphology of nanotubes grown on Ti and its alloys can improve the surface biocompatibility, wettability and corrosion resistance as compared to untreated materials. However, there are few studies on the tribological properties of these films. The purpose of this study was to investigate the friction coefficient and wear rate of nanotubes grown on Ti-35Nb alloy, using a linear reciprocating tribometer. Results were compared with Ti and polished Ti-35Nb alloy. Hardness and elastic modulus of the substrates were measured through instrumented indentation. The produced coatings were also characterized by X-ray diffraction, scanning electron microscopy and metallographic analysis with optical microscopy. Nanotube layers were grown in an electrolyte containing 1 M H_3PO4 + 0.8 wt.% NH_4F, at 20 V for 160 minutes. The nanotubes were annealed at 530 ºC for 3 h. The Ti-35Nb alloy comprises α and β phases. The Ti-35Nb alloy presented higher hardness (3.7 GPa) and lower elastic modulus (96 GPa) than the pure Ti, a consequence of the β phase-containing microstructure. The nanotubes exhibited random diameters and approximately 2 μm thick. The crystal structure of the nanotube layers was a mixture of TiO_2 and Nb_2O_5 oxides. Friction coefficient of the nanotube layers was in the 1.0-1.1 range, lower than that of the polished Ti-35Nb (1.3) and the Ti surfaces. Likewise, wear rate of these coatings was $(0.06 \pm 0.01).10^{-3}$ $mm^3/N.m$, which was much lower than the value obtained for Ti-35Nb alloy [$(1.66 \pm 0.13).10^{-3}$ $mm^3/N.m$]. The wear mechanisms were adhesive and abrasive on Ti and Ti-35Nb alloy. However, the surface coated by the nanotube layers disclosed nor adhesive neither abrasive characteristics, in contrast to the reference surfaces. The low wear rates suggested a good adhesion between layer and substrate.

11:20am **D1-1-5 Designing Hydrogels to Enhance Biomedical Implant Performance**, ***Stephanie Bryant***, University of Colorado, Boulder, USA, United States of America **INVITED**

The foreign body response (FBR) occurs ubiquitously to nearly all implanted non-biological materials and is characterized by fibrous encapsulation. The primary orchestrators of the FBR are macrophages, but efforts to control macrophage phenotype and subsequently the FBR have been challenging. This observation is in part due to the fact that macrophages have highly disparate functions ranging from inflammation to wound healing. It is well accepted that macrophages sense a biomaterial through the adsorbed proteins, but the nature by which adsorbed proteins mediate macrophage phenotype and ultimately the FBR remains poorly understood. While traditional efforts focused on creating 'bioinert' biomaterials as a means to prevent protein adsorption, recent evidence demonstrates that even hydrophilic materials readily adsorb proteins and elicit a FBR. This has led to a shift from 'bioinert' to 'bioactive' materials as means to control macrophages and subsequently the FBR. To this end, our group designs synthetic-based hydrogels to which bioactive molecules (e.g., extracellular matrix (ECM) analogs, small molecules, etc.) are introduced in a highly controllable and tunable manner to create tissue-like mimetic materials.

We use poly(ethylene glycol) (PEG) hydrogels as the base structural component to control the bulk properties. Proteins, glycosaminoglycans, peptides, or other small molecules that are functionalized with polymerizable groups are then tethered into the PEG. Our group has characterized the FBR to PEG hydrogels, in the absence of any bioactive signals, and demonstrated through *in vitro* and *in vivo* experiments, a robust FBR with macrophage recruitment, macrophage activation, and the formation of a fibrous capsule. Incorporating bioactivity, as simply as, a cell adhesion peptide sequence, is sufficient to attenuate the response, but not abrogate the response. Using knockout mice models, we have identified that the initial inflammatory response mediates the long-term fibrotic response suggesting that targeting the early stages of the FBR may be critical to the long-term prevention of the FBR. In addition, we have identified that prostaglandin E2, a molecule that is secreted by stem cells to control inflammation, can significantly reduce the inflammatory macrophage phenotype and the associated FBR *in vivo*. Current efforts are focused on creating biomimetic and anti-inflammatory hydrogels as a means to dynamically control macrophage phenotype at an implant surface and improve the long-term performance of implantable biomaterials.

12:00pm **D1-1-7 Fabrication and Properties of Ca, P Containing Coating on Magnesium Alloy by Micro-arc Oxidation***, **Hui Tang,*** University of Electronic Science and Technology of China, China

As a novel metallic bio-absorbable implant material, magnesium alloy has drawn tremendous interest recently. However, relatively poor corrosion resistance in an environment of physiological fluids restricts their broad applications. In this study, Ca, and P containing coating were prepared on the surface of AZ31 magnesium alloy by micro-arc oxidation. The morphologies, composition, wettability, mechanical properties and corrosion resistance of the coatings were investigated. The corrosion mechanism was studied by long-term immersion in Hank's solution. And the formation mechanism of hydroxyapatite in SBF solution was also studied by combining the ICP and SEM. The results demonstrate that the Ca, P coating could improve the corrosion resistance of magnesium alloy in Hank's solution, and increase the bioactive of the magnesium alloy. The morphologies, composition, wettability and corrosion resistance could be controlled by the composition of the electrolyte and power parameters.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room Royal Palm 4-6 - Session E2-1

Mechanical Properties and Adhesion

Moderators: Gerhard Dehm, Max-Planck Institut für Eisenforschung, Megan Cordill, Erich Schmid Institute of Materials Science, Ming-Tzer Lin, National Chung Hsing University, Taiwan

10:00am **E2-1-1 In-situ Mechanical Testing of Hierarchical and Gradient Nanostructures***, J Wardini, O Donaldson, **Timothy Rupert,*** University of California, Irvine, USA **INVITED**

Recent innovations in materials processing have enabled the creation of nanostructured materials with unique microstructures. In this work, we focus on two promising examples: (1) nanocrystalline metals with amorphous intergranular films and (2) gradient nanograined materials, where grains size is varied near a specimen's surface. Due to the limited volumes of materials that can be made on lab scales or the geometry of typical parts, it is difficult to accurately probe the mechanical properties of these materials. In this talk, we describe the use of in-situ mechanical testing in the scanning electron microscope, with the goal of measuring important properties only from the regions of interest. We focus on properties of fundamental importance, such as yield strength, strain hardening rate, ductility, and rate sensitivity, with measurements made by microtension and microcompression of very small samples. Using these results, we revisit the design of these materials, to suggest paths for improvement in the future.

10:40am **E2-1-3 Mechanical Properties of Molybdenum Incorporated β-Ga_2O_3 Nanocrystalline Films for Extreme Environment Applications***, **Anil Krishna Battu**, S Manandhar, R Chintalapalle,* University of Texas at El Paso, USA

The mechanical properties of the metal-oxide nano films are important to utilize them in extreme environmental applications. The fundamental knowledge about the mechanical behavior in relation to the microstructure and grain growth is required to predict the component life as well as performance in high temperature applications. Thin films and coatings of β-Ga_2O_3, a stable oxide of Ga, are widely used in high temperature sensors, anti-reflection coatings, and solar cells. We recently proposed and demonstrated that the life and performance of Ga coatings can be in high temperature applications by the addition of refractory metals. In this work, we performed a systematic study of the optical and mechanical properties of Mo co-doped β-Ga_2O_3 thin films. A comparative study of as-deposited and annealed samples will be presented and results will be compared to understand the effect of crystal structure, grain growth and oxidation states and how these parameters will affect the mechanical properties, such as hardness, young's modulus and durability.

11:00am **E2-1-4 Experimental Characterization and Finite Element Simulation of Damage in Thin Hard DLC Coatings***, A Choleridis,* Ecole Nationale Supérieure des Mines de St-Etienne, France*; C Héau, M Leroy,* Institut de Recherche en Ingénierie des Surfaces, Groupe HEF, France*; S Sao-Joao, G Kermouche,* Ecole Nationale Supérieure des Mines de St-Etienne, France*; C Donnet,* Université de Lyon, Université Jean Monnet, France*; **Helmut Klöcker,*** Ecole Nationale Supérieure des Mines de St-Etienne, France

While DLC coated components exhibit very little wear having a reduced friction coefficient [1], under severe conditions blistering driven in service delamination can sometimes be observed.

In the present work, first perfectly adherent DLC coatings with high compressive process induced residual stresses were deposited on a M2 steel substrate and a thin under layer.

In a second step, the coated samples were tested under severe loading conditions in a novel friction test facility. The damage induced by these conditions has been characterized by post mortem SEM and FIB observations.

Finally, the novel experimental insight in coating damage allowed modeling coating delamination at a scale defined by the substrate microstructure.

Coating delamination is preceded by intense blistering. FIB cross sections on particular blisters allow analyzing blister nucleation. Blistering occurs close to the under-layer/steel interface, inside steel. After blistering, a thin layer of substrate material is attached to the under-layer. Its thickness is maximal in the center of the blister and decreases moving to its borders. EDX analyses through several zones of this film confirmed the presence of a thin iron-layer. Cracks initiate inside the M2 steel substrate, several nanometers beneath the (M2)-(under-layer) interface. The cracks then propagate towards this interface and propagation ends with interfacial failure. Carbides lead to local crack kinking.

The influence of the local microstructure (grain size, carbide distribution) on the delamination behavior has been analyzed by a mechanical (fe-based) model. This model highlights the blister interaction.

References

[1] Christophe Donnet , Ali Erdemir Editors Tribology of Diamond-Like Carbon Films, Fundamentals and Applications, 2008, Springer, ISBN 978-0-3 G.G.

[2] S. Massl, J. Keckes, R. Pippan, Acta Materialia 55 (2007) 4835–4844

[3] Alexander M. Korsunsky, Marco Sebastiani, Edoardo Bemporad; Surface & Coatings Technology 205 (2010) 2393–2403

[4] R. Treml, D. Kozic, J. Zechner, X. Maeder, B. Sartory, H.-P. Gänser, R. Schöngrundner, J. Michler, R. Brunner, D. Kiener, Acta Materialia 103 (2016) 616–623.

New Horizons in Coatings and Thin Films

Room San Diego - Session F2-1

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Jon Tomas Gudmundsson, University of Iceland

10:00am **F2-1-1 On Recycling in High Power Impulse Sputtering Magnetrons***, **Jon Tomas Gudmundsson,*** University of Iceland, Iceland*; N Brenning, M Raadu,* KTH-Royal Institute of Technology, Sweden*; T Petty, T Minea, D Lundin,* Université Paris–Sud, France

We will discuss a framework on how to quantify and understand large discharge currents in high power impulse magnetron sputtering (HiPIMS) discharges by investigating the role of self-sputter(SS-) recycling and working gas recycling. We find that above a critical current density $J_{crit} \approx 0.2$ A/cm^2, a combination of self-sputter recycling and working gas-recycling is the general case. The relative contributions of these recycling mechanisms,

in turn, influence both the electron energy distribution and the stability of the discharge [1]. For high self-sputtering yields, above $Y_{SS} \approx 1$, the discharges become dominated by SS-recycling, contain only a few hot secondary electrons from sheath energization, and have a relatively low effective electron temperature. Here, stable plateau values of the discharge current develop during long pulses, and these values increase monotonically with the applied voltage. For low self-sputtering yields, below $Y_{SS} \approx 0.2$, the discharges operated above J_{crit} are dominated by working gas recycling, have a significant sheath energization of secondary electrons and a higher effective electron temperature, and the current evolution is generally less stable. For intermediate values of Y_{SS} the discharge character gradually shifts between these two types. In addition, these new insights on ion recycling have been applied to a series of selected sputter materials. For high currents a discharge with Al target develops almost pure self-sputter recycling, while a discharge with Ti target exhibits close to a 50/50 combination of self-sputter recycling and working gas-recycling [2]. However, if the Ti target is operated in a reactive Ar/O_2 gas mixture, it is found that working gas-recycling is dominating [1] and that the Ar^+-ions contribute almost solely to the discharge current [3].

[1] N. Brenning et al. Plasma Sources Sci. Technol. (submitted 2017)

[2] C. Huo et al., J. Phys. D: Appl. Phys. 50 354003 (2017).

[3] J. T. Gudmundsson et al. Plasma Sources Sci. Technol. 25, 065004 (2016).

10:20am **F2-1-2 Electron Density at the Sheath Edge of a HiPIMS Plasma***, A Hecimovic,* ***Julian Held****, V Schulz-von der Gathen, W Breilmann, C Maszl, A von Keudell,* Ruhr-Universität Bochum, Germany

In High power impulse magnetron sputtering (HiPIMS) a magnetron discharge is operated with short, high-voltage pulses with a length in the order of 100 µs at power densities of several kW/cm^2, creating a highly dense plasma. At high discharge currents, the plasma is not homogeneous but is instead organized into distinct zones of high plasma emission which rotate in ExB direction with velocities of about 10 km/s. The strong emission indicates an elevated electron density inside those so called "spokes". Up to now, no measurement of the electron density inside the spokes has been performed. In this contribution, small inserts in the target surface were used to probe the local current density. Simple sheath theory was then applied to derive the electron density at the sheath edge. The electron density was found to be a few 10^{20} m^{-3}. The electron density inside the spokes was about 25% higher than in the plasma between the spokes.

10:40am **F2-1-3 Spatially Resolved Investigation of Transport and Redeposition Processes during HiPIMS by Means of Optical Diagnostics and In-vacuum XPS Analysis of Magnetron Targets***, Sascha Monje, V Layes, A von Keudell,* Ruhr-University Bochum, Germany*; T de los Arcos,* University Paderborn, Germany*; V Schulz-von der Gathen, C Corbella,* Ruhr-University Bochum, Germany

The distribution of redeposited species and their oxidation states were evaluated with in-vacuum X-ray photoelectron spectroscopy (XPS) of magnetron targets after reactive and non-reactive high power impulse magnetron sputtering (HiPIMS). The investigation was performed for various metal targets (all circular with 50 mm diameter). In addition to regular targets, 'composite' targets were used which are made of a regular metal target, where a second cylindrical shaped metal insert is located in the racetrack center. The insert of these targets acts as a marker for the species transport in the plasma.

The HiPiMS discharge was used at several power conditions and was characterized with a fast imaging CCD-camera as well as optical emission spectroscopy (OES). The target surface composition was evaluated with XPS after an in-vacuo transfer to an UHV chamber.

With the characterization of the plasma on one hand and the redistribution of material on the other hand, it was possible to connect the transport and the discharge behavior. It was found that the lateral transport and redeposition of species are influenced by the appearance of spokes. Furthermore, a correlation between oxidation state and the local surface condition has been found.

11:00am **F2-1-4 Time-resolved Ion Energy and Charge Distributions in Pulsed Cathodic Arc Plasmas of Nb-Al Cathodes in High Vacuum.***, Siegfried Zoehrer,* Montanuniversität Leoben, Austria*; A Anders,* Lawrence Berkeley National Laboratory, USA, and now at Leibniz Institute of Surface Engineering (IOM), Germany*; R Franz,* Montanuniversität Leoben, Austria

Cathodic arcs are utilized in industry for a wide variety of applications. For instance, to synthesize functional thin films and coatings, to form energetic metal ion beams for ion implantation, or in high current switches. Although there has been tremendous progress in the last decades, the physics responsible for the observed plasma properties are still a matter of dispute. That is particularly the case for multi-element cathodes, which can play an essential role in all given examples. An often overlooked criterion, especially in DC arc plasma analysis, is the typically occurring neutral background of metal atoms in cathodic arcs. It perturbs initial ion energy and charge distributions, which makes it difficult to get information of the near-cathode plasma and also to relate effects to the cathode composition. Therefore, we use a recently developed method to record time-resolved ion charge state and energy distributions in pulsed vacuum arc plasmas from Nb-Al cathodes. This model system consists out of three different Nb-Al compositions, as well as pure Nb and Al cathodes. The results visualize ion detections of 600 µs plasma pulses, extracted 0.27 m from the cathode resolved in energy and time. They show a heavy influence of neutrals on ion charge state fractions and, to a lesser extent, on ion velocity distributions, which can be observed in the time evolution of these properties. Subsequently, fundamental hypotheses applying to multi-element cathodes, like the „velocity rule“ or the „cohesive energy rule“ are tested on their applicability to early and late stages of the pulse. The results also show a strong material dependency, which appears for initial as well as saturated ion charge states and velocities. That leads to a quite different behavior for single-element cathodes and Nb-rich/Al-rich multi-element cathodes, where the latter generally show lower velocities and less multiply charged Nb ions. Apart from their fundamental character, these findings can be useful for optimizing or designing plasma properties for applications by actively utilizing effects on ion distributions caused by multi-element cathode materials and charge exchange with neutrals.

11:20am **F2-1-5 Investigations on the Substrate Bias Influence on Reactive High Performance Plasmas***, K Bobzin, T Brögelmann, N Kruppe,* ***Martin Engels****,* Surface Engineering Institute - RWTH Aachen University, Germany

High performance plasma processes are subject of several studies. For the high power pulse magnetron sputtering (HPPMS) and hybrid processes composed of HPPMS and direct current magnetron sputtering (dcMS), respectively, investigations regarding correlations between plasma and coating properties and the process parameters have been carried out. These investigations especially focus on the HPPMS pulse parameters frequency f and pulse-on-time t_{on}, the power density at the target and the process gas pressure. However, another important aspect with respect to industrial coating processes is the substrate bias, which is used to accelerate ionized coating forming species to the substrate. This acceleration results in dense and homogeneous coatings due to subplantation of these species into the coating. In order to understand this mechanism, the correlation of substrate-sided plasma properties and the resulting coating properties is a reasonable approach. Nevertheless, it is complicated to implement substrate-sided plasma diagnostics which are closely adapted to industrial coating processes using substrate bias. Hence, the present work focuses on strategies to conduct quantifiable investigations on the high performance plasma properties using substrate bias. These investigations were conducted for reactive HPPMS and dcMS/HPPMS (Cr,Al)N and (Cr,Al)ON processes. The coating systems were chosen, since they are widely used as protective coatings for many tool applications. The strategies were developed for the plasma diagnostics optical emission spectroscopy, Langmuir probe and energy resolved mass spectroscopy in an industrial scale coating unit. A varying substrate bias with values from $U_B = 0$ V to $U_B = -250$ V was used to validate the developed methodology. The results on the substrate-sided plasma properties like the chemical composition, ionization or Debye sheath thickness were correlated with (Cr,Al)N and (Cr,Al)ON coating properties, i.e. the morphology by scanning electron microscopy, the chemical composition by means of glow discharge optical emission spectroscopy, residual stress by means of cantilever sensor chips as well as the universal hardness and the indentation modulus by nanoindentation. The correlation was conducted using an artificial neural network (ANN). With the developed methodology it was possible to identify significantly changing plasma properties at the substrate side when varying the substrate bias. The correlating coatings properties and the output data of the ANN were used to validate the methodology for the analysis of industrial coating processes.

11:40am **F2-1-6 The Impact of a Positive Pulse in HIPIMS Films***, Jason Hrebik,* Kurt J. Lesker Company, USA

HIPIMS technology is on the rise and starting to be qualified in more and more applications in the thin film coating industry. Low power HIPIMS options have enabled more R&D with the technology and as a result, new ways of utilizing and optimizing the technology has been found and published.

Test data will be presented showing various performance advantages of applying a positive pulse (reversing the voltage on the target) during HIPIMS applications. During HIPIMS applications a negative pulse at extremely high densities is applied to the target creating a highly ionized plasma at the target surface. Applying a positive pulse prior to the negative pulse extinguishing extends the plasma and repels metal ions that have not recirculated yet toward the substrate. As a result, higher deposition rates, higher ion fraction, denser films, and less film stress is achieved. In addition, the positive pulse option has a significant effect on reactive coating application in that the positive pulse neutralizes the target resulting in fewer arcs, minimizing the disappearing anode effect.

Data will show that the increase in sputtering rate as a result is approximately 15%. Increasing voltage also has a positive impact on the rate. In addition, the higher density and reduced film stress will be shown in provided performance data.

Parameters can be adjusted to optimize performance for various process requirements such as Height of Pulse, Width of Pulse, and Delay of Pulse. This is a key feature of the technology due to the fact that there are variable requirements based on the application that may need to be tuned and altered. Examples of how these changes can alter performance will be presented.

Surface Engineering - Applied Research and Industrial Applications

Room Sunset - Session G4

Pre-/Post-Treatment and Duplex Technology

Moderators: Hiroshi Tamagaki, NIRO (The New Industry Research Organization), Wan-Yu Wu, Da-Yeh University, Chris Stoessel, Eastman Chemical Company, Inc., USA

10:00am **G4-1 Mechanical Pretreatment before Electroplating of Aluminium Alloy AlSi12***, E Uhlmann,* ***Robert Jaczkowski,*** Technische Universität Berlin, Germany

Electroplating is a coating process which is used to increase the durability of workpieces or to change their appearance. To form a high adhesive bonding between the coating and the workpiece, its surface has to meet certain requirements achieved by a comprehensive pretreatment. The conventional pretreatment process chain consists of different steps to increase the roughness and the surface tension of the workpieces. For this process chain chemicals are used, which are harmful to the environment and health, besides their high costs.

The complexity of the pretreatment and coating process chain differs depending on the used workpiece material. Particularly challenging to coat are Aluminium-Silicon alloys. During the conventional pretreatment of these casting alloys, the Silicon phase enriches on the surface of the workpieces and has to be removed in an additional process step using nitric acid.

This study compares alternative mechanical pretreatment processes for AlSi12–workpieces prior to electroplating. The investigated processes are conventional grinding, double face grinding with planetary kinematics, lapping and dry ice blasting. Subsequent to the structuring, the workpieces are cleaned by carbon dioxide snow blasting. The investigation of the different surface structures and their properties, like roughness, surface tension and wetting behaviour, allowed the determination of their impact on the adhesive strength of the coating by empirical modelling.

By structuring the surfaces of the workpieces they could be coated by electroplating. As a result, the chemicals used in the conventional pretreatment could be substituted. Especially the creation of surfaces, which could be wetted homogenously, showed a satisfactory adhesive strength of the applied coatings. Concluding the study, a comparison of the economic performance of the mechanical and conventional pretreatment processes is created, which confirms the profitability of the mechanical pretreatment for small batch sizes.

10:20am **G4-2 Microstructure Characterization and Mechanical Properties of Gradient AlCrSiN hard Coatings Using Ternary Alloy Targets***, Y Chang,* ***Liang-Chan Chao,*** National Formosa University, Taiwan

Transition metal nitride coatings based on Cr and Al, such as CrN and CrAlN have been attracting great interest for industrial applications as protective coating materials due to their high hardness, impact resistance and thermal stability. CrAlN coatings show high hardness and high thermal stability together with excellent oxidation resistance. However, the properties of the CrAlN coatings may be further improved by addition of Si. The addition of Si suppresses the grain growth and refines it. In this study, AlCrN and AlCrSiN coatings were deposited onto high-speed steels and tungsten carbide tools using AlCr and ternary AlCrSi alloy targets in a Cathodic-arc evaporation (CAE) system. During the coating process of gradient AlCrSiN, CrN and AlCrN were deposited as interlayers to enhance adhesion strength between the coatings and substrates. By controlling the different negative bias voltages and cathode currents, the AlCrSiN via compositional grading and plasma etching possessed different microstructures and mechanical properties. The microstructure of the deposited coatings were investigated by field emission scanning electron microscope (FE-SEM) and field emission gun high resolution transmission electron microscope (FEG-HRTEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS), Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the films. Mechanical properties, such as the hardness and young's modulus, were measured by means of nanoindention. The adhesion strength of the coatings was evaluated by a standard Rockwell indentation test. A ball-on-disc wear test was conducted to evaluate the tribological properties of the deposited coatings. In order to evaluate the impact fatigue behavior of the coated samples, an impact test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. The design of AlCrSiN coatings were anticipated to increase the hardness, toughness, thermal stability and impact resistance by optimizing the coating architecture.

10:40am **G4-3 Integrated Shot Peening, Plasma Nitriding and Gradient PVD TiAlSiN Coating on AISI H13 Molds for Al Die Casting***, Venice Mascariñas,* University of the Philippines, Philippines*; D Quinto,* Beta Nanocoating Philippines Inc., Philippines*; A Salvador,* University of the Philippines, Philippines

Surface engineering that combines processes of a) external shot peening b) plasma nitriding and c) PVD coating – b) and c) comprising duplex treatment done in a continuous process in a commercial PVD cathodic arc machine – has proven to significantly improve the service lifetime of AISI H13 steel molds used for aluminum die casting. Microhardness profiles measured across a spherical taper section (calotte scar) gave a hardness of 2900 $HV_{0.05}$ for the 5 µm TiAlSiN-based multilayer coating while the hardness of the substrate gradually decreased from 1300 $HV_{0.05}$ at the surface across the 40 µm nitrided depth to 600 $HV_{0.05}$ of the base steel. XRD, SEM-EDS analyses confirmed the presence of $Fe_{2-3}N$ and CrN phases within the nitrided diffusion layer of the H13 steel. Shot peening effected by alumina particle microblasting resulted in enhanced nitriding. Rockwell indentation tests at different loads were utilized to compare the adhesion of TiAlSiN coating on the plasma nitrided and non-nitrided H13 samples. Coating removal along circumferential cracks was observed on the non-nitrided sample at 100 kg and 150 kg loads compared to no coating removal on the duplex-treated H13 steel at these loads. The mechanisms of performance improvement of duplex treated H13 molds subjected to thermal fatigue and tribological wear can thus be attributed to the synergies of 1) a high-temperature wear-resistant hard coating, 2) a nitrided layer of increased hardness and in compressive residual stress that inhibits cracking and gives higher load support to the coating against plastic deformation and delamination, and 3) prior shot-peening that enhances nitrogen diffusion during plasma nitriding.

11:00am **G4-4 Effect of Nano-penning Surface Texturing on Self-clean Function***, Nicolas Coniglio,* Arts et Métiers ParisTech d'Aix-en-Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; S Mezghani,* Arts et Métiers ParisTech de Châlons-en-Champagne, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; M El Mansori,* Arts et Métiers ParisTech d'Aix en Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; J Cabrero,* Saint Gobain, CREE, France

Surface texturation at micro and meso scales play an important role in applications where cosmetic, aesthetic and clean functionalities are specified. We are hence dealing with a multiscale surface, in which texturing and texture have a larger influence because they are scaled differently. In this research paper, an experimental method is illustrated to highlight the important effect on the anti-fingerprinting performance (i.e. surface hydrophobicity) rated in term of surface wettability. We examine first, in detail, the wetting response of surfaces textured on aluminum alloy 6063 plates using nano-peening with a range of processing parameters. Roughness was measured by atomic force microscopy (AFM) over a 100 x 100 µm² surface. In addition, the surface wettability was quantified by measuring the contact angles of different liquids using the sessile drop method according to the norm AFNOR EN 828. The calculation takes into

account the wetting behavior of the textured surfaces at different scales. A correlation was made between the micro-scale roughness and the macro-scale apparent solid surface energy.

11:20am **G4-5 Hard Coating and Surface ModificationTechnologies for Piston Ring***, **Hideaki Kamiyama,*** Nippon Piston Ring Co., Ltd., Japan **INVITED**

The technology that achieves abrasion resistance and low friction is essential for improving the product features and the added value of slide members, which are used under severe conditions such as in a high-temperature and high-speed environment. Typically, abrasion resistance and low friction are achieved with the use of the deposition technique, which involves coating of a material surface with a hard coating, and/or the modification technique, which hardens the material surface itself.

A piston ring is an engine component fitted into the groove cut in a piston (piston groove), and moves in a reciprocating motion with the piston inside a cylinder. Specifically, a piston ring has two different surfaces: a surface that contacts the cylinder (peripheral surface), and a surface that contacts the piston (slide faces, or inside surface). These surfaces contact different materials, and different functions are required for these surfaces. It is accordingly very important to have possession of not one but many surface treatment techniques.

The deposition technique used for piston rings often uses chrome plating by a wet process, and CrN, and TiN coating by a dry process (Arc Ion Plating, AIP). Gas nitriding and salt bath nitriding are two processes commonly used for surface modification. Though the deposition and surface modification techniques are often used by themselves, these techniques are also used in combination depending on engine specifications.

In this lecture, we introduce a technology based on both deposition and surface modification, along with the recent composite technology.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B5-2

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Helmut Riedl, TU Wien, Institute of Materials Science and Technology

1:30pm **B5-2-1 Mechanical and Optical Properties of Nanoscale Transparent Metal Oxide Multilayers**, ***Chelsea Appleget***, *A Hodge,* University of Southern California, USA

Optical multilayers are material coatings composed of nanoscale metal oxide layers arranged to alter the way in which the material reflects and transmits light. Optical multilayer coatings can be designed to have virtually any reflectance or transmittance characteristics by tuning layer thicknesses and layer material properties such as index of refraction and film density. These multilayers are promising materials because they offer extraordinary strength, hardness, heat resistance, and most importantly, transparency in both the UV-Vis and NIR wavelengths, which traditionally used silicate glass lacks.

In this work, synthesis of optical multilayers via magnetron sputtering, mechanical properties, residual stresses, and optical properties are discussed. Layer composition, synthesis parameters, and layer thicknesses in these multilayers are examined to tune both mechanical and transmittance in the UV-Vis and NIR wavelengths. The result is further understanding of the relationship between mechanical and optical properties in nanoscale metal oxide multilayers.

1:50pm **B5-2-2 Structure and Properties of Nanocluster Composite Arc Coatings for Hot Die Forging**, ***Marcus Morstein***, *T Schär, J Wehrs,* PLATIT AG Advanced Coating Systems, Switzerland; *M Colliander,* Chalmers University of Technology, Sweden; *J Best,* University of New South Wales, Australia; *M Polyakov, J Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

This contribution outlines recent progress made in designing, characterizing and applying nanostructured PVD multilayer coatings for drop forging of steel parts at about 1300°C.

Hot forging is an efficient, near-net shape process that imparts high strength and reliability to parts made from a wide range of metals and alloys. The economically most important forging processes are commonly run using gas or pulsed plasma (PPN) nitrided hot working steel dies which are hard chrome plated. Electrochemical hard chrome plating, based on Cr(VI), will however soon be banned by European Union and U.S. laws, therefore a viable PVD alternative is urgently being looked for.

In hot forging of steels, the severe mechanical impact and thermal cycling caused by the intermittent contact with the hot ingot, combined with a high abrasive wear, require coatings of good thermal resistance, high thickness, and sufficient energy-absorbing properties. Such coatings were deposited using the high-capacity industrial coating unit π^{1511}, equipped with a combination of cylindrical rotating and planar arc cathodes. An advanced multilayer concept, consisting of alternating nanostructured AlCrTiN- and CrN-based sublayers has been developed, where metallic nanoclusters were embedded into the CrN-based matrix. While the thick Al-rich AlCrTiN sublayers provide good high-temperature anti-wear properties and do act as a thermal barrier, the energy-absorbing CrN-metal composite sublayers reduce the intrinsic coating stress and improve coating compliance, thus allowing for the use of a thick coatings even for this high impact stress application.

Micro- and nanostructure of the multiphase coatings were investigated by SEM-FIB, TEM and atom probe tomography (APT), and the internal stress was analyzed by X-ray diffraction methods. Coating compliance on electro-slag remelted (ESR) grade, plasma-nitrided hot-working tool steel was investigated by high-load impact testing. In addition, nanomechanical tests were carried out for various CrN-metal sublayer types by means of micro-pillar compression.

In hot forging field tests, the optimized nanocluster composite PVD coating system met or exceeded the tool life time of reference hard chrome coated tools. The most common failure mechanism was substrate steel cracking and subsequent loss of coating, at which point the exposed substrate started to be severely worn and thermally attacked.

2:10pm **B5-2-3 New Insights in High Temperature Properties and Oxidation Behaviour of AlCrSi$_x$N Coatings**, ***Nikolaus Jäger***, *S Klima, M Meindlhumer,* Montanuniversität Leoben, Austria; *H Hruby,* eifeler-Vacotec GmbH, Germany; *C Mitterer, J Keckes, R Daniel,* Montanuniversität Leoben, Austria

Hard protective coatings are widely used to protect tools for numerous machining and forming applications. The requirements on the coating properties permanently rise due to the demand of their use under extreme conditions, such as for high-speed machining and dry cutting of hard-to-cut materials. Increasing loads and temperatures in the contact area between tool and work piece create severe challenges with respect to thermal stability and oxidation resistance, claiming for advanced hard coatings suitable for operation temperatures exceeding 1000°C. A solid understanding of the diffusional mechanisms resulting in oxidation and phase transformation of metastable phases is thus the basis to establish strategies for improved high-temperature behaviour of the protective coatings. In order to understand these mechanisms, thermogravimetry and differential scanning calorimetry were used to study the thermal stability and oxidation mechanism during annealing of arc evaporated AlCrSiN coatings with varying Si-content. Furthermore, synchrotron X-ray diffraction in Ar atmosphere was used for in-situ investigation of the high-temperature behaviour at temperatures up to 1100 °C. The results reveal the microstructural evolution, phase transformations and development of residual stresses during thermal loading, and show the positive impact of the Si-content. Additionally, a position resolved synchrotron X-ray nano-diffraction experiment was performed to study the formation of an oxide scale and the development of the microstructure and residual stresses of the $Al_{63}Cr_{27}Si_{10}N$ coating across its thickness. Based on the results of this study, strategies to ensure an increased high-temperature stability and enhanced oxidation resistance of the coatings will be proposed to improve operation performance of the coated tool.

2:30pm **B5-2-4 Magnetron Sputtered High-temperature Hf-B-Si-X-C-N (X = Y, Ho, Mo) Films with Controlled Optical Transparency and Electrical Conductivity**, ***Michal Prochazka***, *V Simova, J Vlček, M Kotrlova, R Čerstvý, J Houska,* University of West Bohemia, Czech Republic

This work focuses on the effect of yttrium, holmium and molybdenum addition into hard and thermally stable Hf-B-Si-C-N films [1] in order to improve their optical transparency or electrical conductivity. The combination of the sufficiently high hardness, high thermal stability in air and optical transparency or electrical conductivity opens up a new scope of applications involving high-temperature protection of electronic and optical elements or capacitive pressure and tip clearance sensors for severe oxidation environments.

Hf-B-Si-X-C-N films were deposited onto Si(100), SiC and glass substrates using pulsed magnetron co-sputtering of a single B_4C-Hf–Si-X target (at a fixed 15% Hf fraction and a varying Si + X fraction in the target erosion area) in Ar + N_2 gas mixtures at the N_2 fraction of 15% and 25%. A planar unbalanced magnetron (127 × 254 mm^2 target) was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with a fixed voltage pulse length of 50 μs (duty cycle of 50%). The total pressure was 0.5 Pa and the substrate temperature was adjusted to 450 °C during the deposition on the substrates at a floating potential.

All Hf-B-Si-X-C-N films possessed a sufficiently high hardness (close to 20 GPa), low compressive stress, high elastic recovery and high oxidation resistance in air at elevated temperatures (above 1000 °C). Addition of Y and Ho into the Hf-B-Si-C-N films prepared at the 25% N_2 fraction in the gas mixture resulted in enhancement of the optical transparency. Addition of Mo into the Hf-B-Si-C-N films prepared at the 15% N_2 fraction in the gas mixture led to an increase in the electrical conductivity.

[1] V. Simova, J. Vlcek, S. Zuzjakova, J. Houska, Y. Shen, J. Jiang, E. I. Meletis, V. Perina, Magnetron sputtered Hf-B-Si-C-N films with controlled electrical conductivity and optical transparency, and with ultrahigh oxidation resistance, Thin Solid Films (submitted).

2:50pm **B5-2-5 Holistic Design of Multifunctional Nitrides, Oxides, and Oxynitrides**, ***Denis Music***, *J Schneider,* RWTH Aachen University, Germany **INVITED**

Research fields are commonly congregated around key physical and chemical properties, but often correlative approaches are lacking. Here, we discuss density functional theory aspects of isostructural cubic phases M-Al-O-N (M = Ti, Cr, Nb). Besides considering hardness, a design methodology for hard coatings must include additional physical and chemical properties, such as thermal conductivity, as well as interaction

with environment. In the case of M = Ti (TiAlN), atomic scale understanding of the phase stability, formation of defects and interfaces, enhancement of toughness, initial stages of oxidation, including formation of oxynitrides, and interaction with molten polymers are investigated. The second system (M = Cr, CrAlN) is discussed in terms of a plasma-surface model. This plasma-surface model relates plasma energetics with film composition, crystal structure, mass density, stress state, and elastic properties. It is predicted that N Frenkel pairs form during growth due to high-energy ion irradiation. Based on stress-induced fluctuations of Young's modulus, we are able to explain the extensive variation of the reported data from literature. The third coating discussed here (M = Nb, NbO) is a promising thermoelectric oxide. Its thermoelectric properties can be enhanced by filling vacant sites with N and forming amorphous and multiplayer coatings. Even though transport properties are central in designing efficient thermoelectrics, mechanical properties should also be considered to minimize their thermal fatigue during multiple heating/cooling cycles. Based on the elastic response, this system can be perceived as ductile and resistant to thermal fatigue. Only by applying holistic approach, where correlative treatment of many properties and phenomena occurring at different scales ranging from nanoscale to continuum as well as explicitly including plasma-surface and environmental interactions, it is possible to design novel materials for specific applications.

3:30pm **B5-2-7 Improved Mechanical Properties and Thermal Stability of Ti-Al-N through Alloying with La-borides**, ***Hidetoshi Asanuma,*** Mitsubishi Materials Corporation, Austria*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; F Klimashin, H Riedl, P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

After discovering the positive effect of Al on many properties (such as oxidation resistance) of Ti–N in 1986, Ti–Al–N hard coatings quickly conquered the market for protective coatings. The progress made in research provides a wealth of variations, such as alloyed Ti–Al–N. Just recently we showed the enormous improvement in deposition rate, mechanical strength, and thermal stability of Ti–Al–N when using Ce-alloyed Ti-Al composite targets. Here, we further follow this concept by studying coatings, developed by sputtering a 2% LaB_6 alloyed $Ti_{0.50}Al_{0.50}$ composite target in a mixed Ar/N_2 atmosphere.

We achieved a dramatic increase in film growth rate from 4.8 to 8.4 µm/h when sputtering a $Ti_{0.49}Al_{0.49}(LaB_6)_{0.02}$ instead of a $Ti_{0.50}Al_{0.50}$ target, while keeping all other deposition parameters unchanged. Due to the different poisoning behavior of Ti and Al, the Al-fractions of our coatings ($Ti_{0.42}Al_{0.58}N$ and $Ti_{0.42}Al_{0.56}La_{0.02}$–B–N) is higher as that of the respective target. Furthermore, the hardness increased from 34 to 40 GPa, the maximum annealing temperature (before a significant hardness reduction sets in) increased from 800 to 1100 °C, and also the oxidation resistance was significantly improved. After exposure to ambient air at 950 °C for 1 h the oxide scale thickness is only 0.50 µm on our Ti Al La –B–N coatings, whereas the Ti Al N coatings were already fully oxidized. The results obtained even outperform the already excellent properties of Ce-alloyed Ti–Al–N.

Based on our results we can conclude, that the addition of 2% LaB_6 to $Ti_{0.5}Al_{0.5}$ composite targets, not only leads to coatings with significantly improved mechanical properties and thermal stability, but also boosts the deposition rate.

3:50pm **B5-2-8 Thermal Evolution of Nanometallic Multilayers**, ***J. Sebastian Riano Z.,*** *A Hodge,* University of Southern California, USA

Although nanocrystalline thin films have interesting mechanical properties, they usually have low thermal stability due to their high density of interfaces which act as channels for diffusion and drive grain growth. The application of nanocrystalline coatings is usually limited to temperatures below half the melting point of the constituent metals. At higher temperatures, several processes cause deterioration of the nanograin structure, which results in degradation of the exceptional properties of the film. Therefore, to expand the usage of nanocrystalline coatings, it is imperative to enhance their thermal stability by controlling the microstructural transformations that could lead to grain growth.

In this talk, we will show the thermal evolution of nanometallic multilayers (NMMs) with the goal of elucidating on the microstructural transitions that occur during annealing; in turn, these findings will allow for a better understating of possible paths that could aid thermal stabilization. NMMs are nanostructured thin films that can be tailored to control the grain size and the local composition. Thus, NMMs configurations that favor selected kinetic paths were selected to resolve microstructures during thermal transitions. In this study, Hf-Ti and Mo-Au NMMs, deposited by magnetron sputtering, were annealed at critical temperatures identified using DSC scans. The heat-treated samples were characterized by TEM and EDS techniques. The results provide insight into the mechanisms controlling the thermal evolution of nanocrystalline thin films.

4:10pm **B5-2-9 Nanostructured TiAlN/TaN Multilayer Coatings Deposited by DC Magnetron Sputtering: Effect of Bilayer Period**, ***Elbert Contreras,*** *M Gómez,* Universidad de Antioquia, Colombia

TiAlN have been one of the most protective coatings used in the industry due to their excellent mechanical and thermal properties; in the same way TaN have been a great alternative to the conventional Me-N (Me: Ti, Al, Cr), showing a high hardness, chemical stability, excellent corrosion and thermal resistance. The constant search by development coatings with higher properties opened the doors to the research these monolayer coatings in nanostructured multilayers configuration, in order to improve, even more, their mechanical, tribological and heat resistant properties. In this research, nanostructured TiAlN/TaN multilayer coatings were deposited onto AISI H13 steel substrates using a DC UBMS, a power density of 3.4 W/cm^2 was applied at both TiAl (50-50 wt.%) and Ta (99.9 wt.%) targets. A N_2 gas flow of 7 sccm and Ar gas flow of 30 sccm was; the working pressure was 0.5 Pa, deposition temperature was 523 °K and a fixed bias voltage of -100V. In order to varying the bilayer period a Variable Frequency Drive (VFD) was used to control the speed rotation of the substrates, four different speed rotation was used: 1, 2, 3 and 4 rpm, looking for some different bilayer periods, TiAlN and TaN monolayer coatings were also deposited for comparison purpose. X-ray diffraction (XRD) showed that both monolayer and multilayer coatings showed a fcc crystal structure with (111) preferential orientation corresponding to TiAlN and TaN lattice. Using AFM technique, a decrease in roughness and grain size with decreasing in the bilayer period was observed, in addition, all multilayer coatings showed lower values of roughness and grain size compare to monolayer TiAlN and TaN coatings. SEM images revealed columnar, dense and homogenous structure for all coatings, both monolayers and multilayer coatings. Tribological properties of the coatings were investigated using Pin-on-disk, all the multilayer coatings showed lower friction coefficients and wear rates compared with the monolayer coatings. As to mechanical properties, an increase in hardness and young modulus was observed when the bilayer period decrease, furthermore, all coatings show hardness over 20 GPa and really good adherence with Lc values over 40 N.

4:30pm **B5-2-10 The Relationship between Mechanical Property and Phase Composition of Cr-Al-C Coating**, ***Jingzhou Liu,*** *P Ke, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Cr_2AlC MAX phase has aroused worldwide concern these years as the ternary nano-laminate structure enabled them with combined properties of both metal and ceramic. In the present work, in order to study influence of Al content on coatings property, coatings with different Al content were prepared by a post heat treatment of pre-deposited Cr-Al-C coatings. Rietveld refinement of XRD was used to quantitively analyse the phase composition. Results showed that the coatings were composed of Cr_2AlC, Al_8Cr_5 and Cr_7C_3 with different percentage. The hardness of Cr_2AlC coating varied from 10.17 to 19.00 GPa, the modulus changed from 198.43 to 267.62 GPa. The relationship between phase composition and electrochemical corrosion behavior were also studied.

4:50pm **B5-2-11 Microstructure and Mechanical Properties of Ta-Si-N Coatings Prepared by Reactive Magnetron Sputtering**, ***Anna Zaman,*** *Y Shen, E Meletis,* University of Texas at Arlington, USA

Nanocrystalline or quasi-amorphous ternary Me-Si-N (metal Silicon Nitride) systems have gained considerable interest because of their impressive physical, chemical and mechanical properties. In this article, the structural and mechanical properties of Ta–Si–N coatings prepared via reactive magnetron sputtering have been investigated as a function of varying N_2 percentage in the N_2/Ar gas mixture. It was demonstrated that decreasing the N_2 content in the gas mixture resulted in changing the film structure from face centered cubic (fcc) TaN (at 20% N_2) to a mixture of fcc $TaN_{1.13}$ and hexagonal (hex) Ta_2N (at 15% N_2), to hex Ta_2N (at 13% and 10% N_2) and finally to textured hex Ta_2N (at 7% N_2). X-Ray photoelectron spectroscopy revealed both Tantalum-Nitride and Silicon-Nitride binding states in the films. The hardness of the films varied from ~25 Gpa to ~35 Gpa with N_2 content varying from 7% to 15%. Especially the film deposited with 13% N_2 besides possessing highest hardness of ~ 35 Gpa, exhibited the highest hardness/modulus ratio (0.133), elastic recovery of ~60% and very low wear rate (7×10^{-6} mm^3/Nm). This film exhibited nanocolumnar structure,

with columns being separated by an amorphous matrix 5-10 nm in width. Oxidation resistance of the Ta–Si–N coating was assessed by means of thermogravimetric analysis in a flowing air up to an annealing temperature of 1300 °C and the film depicted no increase in mass upto 800 °C. Consequently, the films maybe used as a new class of hard and oxidation resistant coatings.

5:10pm **B5-2-12 Five Typical Mistakes during the Nanoindentation of Coatings**, ***Esteban Broitman,*** SKF Engineering and Research Centre, Netherlands

Nowadays, nanoindentation has become a routinely technique for the mechanical characterization of thin films and small-scale volumes. Thanks to the development of friendly analysis software and advances in high sensitive instrumentation, it feels like the measurement and calculation of hardness and elastic modulus can be easily done by just *"the pushing of one button."* However, the consequences of easy procedures have led many researchers to multiple publications with erroneous data.

Recently, we have reviewed the indentation hardness of materials at macro, micro, and nanoscale (E. Broitman, Tribology Letters, vol. 65, 2017, p. 23). Misconceptions in the nanoindentation technique were highlighted, and solutions to errors were proposed. In this paper, five typical mistakes in the measurement and data analysis during the instrumented nanoindentation of thin films will be critically reviewed, and the possible ways to correct them will be discussed: 1) the wrong area selection to calculate instrumented indentation hardness; 2) the wrong data conversion from Vickers microindentation to Berkovich nanoindentation; 3) the confusion of thermal drift with creep and viscoelastic effects; 4) the wrong correlation of hardness with tip penetration; 5) the preconceptions about a direct relationship between elastic modulus and hardness.

The origins of the aforementioned mistakes will be elucidated from the lack of understanding on contacts mechanics theory, the limits and validation of the Oliver and Pharr's method, and preconceptions transmitted from generation to generation of nanoindenter users. At the whole, it will be stressed that it is not enough to know *"how to push the button"* in order to measure the nanoscale mechanical properties of coatings.

Coatings for Biomedical and Healthcare Applications
Room California - Session D1-2

Surface Coatings and Surface Modifications in Biological Environments

Moderators: Kerstin Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

1:30pm **D1-2-1 Optimisation of Antimicrobial Silver Nanocomposite Coatings on Orthopaedic Grade Cobalt Chromium Alloys and the Related Simulator Analyses in Knee Surgery**, ***Liuquan Yang,*** Wallwork Cambridge Ltd, UK*; L Richards,* MatOrtho Limited, UK*; J Shelton,* Queen Mary University of London, UK*; H Hothi,* University College London, UK*; S Collins,* MatOrtho Limited, UK*; J Housden,* Wallwork Cambridge Ltd, UK*; A Hart,* University College London, UK*; L Espitalier,* Wallwork Cambridge Ltd, UK

Hard wearing PVD silver nanocomposite coating has shown the antimicrobial effect in previous research and a good ion barrier for the release of heavy metal ions from the conventional orthopaedic grade cobalt chromium (CoCr) alloy. Therefore, such a coating family may be considered as a promising candidate in orthopaedic applications with bearing surfaces and in particular may lower the risk of post-operation infection. The control of silver release and the overall tribological friction/wear performances are critical for the safety and longevity of the orthopaedic implant research. This is study focuses on optimisation of four the electron beam physical vapour deposition (EBPVD) coatings deposited on the medial rotation knee (MRK™) surface with different levels of silver contents in the coating structure. The overall coating assessments are carried out on simulator testing in vitro for antimicrobial effectiveness, i.e., silver ion and particle release, and wear characterisations against ultra-high molecular weight polyethylene (UHMWPE). The proposed optimised coating structure will be subject to biocompatibility tests and clinical trials.

1:50pm **D1-2-2 Structure and Properties of Novel Hydrophobic Cr-Ag Antibacterial Coatings Deposited by Closed-field Unbalanced Magnetron Sputtering**, ***MohammadSharear Kabir,*** University of New South Wales, Australia*; A Karami,* University of Adelaide, Australia*; P Munroe,* University of New South Wales, Australia*; Z Zhou,* City University of Hong Kong, Hong Kong*; Z Xie,* University of Adelaide, Australia

Antibacterial coatings are defined as surface coatings that can repel or resist the attachment of bacteria by exhibiting bactericidal or anti-biofouling effects. They are emerging as a primary component in surface applications to mitigate problems related to bacterial pathogens. In this study, we have investigated the structure and properties of Ag-doped Cr coatings. These coatings were deposited by closed-field unbalanced magnetron sputtering method using pure (99.99 %) Cr and Ag targets. The structure and mechanical properties of the coatings were investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM), focused ion beam microscopy (FIB) as well as nanoindentation. XRD analysis revealed Cr (110) as the dominant texture with the emergence of Ag (111) as the Ag content increases. TEM analysis revealed that the coatings were composed of distinct columnar grains several hundred nanometres in length. Furthermore, the coatings exhibited a hardness of around ~8 GPa with significant abrasion resistance and hydrophobic behaviour with a contact angle of ~114^0. Ongoing work is investigating the behaviour of these coatings under conditions of bacterial colonization.

2:10pm **D1-2-3 Thin Film Metallic Glass : A Lubricated Coating on Medical Needle for Reducing Fracture Toughness and Damage of Phantom Materials**, ***Berhane Gebru,*** *J Chu, C Yu,* National Taiwan University of Science and Technology (NTUST), Taiwan

A two successive insertion of bare and thin film metallic glass (TFMG) coated needles was used to measure the fracture toughness of polyurethane rubber block and porcine skin. We found that the TFMG coating reduced the fracture toughness of polyurethane rubber block and porcine tissue by more than 10 % compared to a bare needle. In both testing materials, a reduction in the cutting and frictional force is observed for insertion of TFMG-coated needle. The reduced cutting and frictional force can be ascribed to the low coefficient of friction (COF) of TFMG measured by nano-scratch tests. In addition, compared with bare needle, the crack area created on polyurethane rubber and porcine tissue for insertion of TFMG-coated needle is noticeably reduced. The results imply that by employing TFMG coating on the medical needle is capable of reducing the trauma of human tissue.

2:30pm **D1-2-4 Biocompatibility and Antimicrobial Performance of a Durable Super-hydrophobic Surface Modified Stainless Steel**, ***Cheng-Wei Lin,*** Feng Chia University; Central Taiwan University of Science and Technology, Taiwan*; C Chou,* Taichung Veterans General Hospital; National Yang-Ming University, Taiwan*; C Chung,* Central Taiwan University of Science and Technology, Taiwan*; J He,* Feng Chia University, Taiwan

For orthodontic application, a durable super-hydrophobic surface has been developed on AISI 304 stainless steel by sandblasting, electrochemical treatment and fluorocarbon plasma polymerization (SEP). The hybrid surface possesses nano/micro coexisting structure and present super-hydrophobicity (water contact angle 154°) and good abrasion durability. In this study, the *in vitro* tests for cell compatibility and antimicrobial behavior were performed by using fibroblast cell culture and bacterial cell culture, respectively.

The results reveal that the obtained hybrid surface exhibit better cell proliferation in comparison with the bare AISI 304 stainless steel (SS). In the antimicrobial test, the SEP surface also exhibit a comparatively lower level of bacterial adhesion than SS. These results suggest that the hybrid SEP treated AISI 304 stainless steel present good cell compatibility and antimicrobial performance, which are essential for orthodontic application.

2:50pm **D1-2-5 Immobilization of Carboxylic Acid Groups on Polymeric Substrates by Plasma-enhanced Chemical Vapor or Atmospheric Pressure Plasma Deposition of Acetic Acid**, ***Wei-Yu Chen,*** *A Matthews,* University of Manchester, UK*; F Jones,* University of Sheffield, UK*; K Chen,* Tatung University, Taiwan

Low-pressure plasma-enhanced chemical vapor deposition (PECVD) is a process that activates the precursor in the plasma state to deposit films on the surface. Introducing carboxylic acid functional groups via PECVD has been widely applied in various applications, such as the enhancement of interfacial adhesion between fillers and matrices in composite materials, molecular grafting for biosensors and biocompatibility improvement. To develop a compatible surface for cell adhesion, polymeric substrates, poly (lactic-co-glycolic acid) (PLGA) and polyethylene terephthalate (PET), were

modified by a low-pressure acetic acid plasma to improve surface hydrophilicity and biocompatibility. The acetic acid plasma deposited film maintained stability on a hydrophilic surface for long-term aging and possessed good biocompatibility. If the acetic acid film can be deposited by process using atmospheric pressure plasma (APP), a more rapid, economic and power-saving method can be achieved. In this study, a remote APP system using a bespoke Pyrex APP chamber was utilized to deposit acetic acid film onto the surfaces of polymeric substrates. The wettability, stability of hydrophilicity and surface elemental composition of the APP-deposited film will be reported and compared with that prepared via low-pressure acetic acid plasma.

3:10pm **D1-2-6 Coatings Deposition by RF Magnetron Sputtering of Loosely Packed Hydroxyapatite Powder Target***, **Laurynas Lukosevicius,*** The University of Manchester, UK*; S Mráz, J Schneider,* RWTH Aachen University, Germany*; A Matthews,* The University of Manchester, UK

It is well known that hydroxyapatite (HA), which is the major mineral compound of bone tissue, promotes orthopedic implants osteointegration when applied in a mixture or composite material compound. HA target preparation can be difficult and target cracking can occur. Therefore, many different target preparation techniques such as sintering, mixing HA with additional materials, HA plasma spraying copper discs prior the deposition or directly sputtering from the powder have been employed during previous research. Also, the deposition of HA is complicated due to the target and grown film decomposition as well as low bonding strength of the coating to the substrate.

In this study, amorphous HA coatings were deposited on Titanium, Magnesium and Silicon substrates from three different loosely packed powder target electrodes arrangements by radio frequency magnetron sputtering in an argon environment pressure of 5–50 mTorr and magnetron power of 30-381 W (1.5-6 W/cm^2). Deposition from solid and powder target materials has been evaluated and compared. Furthermore, the influence of the deposition parameters on the coating phase and elemental composition has been investigated.

The Ca/P ratio has been evaluated by means of EDS and XPS. FTIR and Raman analysis revealed that deposited coatings contain a typical calcium phosphate structure. The analysis showed that coatings of a multiphasic mixture containing HA, TCP, pyrophosphate and CaO have been formed. Furthermore, pyrophosphate was the major compound of the coating deposited at 50 mTorr process pressure. Heat treatment of the HA and titanium composites at 550 ^{o}C in air medium led to the crystallization of the coating.

3:30pm **D1-2-7 Advanced Medical Biosensing Systems with Soft/Stretchable Materials and Assemblies***, J Rogers, **Roozbeh Ghaffari,*** Northwestern University, USA **INVITED**

Unusual classes of electronics and electrochemical sensors enabled by recent advances in materials science and mechanics have been designed with 'skin-like' physical properties. These systems are highly conformal and wearable by virtue of their soft mechanics compared to conventional packaged electronics and sensors. In this talk, we present an overview of recent advances in novel materials, mechanics and designs for emerging classes of fully-integrated soft bio-electronics. These devices incorporate microfluidics and microfabricated arrays of sensors configured in ultrathin, stretchable formats for monitoring of hydration and (electro-)physiology. Quantitative analyses of strain distributions and electronics performances under mechanical stress highlight the utility of these advanced medical systems in the clinical and remote environments. We will conclude with representative examples of epidermal systems being tested in clinical studies and sports field trials.

4:10pm **D1-2-9 Cyclic Voltammetry Study of Electrolytic Plasma Processing of Porous Ti***, M Shbeh,* University of Sheffield, UK*; **Aleksey Yerokhin,*** University of Manchester, UK*; R Goodall,* University of Sheffield, UK

Titanium is one of the most commonly used materials for biomedical applications. However, there are two issues associated with the use of it, namely its bio-inertness and high elastic modulus compared to the elastic modulus of the natural bone. Both of these hurdles could potentially be overcome by introducing a number of pores in the structure of the Ti implant to match the properties of the bone as well as improve the mechanical integration between the bone and implant, and subsequently coating it with a biologically active ceramic coating to promote chemical integration. This study has investigated the utility of cyclic voltammetry to understand processes that occur during electrolytic plasma surface treatments of porous Ti parts with different amounts of porosity produced by Metal Injection Moulding. Anodic behaviour of the porous Ti substrates was studied in aqueous solutions of disodium hydrogen phosphate in the voltage range 0 to 500 V. The shapes of the cyclic voltammograms for the relatively dense samples were relatively steady and not sensitive to the change in the scan rate, with more distinctive peaks indicating occurrence of complex multi-electron transfer processes observed. In contrast, for more porous samples the voltammogramms had hump-shaped start and less distinctive peaks. The treatment of porous samples with higher porosity and open pores resulted in much thicker surface oxide layers that penetrate through the inner structure of the samples forming a network of surface and subsurface coatings. The results are of potential benefit in producing surface engineered porous samples for biomedical applications which not only address the stress shielding problem, but also improve the chemical integration with the bone matrix.

4:30pm **D1-2-10 Corrosion and Degradation Behavior of dahp pre-treated PCL Composite Coatings on Pure Magnesium***, **Yuyun Yang,*** Institute for Corrosion Science and Surface Technology, China*; K Zheng,* Institute of Biomaterials, Germany*; G Jin, X Cui,* Institute for Corrosion Science and Surface Technology, China*; S Virtanen,* Institute for Surface Science and Corrosion, Germany*; A Boccaccini,* Institute of Biomaterials, Germany

Application demands for magnesium have increased dramatically recently due to its favorable mechanical properties. However, the poor corrosion resistance of magnesium under corrosive environment strongly impedes numerous applications, particularly in the biomedical field. Numerous efforts have been made to improve the anticorrosion property of magnesium, such as increasing purity level, modifying composition, and altering the microstructure by heat treatments. Surface modification has been proved to be an efficient and cost-effective approach in enhancing corrosion resistance and degradation behavior of magnesium. Polymeric coatings are attracting increasing attention because of their pronounced protective effect on magnesium matrix. Polycaprolactone (PCL) has been employed in a series of composite coating systems developed in our group to control the dissolution of magnesium. However, the main weakness of polymeric coatings is the unsatisfied adhesion to the bulk matrix. Therefore, pretreatment of magnesium is required to enhance the interaction between the magnesium matrix and polymeric coatings. Di-ammonium hydrogen phosphate (DAHP) is commonly used to synthesis hydroxyapatite in the hydrothermal method as an essential compound. In this study, DAHP was used to pre-treat magnesium under hydrothermal condition prior to PCL coating for enhancing the adhesion. It is also expected that DAHP pretreatment would facilitate the phosphate deposition and induce hydroxyapatite formation in further. In addition, nanoscaled bioactive glass particles (BGN) that were synthesized by a modified Stöber method were incorporated in the PCL coating to improve biological activities of the coated magnesium. The results showed that DAHP/PCL composite coatings offer magnesium significant protection against corrosion in comparison to the DAHP pre-coating and PCL composite coating. The DAHP/PCL composite coating shows great potential in improving corrosion resistance of magensium for biomedical applications.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Royal Palm 4-6 - Session E2-2

Mechanical Properties and Adhesion

Moderators: Gerhard Dehm, Max-Planck Institut für Eisenforschung, Megan Cordill, Erich Schmid Institute of Materials Science, Ming-Tzer Lin, National Chung Hsing University, Taiwan

1:30pm **E2-2-1 Controlling the Chemomechanical Effects in Sapphire by Ion-implantation***, **Steve Bull,*** *A Yadav,* Newcastle University, UK

Modification of the chemomechanical behaviour of the surface of sapphire by ion implantation has been investigated to improve its near-surface mechanical properties (i.e. hardness). 300keV Ti^+ ions at various doses have been implanted and the concentration and damage profiles characterised using Rutherford Backscattering (RBS). At high doses (≥3×10^{16} Ti^+cm^{-2}), a surface amorphous layer has formed due to implantation-induced damage. Nanoindentation has been used to determine the hardness behaviour of the ion-implanted single crystal sapphire. It has been found that hardness increases at low implanted doses, which is associated with implantation-induced damage but that also chemomechanical softening of the surface is

reduced due to the removal of adsorbed water layer. In-situ Raman scattering measurements demonstrate the removal of the adsorbed water at low doses, and existence of the readsorbed water at high doses. For the optimum implanted dose the water readsorption does not recur even several years after the implantation treatment. Based on this study, it is concluded that ion implantation with an appropriate ion species and dose can control the chemomechanical effect and improve the hardness of ceramics such as sapphire.

1:50pm **E2-2-2 Magnetron Sputtering of Refractory Metal Thin Films on NiTi Shape Memory Alloy Sheets**, ***Fabian Seifried***, Karlsruhe Institute of Technology (KIT), Germany; *H Riedl,* Technische Universität Wien, Austria; *S Baumgaertner, H Leiste, R Schwaiger, S Ulrich, H Seifert,* Karlsruhe Institute of Technology (KIT), Germany; *P Mayrhofer,* Technische Universität Wien, Austria; *M Stüber,* Karlsruhe Institute of Technology (KIT), Germany

In this study, pseudo-elastic Ni 50.8 at.%-Ti alloy sheets of 1000 microns thickness were coated with 10 microns thick refractory metal thin films (e.g. Mo, Ta and Nb thin films), by non-reactive d.c. magnetron sputtering. These thin films were characterized with regard to their microstructure and selected mechanical properties. Microstructural characterization of the thin films included X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) analyses. Mo thin films grow in a densely packed, (110) textured b.c.c. structure with columnar grains and large crystallite size (columnar width: 280-300 nm) on the NiTi substrate. Ta and Nb thin films grow as well in a dense columnar structure; however they show X-Ray diffraction peaks of various lattice planes of the b.c.c. structures (i.e. no texture) and exhibit much smaller crystallite sizes (columnar width: 30-40 nm). Considering the specific thin film/substrate thickness ratio (1:100) of the samples, the mechanical properties of both the thin films and thin film/substrate composites were investigated on different length scales, using nano- and microindentation techniques. Nanoindentation results confirm that the values of the Young's modulus of all thin film materials are identical with the values of the related bulk metals. Microindentation revealed that the Young`s modulus of the Nb/NiTi composite is closest to that of the pure NiTi substrate. Progressive scratch tests indicate excellent adhesion of all metal thin films on NiTi. To further evaluate the elasticity of the metal films and the integrity of the composites during elastic deformation tensile tests were performed on the thin film/NiTi composites. These pre-strained samples were subsequently used for cycle fatigue testing. To evaluate the potential impact of the surface coating and the deposition process on the phase transformation behaviour of the NiTi shape memory alloy, differential scanning calorimetry (DSC) analyses were done. We will discuss in detail the correlation of microstructure and static and dynamic mechanical properties of metal coated NiTi shape memory alloys. Conclusions and recommendations will be given for a material selection of refractory thin films design as radiopaque coatings on NiTi substrates for medical applications.

2:10pm **E2-2-3 Quantitative *In Situ* SEM MEMS High Cycle Fatigue: the Critical Role of Oxygen on the Nanoscale-Void-Driven Nucleation and Propagation of Small Cracks in Ni Microbeams**, *A Barrios Santos, S Gupta,* Georgia Institute of Technology, USA; *G Castelluccio,* Cranfield University, UK; ***Olivier Pierron***, Georgia Institute of Technology, USA **INVITED**

Small-scale fatigue is an active research area due to the widespread use of metallic films and micrometer-scale structures in applications such as flexible/stretchable electronics, micro and nano electromechanical systems (MEMS and NEMS), and microelectronics. This work presents an advanced small-scale, *in situ* scanning electron microscope (SEM) fatigue testing technique to characterize the fatigue behavior of electroplated Ni microbeams (with an ultrafine grained microstructure) subjected to high / very high cycle fatigue loading conditions, with and without a protective Au coating. The fatigue devices consist of MEMS microresonators that are driven at resonance inside the SEM, leading to fully-reversed loading of the microbeams at a frequency of ~8 kHz. The fatigue damage leads to a decrease of the microresonator's resonance frequency, which can be measured and used as a metric to quantify the crack growth rates. In addition, the *in situ* SEM observations allow direct evaluation of fatigue crack nucleation and propagation rates. Fatigue tests on the Ni microbeams provided direct measurement of ultraslow fatigue crack growth (average values down to 10^{-14} m/cycle) that have heretofore not been reported and highlighted strong environmental effects on fatigue lives that are three orders of magnitude longer in air than in vacuum. This ultraslow fatigue regime does not follow the well documented fatigue mechanisms that rely on large cyclic plastic zones and that are associated with larger crack growth rates (>~10^{-10} m/cycle). Instead, our study reveals fatigue nucleation and propagation mechanisms that mainly rely on room temperature vacancy condensation leading to voids, whose nucleation process is strongly affected by oxygen. The presence of a protective Au coating also increased the fatigue life in air by one order of magnitude, by delaying the crack nucleation process in the underlying Ni microbeam. The improvement in fatigue life is related to the fatigue degradation of the Au coating and its delamination from Ni once a fatigue crack reaches the interface. This work highlights significant size-dependent fatigue behaviors, whose origin will be discussed in this talk.

2:50pm **E2-2-5 Role of Microstructure on the Interface Stability of Copper Thin Films on Brittle Substrates**, ***Alice Lassnig***, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *V Terziyska,* Montanuniversität Leoben, Austria; *C Gammer,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *D Kiener, C Mitterer,* Montanuniversität Leoben, Austria; *M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Thin ductile films on brittle substrates are widely used in different technological applications such as in microelectronics and energy sectors. Of particular interest is the stability of the interface between the two materials, since it is the weakest site determining the overall reliability of the material system. To decouple extrinsic from intrinsic size effects, a model ductile thin film on a brittle, chemically inert substrate was investigated. Therefore, 100 nm copper thin films were deposited by magnetron sputtering where the deposition process was optimized to maintain the same thin film thickness but a significant variation of the microstructure (bimodal). Further variations of the microstructures could be achieved by means of heat treatments leading to a uniform, coarse-grained microstructure. A thorough characterization of the film microstructures and interfaces was conducted by means of SEM and TEM.

To determine the adhesion, stressed overlayers were deposited, leading to the formation of spontaneous buckles with straight and telephone cord buckle morphologies. These buckles were measured by means of confocal laser scanning microscopy, allowing for the determination of the adhesion energy with the well-known Hutchinson & Suo model.

We could show that the adhesion values of the same thin film – brittle substrate system increased a factor of almost 2 with decreasing grain size but same thin film thickness.

A detailed study explaining the change of interface adhesion energy by means of a thorough characterization of the thin films will be presented, including a TEM study to reveal the delamination processes in-situ.

Abstract #3863

3:10pm **E2-2-6 Mechanical Reliability of Barrier Films for Flexible Electronics**, ***Kyungjin Kim***, *H Luo, T Zhu, S Graham, O Pierron,* Georgia Institute of Technology, USA

PECVD SiN_x thin film coatings have been developed to protect flexible electronics devices from environmental exposure. While most of the study has leaned on water vapor transport properties, the mechanical reliability during flexural deformation is another critical aspect for the coatings. Previously, we investigated the time-dependent channel crack growth behavior of silicon nitride (SiN_x) barrier films on polyethylene terephthalate (PET) substrates in humid and dry air and showed that crack growth can occur at strains that are much lower than the standard measured crack onset strains. In this work, we demonstrate the long-term time dependent fracture of PECVD SiN_x barrier films on polyethylene terephthalate (PET) and polyimide (PI) substrates by measuring crack growth rates under fixed strain as a function of time using in-situ microscopy tensile test. Our study highlights the interplay between neighboring cracks and substrate damage on the long term crack growth rates. For isolated cracks in SiN_x with PET damage, the growth rates were found to increase with time due to the loss of constraint on the SiN_x channel cracks as the corresponding crack grew in the PET. For multiple cracks growing on PET, decrease in the subcritical crack growth rates was found by up to 2 orders of magnitude until reaching steady-state rates due to substrate cracking in the interacting cracks. For SiN_x on PI, crack growth rates were observed to be nearly constant due to the lack of substrate cracking in PI as compared to PET.

3:30pm **E2-2-7 Molecularly Grafted, Structurally Integrated Multifunctional Polymer Thin Films with Improved Adhesion**, *A Lassnig,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *P Smith,* Carnegie Mellon University, USA; *M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; ***B.Reeja Jayan***, Carnegie Mellon University, USA

We present a novel molecular scale grafting technique using chemical vapor deposition (CVD) polymerization to enhance the adhesion of thin

polymer films to various substrates. Such engineered coatings can find applications in structurally integrated batteries and sensors that can carry mechanical loads in addition to performing energy conversion functions. Conventional un-grafted polymer thin films are loosely anchored to surfaces by weak physical interactions like Van der Walls forces or physisorption, which are easily disrupted by mechanical forces. We show that grafting can deploy strong chemical bonds or chemisorption to permanently anchor the film to the substrate. Until now, direct measurements of these bonds have not been possible because the materials used are very thick (typically 10-100 µm) and are difficult to access by surface characterization methods like x-ray photoelectron spectroscopy. Also, in previous attempts these bonds were made on small (localized) scale (e.g., polymer brushes grafted on nanoparticles) and thus large spatial variations in stresses that arise under real operating conditions in a device could not be investigated.

Herein, we use a novel non-line-of-sight oxidative CVD (oCVD) polymerization technique to simultaneously graft and polymerize monomers of EDOT onto radical (reactive) sites present on a Silicon substrate, resulting in conducting poly(3,4-ethylenedioxythiophene) (PEDOT) films. This grafting improves adhesion of coatings to the substrate surface. Films without the graft spalled and delaminated in the form of spontaneous buckles, after the application of Molybdenum stressed overlayer. Similar PEDOT films with the graft only spontaneously delaminated after the same stressed overlayer was added. From the spontaneous buckling the adhesion energy of the PEDOT-Silicon interface can be evaluated using the well-known Hutchinson and Suo model. It will be demonstrated that the addition of the graft significantly increases the adhesion of the PEDOT to a Silicon substrate

3:50pm **E2-2-8 Thin-film Adhesion Characterization by Colored Picosecond Acoustics***, **Arnaud Devos**,* IEMN UMR CNRS 8520 / MENAPiC, France*; P Emery,* MENAPiC, 41 Bd Vauban, France

Thin-film characterization is a main issue for a broad range of industrial applications related to the microelectronic industry or coatings for optics or glass industry or photovoltaics. All these technologies have in common to develop new products based on complex stacks made of various thin-film materials thinner and thinner. Thickness, elasticity, composition and adhesion at interfaces must be controlled if possible in a non-destructive way. Increased efforts are being made to develop measurement methods compatible with “real life conditions”.

This paper will present a new technique so-called the Colored Picosecond Acoustics (APiC), a unique combination of optics and acoustics, which implements a SONAR at the nanoscale using a tunable ultrafast laser. From the experimental point of view, it is a full optical setup, acoustics taking place in the sample only. Very high frequency acoustic waves are emitted and detected using ultra-short laser pulses. The acoustic waves propagate indifferently in transparent or opaque materials. These “hypersonic waves” have such a short wavelength that they suit very well the characterization of thin films, multi-layers, nanostructures and interfaces.[1-2]

In this paper, we will present some results to show useful can be the APiC technique for controlling thin-film thickness and adhesion at interface on complex samples related to various industrial objects: radio-frequency filters, thin-film solar cell, advanced mirrors, semiconductor lasers.

References:

[1] A. Devos, R. Cote, G. Caruyer, and A. Lefevre, Appl. Phys. Lett. 86, 211903 (2005).

[2] A. Devos, Ultrasonics 56, pp. 90-97 (2015) DOI 10.1016/j.ultras.2014.02.009

4:10pm **E2-2-9 Imaging Thin Film Adhesion with Picosecond Ultrasonics***, **Allaoua Abbas**, X Tridon, J Michelon,* Neta, France

In the middle of the eighties, it has been demonstrated that femtosecond lasers are able to generate and to detect ultrasounds which frequencies can extend up to serval TeraHertz. Thanks to their very small wavelengths, these ultrasounds can perform measurement of the mechanical properties of structures with nanometric resolution. These measurements have serval application in industries which use thin films, as the photovoltaic or the electronic ones.

In this presentation, utilization of these ultra-high frequencies ultrasounds as a tool for nondestructive testing will be overlined. It will be shown how photo-generated and photo-detected ultrasounds are able to probe, without any contact, the bounding quality and the thickness of a thin metallic film deposited on a dielectric substrate. Cartographies, which illustrate the thickness inhomogeneities and the bounding quality adhesion of a 255 nm Tungsten thin film deposited on a Silicon substrate will be presented to support these points.

4:30pm **E2-2-10 Mechanical Property Evaluation of Zr-Ti- Fe Thin Film Metallic Glasses***, **Yi-Jie Liao**,* Ming Chi University of Technology, Taiwan*; D Tseng, T Wu, M Lin,* National Chung Hsing University, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Recently, thin film metallic glass (TFMGs) have drawn lots of attention from academia and industries due to their unique properties and possible applications. In this study, four ternary Zr-Ti-Fe TFMGs were fabricated on Si wafer and AISI304 stainless steel disk substrates using a magnetron co-sputtering system. The power of iron target was adjusted to grow TFMGs with different Fe contents. The effects of iron content on the microstructure and mechanical properties of Zr-Ti-Fe TFMGs were discussion. The thin film metallic glass materials consisted of an amorphous structure, with an absence of any detectable peak corresponding to crystalline phases. The surface morphology of TFMGs showed a very smooth surface by the analysis of atomic force microscopy. The hardness and elastic modulus of TFMGs were analyzed by nanoindentation. Furthermore, the bulge test was carried out to determine the residual stress, elastic modulus and deformation behavior of TFMGs from the pressure–deflection curves. The influence of Fe concentration on the mechanical property and deformation behavior of ternary Zr-Ti-Fe TFMGs was discussed.

4:50pm **E2-2-11 Mechanical Properties Measurement of Submicron Ti-Ni Shape Memory Alloys Thin Films***, T Wu, **Ming-Tzer Lin**,* National Chung Hsing University, Taiwan*; T Chen,* Chaoyang University of Technology, Taiwan*; T Lin,* National Chung Hsing University, Taiwan

Ti-60at%Ni thin films with thickness of 600nm were deposited on silicon nitride with and without chromium interlayer. Static and dynamic mechanical properties of these films were investigated using bulge test and observed their microstructure and crystalline phase orientation from SEM and XRD. It was found that with the adhesion of chromium interlayer the Ti-Ni films have the lowest residual stress and the highest Young’s modulus. The addition of chromium interlayer between Ti-Ni film and silicon nitrite introduces R phase transformation in room temperature. Microstructure analysis revealed that the surface trenches could be significantly reduced if the film has chromium interlayer, which indicates that chromium interlayer can minimize the stress development on Ti-Ni films during deposition. Thermal cycling stress evolution test results showed that chromium interlayer can be a buffer layer between TiNi and SiNx thermal mismatch. Moreover, the thermal cycling bulge test can be used to measure the thermal expansion coefficient of the films. In addition, the fatigue test showed that the interlayer of Cr can enhance the fatigue strength of TiNi films.

New Horizons in Coatings and Thin Films
Room San Diego - Session F2-2

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Jon Tomas Gudmundsson, University of Iceland

1:30pm **F2-2-1 Effect of Bias Voltage during Deposition by Deep Oscillation Magnetron Sputtering of AlN Films for Acoustic Biosensors***, L Melo-Máximo,* ITESM-CEM, Mexico*; J Lin,* Southwest Research Institute, USA*; **AbrilErendira Murillo**, O Salas, J Oliva-Ramírez, J Oseguera, B Garcia-Farrera,* ITESM-CEM, Mexico*; D Melo-Máximo,* Tecnológico de Monterrey-Campus Estado de México, Mexico

Deep Oscillation Magnetron Sputtering (DOMS) has an excellent potential to produce AlN films with the required features for biosensing applications. In the present study, AlN films deposited on Si wafers were extensively characterized to assess this potential. The films were produced varying the substrate potential and the resulting microstructures examined by glancing angle x-ray diffraction, scanning electron microscopy coupled with energy dispersive microanalysis, optical profilometry, scratch testing and atomic force microscopy. The results indicate that there is a strong effect of the potential applied to the substrate on the structure of the Al/AlN/Al films an intermediate bias voltage results in the highest (002) oriented films.

1:50pm **F2-2-2 Modification of Niobium Surface Properties by High-temperature Nitrogen Plasma based Ion Implantation Aiming Aerospace Applications**, ***Rogerio Oliveira***, *O Aguiar,* National Institute for Space Research - INPE, Brazil*; A Oliveira,* Federal University of São Paulo, Brazil*; L Hoshida,* Plasma Laboratory, Brazil*; M Araujo, M Silva, C Mello, E Ferreira,* National Institute for Space Research - INPE, Brazil*; V Liccardo,* Aeronautical Institute of Technology, Brazil

High temperature nitrogen plasma based ion implantation (HT-NPBII) has been successfully used to treat pristine niobium. The method has shown to be a convenient alternative to treat the surface of Nb in comparison with coating and alloying, mainly when physical and chemical properties of the raw metal must be preserved, as required in many technological applications, like in aerospace sector. In this non-line-of-sight process, the workpiece immersed in plasma is heated by electron bombardment during the off-time of high negative voltage pulses used to implant nitrogen positive ions into the surface of niobium. The precise control of the heating temperature and the adjustment of the implantation energy and duty cycle of the pulses allow to tailoring the N-implantation depth and its concentration. Thus, relatively thick (6-7 µm) layers enriched with nitrogen and very thin ones (less than a hundred of nanometers) can be achieved. It is reported for the first case, a remarkable presence of niobium nitrides for samples treated by HT-NPBII at 1200 °C, 7 keV/ 30 µs/ 400 Hz, leading to the improvement of mechanical and tribological properties of the metal, as well as the enhancement of the oxidation resistance. For the second case (700 °C/ 5 keV/ 20 µs/ 300 Hz), nitrogen atoms occupy interstitial spaces in the crystal lattice. The treatment of superconducting niobium cavities under these parameters caused the enhancement of two orders of magnitude of the respective quality factors. Such cavities find application in particle accelerators or playing the role of electromechanical transducers of resonant-mass gravitational wave detectors. A complete set of characterization is presented herein, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), glow discharge optical emission spectroscopy (GDOES), scanning electron microscopy (SEM/FEG), Vickers hardness, thermogravimetric analysis (TGA) and tribology measurements.

2:10pm **F2-2-3 High-Power Impulse Magnetron Sputtering Coatings for Extreme Environments**, ***Frédéric Schuster***, CEA, France*; A Ferrec,* Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, France*; J Wang,* Nanyang Technological University, Singapore*; M Ougier,* CEA, France*; A Quenardel,* Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, France*; M Sall, M Schlegel, F Lomello, A Michau, H Maskrot, F Balbaud,* CEA, France

The rise of low carbon energy, in particular nuclear energy, requires the development of new materials resistant to extreme environments with very often combined stresses: high-temperature oxidation, irradiation, wear and corrosion, frequently in concentrated media. During the last years and especially due to the development of HiPIMS (High Power Impulse Magnetron Sputtering) technologies, industrial developments that could not be considered in the past are now possible thanks to the progresses made by PVD (Physical Vapor Deposition) processes.

Applications for protective coatings concern the whole nuclear fuel cycle, specifically the development of EATFs (Enhanced Accident Tolerant Fuels) in order to increase the resistance in loss of coolant accidental conditions. The protection of components operating in concentrated nitric acid in case of reprocessing plants is also of particular interest to increase drastically their lifespan, as wear-resistant components for valves and the protection against corrosion of nuclear waste storage steel containers.

To address these issues, various studies led CEA to develop over the last few years a wide range of HiPIMS coatings, from simple monolithic metals, metallic alloys, self-healing Cr/Ta nanometric multilayers, to more complex nanocomposites compositions in Cr-Si-N and Ti-Si-N ternary systems but also simple and mixed oxides such as ZrO_2 and $ZrSiO_4$.

HiPIMS benefits from several advantages in comparison with conventional cathodic magnetron sputtering because of its highly energetic and ionized nature. HiPIMS combines the assets of ionized and pulsed PVD processes to achieve denser coatings, stronger adherence with substrates and better thickness conformities which can be crucial for coatings exposed to harsh environments.

The main driver of the integrated and agile approach we elaborated is rapid industrialization of coating processes. That is the reason why we carry out technological demonstration of components at industrial scale very quickly. This whole research is therefore executed in pilot-scale installations followed by industrial prototype facilities.

2:30pm **F2-2-4 Reactive High-power Impulse Magnetron Sputtering of Al-O-N Films with Tunable Composition and Properties**, ***Jaroslav Vlček***, *A Belosludtsev, J Houska, R Čerstvý, S Haviar,* University of West Bohemia, Czech Republic

Oxynitrides are a class of materials with yet unexplored physical, chemical and functional properties, and a great potential for industrial applications [1,2].

In this work, a modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, with a feedback pulsed reactive gas (oxygen and nitrogen) flow control and an optimized location (high-density plasma) of the reactive gas inlets in front of the target and their orientation toward the substrate made it possible to produce high-quality Al-O-N films with a tunable elemental composition, structure and properties. We give the basic principles of this method, maximizing the degree of dissociation of both O_2 and N_2 molecules in a discharge plasma, which leads to a replacement of very different reactivities of the O_2 and N_2 molecules with metal atoms on the surface of growing films by similar (high) reactivities of atomic O and N.

The depositions were performed using a strongly unbalanced magnetron with a planar aluminium target of 100 mm diameter in argon-oxygen-nitrogen gas mixtures at the argon pressure of 2 Pa. The nitrogen fractions in the reactive gas flow were in the range from 0 % to 100 %. Voltage macro-pulses, composed of 10 voltage micro-pulses (pulse-on time of 20 µs and pulse-off time of 30µs), with a total length of 500 µs and repetition frequency of 350 Hz were used for all depositions with a maximum target power density up to 675 Wcm^{-2} during pulses at a deposition-averaged target power density of 8.5 Wcm^{-2}. The substrate temperatures were less than 120°C (no external heater) during the depositions of films on a floating substrate at the distance of 100 mm from the target. A pulsed reactive gas (O_2 and N_2) flow control made it possible to produce hard (11–19 GPa) and highly optically transparent (extinction coefficient ≤ 1 x 10^{-4} at 550 nm) Al-O-N films with gradually changed elemental compositions from Al_2O_3 into AlN.

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[2] A. Belosludtsev, J. Houska, J. Vlcek, S. Haviar, R. Cerstvy, J. Rezek, M. Kettner,

Structure and properties of Hf-O-N films prepared by high-rate reactive HiPIMS with

smoothly controlled composition, Ceram. Int. 43 (2017) 5661–5667.

2:50pm **F2-2-5 Fabrication of Ti BC N Coatings using a Superimposed HiPIMS and MF Deposition System**, ***Yu-Wen Su***, *J Lee,* Ming Chi University of Technology, Taiwan

Recently, the TiBCN hard coating has attracted lots of attentions owing to its wide range of hardness and coefficient of friction values, which are caused by adjusting the chemical composition of N and C and resulting phases. Meanwhile, the superimposed high power impulse magnetron sputtering (HiPIMS) and middle frequency (MF) power system has been developed to improve the low deposition rate of traditional HiPIMS without sacrificing its high target peak power density. In this study, a superimposed HiPIMS and MF power system was used to grow TiBCN coatings. The pure Ti and TiB_2 targets were adopted during deposition. The reactive gas mixture consisted of nitrogen and acetylene. A plasma emission monitoring system was employed to grow coatings under different Ti target poisoning regime. Various acetylene gas flow rates were added during deposition. The phase of each coating was studied using the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy and transmission electron microscopy. Atomic force microscopy was employed to analyze the surface roughness of films. The nanoindentation, scratch and pin-on-disk wear tests were used to evaluate the hardness, adhesion and tribological properties of thin films, respectively. Effects of the Ti target poisoning status and flow rates of acetylene on the microstructure, chemical composition, phase, deposition rate and mechanical properties of TiBCN were studied in this work.

3:10pm **F2-2-6 Effect of Peak Current on the Ti-Cu Thin Film Deposition by High Power Impulse Magnetron Sputter Deposition***, **Ying-Chai Chen**, Y Lin,* National Changhua University of Education, Taiwan*; W Wu,* Da-Yeh University, Taiwan

The improvement in the performance and durability of medical implants and surgical tools is an important issue. Therefore, various surface coatings have been applied onto these implants and tools to enhance their functional properties and lifetime. It is known that several metal ions (Cu^{2+}, Ag^{+}, Zn^{+}) exhibit antibacterial effect which fit such a purpose. Among these metal ions, Cu represents a very promising one because of its lower toxicity and higher cytocompatibility. However, the hardness and the adhesion of Cu thin film to the Ti6Al4V substrates require further improvement. As a result, an asymmetric bipolar high-power magnetron sputtering (HiPIMS) technique was used to deposition Ti-Cu thin films using two different targets of Ti and Cu due to Ti can provide a better mechanical property. The peak currents of the Ti and Cu targets were individually varied from 80 to 200A. The thin films were deposited on different substrates, including Si wafer, Ti6Al4V, and a flexible substrate. The microstructure, composition, mechanical properties, antibacterial effect, and biocompatibility of the resulting Ti-Cu thin films were then investigated and reported.

3:30pm **F2-2-7 Deposition of Ag-Cu Thin Film on Flexible Substrate using High Power Impulse Magnetron Sputtering***, **Yu-Hsuan Hsu**, W Wu,* Da-Yeh University, Taiwan

In high power impulse magnetron sputtering (HiPIMS) technique, a highly ionized flux from both the sputtering gas and target material occurs due to the input of a high power in a short pulse. The quality of the deposited film is thus improved, especially the adhesion, density, and surface roughness. Furthermore, the deposition temperature of HiPIMS is much lower than that of the conventional magnetron sputtering. Therefore, the selection of substrates is much wider. In this study, a HiPIMS technique was used to deposit bimetallic Ag-Cu coatings under an asymmetric bipolar mode. The Cu target current was varied from 80 to 200 A as the Ag target current was fixed at 50 A. The deposition temperature is lower than 50°C. During the deposition, the plasma was diagnosed using optical emission spectroscopy (OES). Flexible substrates, including plastic PET and PEN were used for the deposition. The bioapplication of the Ag-Cu thin films were examined and reported.

3:50pm **F2-2-8 Preparation of Anatase TiO_2 Thin Films by Reactive HiPIMS***, F Cemin,* Université Paris-Sud, France*; J Keraudy,* Linköping University, Sweden*; T Minea,* Université Paris-Sud, France*; **Daniel Lundin**,* Université Paris-Sud/CNRS, France

Titanium dioxide (TiO_2) is one of the most investigated semiconducting materials for a wide range of applications, *e.g.*, in photocatalysis (for water splitting, decomposition of pollutants, self-cleaning windows), memory capacitors and transistors (dielectric material), lithium-ion batteries (as anode material), gas and humidity sensors, anti-reflective coatings, etc. Compared to the rutile phase, the anatase phase possesses the highest photocatalytic activity and the best properties for lithium-ion intercalation, which are critical factors for the performance of energy-related devices/applications. Although most HiPIMS studies on TiO_2 phase formation are focused on the rutile phase, there is some evidence that anatase (or a mixture of anatase-rutile) grows preferentially under conditions of relatively weak ion bombardment of the growing film. However, the reported deposition conditions are often contradictory with no obvious choice of pulse parameters, gas pressure, substrate-to-target distance, etc. In this contribution we have therefore investigated the HiPIMS growth conditions required specifically for anatase TiO_2 and systematically studied the phase formation, microstructure and chemical composition as a function of mode of target operation (metal-transition-compound modes) as well as of external process parameters (substrate temperature, working pressure, and peak current density). Phase pure anatase films were deposited at power normalized deposition rates of more than a factor 10 higher compared to what has previously been reported. Also the crystal quality was improved by using ion bombardment of weak to moderate intensity. Furthermore, the reactive HiPIMS process of TiO_2 was characterized using a new reactive ionization region model (R-IRM). The model provided insight into the temporal behavior of the discharge plasma parameters such as electron density, the neutral and ion composition, the ionization fraction of the sputtered vapor, the oxygen dissociation fraction, and the composition of the discharge current for various discharge conditions.

4:10pm **F2-2-9 Vapor Phase Nanoparticle Synthesis, Guiding and Self-assembly***, **Ulf Helmersson**,* Linköping University, Sweden **INVITED**

The synthesis of nanoparticles using low-pressure plasma have the reputation that it “cannot be easily managed for production of material in large quantities”. [1] However, it has recently been shown, independently by two groups, that it is possible to achieve a dramatic increase in nanoparticle productivity in using pulsed plasmas. [2,3] This is of great interest since low-pressure plasma methods opens up the potential for design of a diversity of nanoparticles directly followed by the distribution of the generated nanoparticles on surfaces or in the assembly of the nanoparticles into nanostructures using guiding electric or magnetic fields. Electric field can be used since nanoparticles in a plasma generally attains a negative potential, while magnetic fields require that the nanoparticles have ferromagnetic properties. In this presentation, the role of high-power pulsed plasmas for the increased nanoparticle yield, will be discussed and results of nanoparticle assembly into pillars, nanowire and nanotrusses, will be presented. Matrixes of pillars assembled from Ag-nanoparticles are generated by the use of a grid in front of the substrate forming an electrostatic lens by applying suitable potentials on the grid and the substrate. By placing the grid on a movable stage, 3D-printing behavior can be achieved. In the synthesis of ferromagnetic Fe- and Ni-nanoparticles, the use of an external magnet placed behind the substrate promotes the self-assembly of the nanoparticles into wires and trusses, forming conducting nanostructures with large surfaces. The use of these structures in a electrocatalytic water-splitting experiment demonstrates the structures great potential for the use as different electrodes.

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Surface Engineering - Applied Research and Industrial Applications

Room Sunset - Session G3

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

Moderators: Heidrun Klostermann, Fraunhofer FEP, Holger Gerdes, Fraunhofer Institute for Surface Engineering and Thin Films IST, Mirjam Arndt, OC Oerlikon Balzers AG, Liechtenstein

1:30pm **G3-1 On the Synergies Between Coating and Tool Material Substrate: A Strategy to Optimize Coated Tools Performance in Cold Forming***, D Casellas,* Fundació CTM Centre Tecnològic, Spain*; A Mueller,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; **Giselle Ramirez**, M Vilaseca,* Fundació CTM Centre Tecnològic, Spain **INVITED**

In recent years hard coatings have acquired a significant importance in the microstructural and micromechanical design of tools and components. Among the wide range of surface modification techniques, PVD (Physical Vapour Deposition) is one of the most suitable routes to meet the demanding requirements of surface finish and dimensional tolerances that need some specific tools and components, such as those for the automotive sector. However, although thin films tend to reduce the wear mechanisms under service conditions, improved resistance against contact fatigue failure still remains a challenge. The latter has been emphasized in punching and forming processes, where the introduction of advanced materials (such as high strength steels, thick stainless steel strips, etc.) requires higher impact pressures than those used in conventional materials. In those cases, the load is mainly supported by the substrate. Thus, if any subsurface damage occurs in coated tools, then a premature detachment of the layer, or even more, chipping of material could be produced accelerating the wear damage mechanism.

Attempting to ensure the effective usage of coated steels under complex service conditions, where wear is accompanied by contact loads of cyclic nature, it is important to understand and document the interaction between coating and substrate of industrial components. Once the main

mechanism of damage is identified on cold forming tools, the following step is the selection of the optimum configuration of coating, interface and steel. But the selection process is not trivial task, and a wrong decision can produce bad experience in the application of coating technology. Recent studies have demonstrated that topography and mechanical properties of the PVD coated surfaces is strongly dependent on the tool steel microstructure as a substrate. This was mainly attributed to a difference in sputtering rates of phases and the metal-matrix of steels during ion etching process, and also due to the size, morphology and structure type of primary carbides.

The main objective of this work is to address the interaction between tool steel and thin coating during cold forming and discern the most relevant microstructural and topographical aspects leading to high tool performance. Detailed microstructural analysis will be complemented with industrial tool behavior to properly understand the synergies between coating and tool material substrate.

2:10pm **G3-3 Deposition of ta-C Coating by Arc Ion Plating for Machining of Al Alloys***, **Yoshiyuki Isomura**, T Takahashi, S Kujime,* Kobe Steel, Ltd., Japan

Al-alloy is soft metallic material and exhibits good machinability. However welding adhesion and building-up edge (BUE) tend to form easily at a surface of cutting tool due to its low melting point. To prevent the formation of BUE, dry cutting tool for Al-alloy requires high resistance against welding adhesion. For this purpose Diamond-Like Carbon, DLC, coating draws a great practical attention. DLC is known to exhibit low friction and high resistance to welding adhesion. Among various types of DLC coatings practically available in recent years, hydrogen free DLC, also referred to as ta-C, tetrahedral amorphous carbon, shows high sp3 content and hence high hardness as compared to conventional hydrogen containing DLC coatings.

In this study, we deposited ta-C coatings by cathodic arc process, also referred to as arc ion plating, in a middle sized industrial coating unit. The unit was equipped with a round-bar type cathode with a typical target diameter of 20 mm. Pure graphite was used as the target material. ta-C coatings were deposited at different bias voltage and film thickness. The sp3/sp2 fraction, hydrogen content, and film density were studied by XPS, RBS, and XRR method, respectively. These coatings were also deposited on cutting tools for machining of Al alloys. Correlation of the film properties to cutting performance is discussed.

2:30pm **G3-4 Laser Structured High Performance PVD Coatings for Injection Molds***, K Bobzin, T Brögelmann, N Kruppe, **Mona Naderi**,* Surface Engineering Institute - RWTH Aachen University, Germany

Structured plastic components, which are used for flow-optimization, self-cleaning surfaces and optical applications, are usually produced by injection molding using structured tools. A suitable technique for structuring is laser ablation, which offers a high level of accuracy and flexibility. Moreover, the dimension of structures fabricated by laser in the order of a few micro- and nano-meters can significantly change surface properties such as topography, mechanical properties and wetting. Specifically, adhesive and abrasive wear of the mold surface are important failure mechanisms in plastics processing. The key to overcome the aforementioned challenges is to modify the surface of the mold using innovative surface engineering such as physical vapor deposition (PVD). However, coating deposition on nanostructures leads to a decisive change in the surface topography and the surface functionality. For this reason a direct structuring of PVD coated tools is beneficial.

This work deals with the influence of laser structuring on the properties of nitride and oxinitride chromium-based coatings. For this purpose, three coatings with different chemical composition were synthesized on tool steel AISI 420 (X42Cr13, 1.2083) by means of high power pulsed magnetron sputtering process. The coatings were structured by means of ultra-short pulsed laser under variation of the parameters, such as pulse energy, repetition rate of laser and structuring speed. It could be observed that a decrease of the laser intensity results in a reduction in the structural depth observed with scanning electron microscopy. This, on the other hand, leads to a decrease of the surface roughness measured through confocal laser scanning microscopy. Structural changes at the surface of the coating as a result of thermal effects during laser structuring were characterized using Raman spectroscopy and in-situ high-temperature X-ray diffraction.

Based on the results of the laser-surface interaction one set of laser parameter was selected. With these parameters, the samples were structured over a large area for the tribological investigations. On these samples, friction behavior was measured by using a pin on disc tribometer in contact with polycarbonate and polymethyl methacrylate. Furthermore, the wetting behavior of plastics melts on the structured coatings was investigated by means of high temperature contact angle measurements. The shear energy while shearing the solidified plastics from the surface was determined. The results for the structured coatings are promising with regard to the production of optical plastics components.

2:50pm **G3-5 Effect of Layer Sequence on Wear Behavior of AlTiSiN Hard Coatings***, **Joern Kohlscheen**, C Bareiss,* Kennametal GmbH, Germany*; C Charlton, D Banerjee,* Kennametal Inc., USA

The aim of this study is to understand the effect of different silicon contents and layer sequences on the resulting wear behavior of AlTiN based coatings. Deposition was done in an industrial scale PVD unit using cathodic arc evaporation of AlTi and TiSi materials. Silicon contents ranging from 3 to 15 at. % (metal fraction of the nitride compound) were adjusted. Monolithic and multilayers were deposited keeping the coating thickness between 3 to 4 micron. Coating hardness and elastic modulus were determined by nanoindentation. Adhesion and toughness were characterized by indentation with a diamond tip. Film structure and chemistry was determined using EDX and XRD. In some cases TEM images were prepared to clarify film structure in the nanometer range. Using fatigue testing at room temperature and T ~ 700 C it could be shown that multi-layers tend to be more wear resistant especially for moderate silicon contents below 10 at. %. In order to tailor the wear resistance in the contact zone of a cutting tool, we varied the silicon content and selectively removed the outer layer to obtain harder and tougher zones at the flank and rake face of carbide inserts (ISO K grade). Turning of high strength cast iron material was performed to show the beneficial effect of this method. The resulting wear patterns will be discussed.

3:10pm **G3-6 Structural, Mechanical, and Cutting Properties of AlCrN Coatings Deposited by Arc Ion Plating***, N Ohba, T Takahashi, **Susumu Kujime**,* Kobe Steel, Ltd., Japan

High aluminum containing transition metal nitride such as AlCrN and AlTiN has widely been used for cutting tool application due to their high hardness and oxidation resistance at elevated temperatures. The intrinsic properties of the coatings, and hence cutting performance thereof is highly dependent on Al content and its crystallographic structure. It is of practically significance to increase Al content in the coating in a vacuum deposition process whereas the metastable cubic phase is preferred to be remained and the possible formation of AlN hexagonal phase should be suppressed during deposition as well as cutting operational condition.

In this study we investigate the correlation between deposition conditions, coating properties, and cutting performance. AlCrN coatings were deposited by cathodic arc, also referred to as arc ion plating. As for coating process we employed new industrial arc ion plating system having a reasonably compact batch volume for production, but yet high productivity. Al content x in $Al_xCr_{1-x}N$ was systematically varied by changing the target composition from 65 up to 73 at at.% Al. Bias voltage of 40, 70, and 150 V were applied at a given composition of Al. The structural, compositional, and mechanical properties of the coatings were studied by X-ray diffraction, SEM-EDX, as well as nanoindentation. Residual stress of the coating was also evaluated from curvature measurement of a plate sample. For cutting test evaluation the depositions were also performed on micro-endmills with a diameter of 1 mm. Cutting performance with respect to the coating properties will be discussed.

3:30pm **G3-7 Physical Properties and Cutting Performances Relation to Coating Conditions of AlCrN Coating Deposited by HiPIMS and Cathodic Arc***, **Keizo Tanaka**, S Imamura, M Setoyama, H Fukui,* Sumitomo Electric Hardmetal Corp., Japan

Recently Aluminum Chromium Nitride (AlCrN) coating is widely used in cutting tool industry. And HiPIMS technology has been seen as a probable alternative to the cathodic arc technology. In this study, physical properties and cutting performances was examined and the results explained in terms of coating conditions compared HiPIMS to cathodic arc technology.

HiPIMS coating showed valuable surface morphology, hardness ; 22.9 to 41.6GPa, compressive residual stress; 0.3 to 3.3GPa by bias voltage ; 30 to 100V, peak pulse power ; 30 to 60kW and nitrogen partial pressure.

HiPIMS coating showed higher hardness and more stable tool damage than cathodic arc by higher bias voltage or higher peak pulse power. These results were considered argon ion bombardment assist during film deposition. This consideration indicates further usability of HiPIMS technology in cutting tool industry.

4:50pm **G3-11 Nanoscale Multilayer PVD Coatings to Serve in Demanding Environments**, ***Papken Hovsepian***, *A Ehiasarian,* Sheffield Hallam University, UK **INVITED**

Superlattices were discovered in 1925 by Johansson and Linde as periodic structures of layers of two (or more) materials. In 1970 J.S. Koehler theoretically predicted that if these materials were selected to be with high and low elastic constants a super strong man made material could be produced. Various theories and models have been put forward to explain the super hardening and super toughening effects and a large variety of coatings have been explored both on laboratory and industrial scale. This work summarises results on the properties and performance of novel nanoscale multilayer structured coatings produced by High Power Impulse Magnetron Sputtering, (HIPIMS) dedicated to serve in demanding environments.

To protect Gamma-TiAl components used in automotive and aero engines against environmental attack dense oxide forming elements such as Cr and Al were combined to produce **CrAlYN/CrN** nanoscale multilayer coatings. Coatings with very low layer waviness and strongly improved density have been successfully grown by HIPIMS. These coatings provide excellent oxidation resistance up to 850°C and reduce the fatigue deficit of the aerospace turbine blade material to less than 9%.

TiAlCN/VCN represents a new class of superlatice coatings where enhanced performance is achieved by lateral segregation of small atom material (in this case Carbon) at the interfaces between the individual layers producing low shear strength interfaces. These coatings provide excellent tool protection against build-up edge formation during machining of Aluminium alloys, Titanium alloys and MMCs widely used in aerospace and automotive applications.

In **Me doped Carbon films** a unique nanoscale multilayer structure was produced by unconventional method of coating growth based on dynamic segregation driven by intensive ion irradiation. By varying the ion energy and ionisation degree, layered structures with bi-layer period of up to 25 nm were grown. With Cr/C and Mo-W doped Carbon nanoscale multilayer films enhanced tribological performance in boundary lubricated conditions at elevated temperatures, (up to 200°C) was achieved. Smart material selection allowed *in- situ* formation of lubricious phases at the asperity contacts due to tribochemical reactions between the dopants and the oil and improved the coatings high temperature stability.

CrN/NbN combining the electrochemically stable Nb with the wear resistant Cr was initially developed as a replacement of hard Cr, however its unique properties allowed the coating to be used in many other demanding applications described here.

CrN/NbN provided reliable protection against high pressure, (50 bar) , high temperature, (600°C) pure steam attack on P92 steel used in steam turbines and showed high resistance against water droplet erosion. Furthermore, the coating did not deteriorate the mechanical properties such as Ultimate Tensile, Low Cycle Fatigue and Creep Strength, which is of paramount importance in turbine blade applications.

The performance of medical implants was enhanced by the application of **CrN/NbN** coatings. Metal ion release studies showed a reduction in Co, Cr and Mo release at physiological and elevated temperatures to undetectable levels (<1 ppb). Thorough *in vitro* biological, cytotoxicity, genotoxicity and sensitisation testing proved the safety of the coating in biological environment.

Topical Symposia
Room Sunrise - Session TS4
Materials Modeling and Simulation

Moderators: Thomas Mussenbrock, BTU Cottbus, David Holec, Montanuniversität Leoben, Austria

1:30pm **TS4-1 From the Atomic Interaction to Thermodynamic and Mechanical Properties of Materials**, ***Ralf Drautz***, Ruhr-Universität Bochum, Germany **INVITED**

Density functional theory (DFT) provides a solid basis for the simulation of materials properties. In some cases the computational expense of DFT makes the sampling of thermodynamic observables or the calculation of dynamic variables difficult. We coarse grain the interatomic interaction from DFT at two levels of approximation to allow for faster and larger simulations. First, a tight-binding model is derived from a second-order expansion of DFT in a minimal basis. The parameters in the tight-binding model are obtained directly from minimal basis DFT calculations. In a second step the tight-binding model is approximated locally and analytically, resulting in the analytic Bond-Order Potentials (BOPs). Because of the derivation of BOPs from DFT, the contributions of magnetism and charge transfer to bond formation are directly taken into account. The BOPs are orders of magnitude faster than DFT and allow for the direct sampling of thermodynamic observables.

I will discuss the application of the BOPs to simulating finite temperature magnetism in iron, in particular the ferromagnetic to paramagnetic phase transformation and the alpha-gamma transition and the prediction of some mechanical properties. I will further discuss atomic simulations for phase stability, nucleation and solid-solid transformations with relevance to high-temperature materials.

2:10pm **TS4-3 Molecular Dynamics Study of Titanium Oxynitride Surface Properties**, ***Tobias Gergs***, *J Trieschmann,* Ruhr University Bochum, Germany*; T Mussenbrock,* BTU Cottbus, Germany

Mechanical properties of metal oxynitride hard coatings depend on the preceding film growth through fundamental surface processes and thermodynamic driving forces. While the latter aspects were recently studied for titanium nitrides, the influence of substitutional oxygen requires further investigation. The absence of theoretical approaches reported in the literature is mainly due to unavailable purely classical potentials to describe titanium oxynitrides. A second reason might be computational limitations of ab-initio methods. So far solely the bulk properties have been addressed by means of density functional theory in the literature. Initially in this work, on the basis of these referenced calculations [1], the recently published COMB3 (3rd generation charge optimized many body) semi-classical potential for heterogeneous titania/titanium nitride systems is characterized and validated. Subsequently, the validated potential is utilized to systematically investigate the inherent thermodynamic driving forces for varying nitrogen/oxygen compositions at the surface. For this study, independent atom configurations are generated with a modified version of the combinatorial SOD (site-occupancy disorder) code, taking into account the broken symmetries of the (001), (110) and (111) surfaces. The resulting slabs are relaxed and characterized with the molecular dynamics code LAMMPS (large-scale atomic/molecular massively parallel simulator). With the validation of the semi-classical potential for titanium oxynitride and a discussion of the influence of a substitutional oxygen contribution, a first step towards the modeling of the corresponding film growth is presented.

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2:30pm **TS4-4 Distribution of O Atoms on Partially Oxidized Metal Surfaces According to Ab-initio Calculations, and the Consequences for Sputtering of Individual Metal Oxides**, ***Jiri Houska***, *T Kozak,* University of West Bohemia, Czech Republic

We investigate the oxidation of a wide range of metal surfaces by density functional theory. The metals of interest will include those studied in Ref. 1 (Al, Ag, Cu, Ti, Zr, Hf) as well as those studied more recently. We go through a wide range (235 per metal) distributions of O atoms on a partially oxidized metal surface. First, we focus on the qualitative information whether the preferred distribution of O atoms is heterogeneous (stoichiometric oxide + metal) or homogeneous (substoichiometric oxide). We find that the former is energetically preferred e.g. for Al, while the latter is energetically preferred e.g. for Ti, Zr and Hf. Second, we correlate these qualitative results with the known formation enthalpies of oxides of various compositions. Third, we provide the quantitative values of adsorption energies corresponding to the energetically preferred O atom distribution for various partial coverages of various metals by O. We find that the absolute values of the adsorption energies increase with the surface oxygen coverage e.g. for Al, and decrease e.g. for Ti, Zr and Hf. Fourth, we demonstrate one use of these results by presenting Monte Carlo simulations of sputtering. Fifth, we utilize the theoretical results in order to explain the experimental results, such as the time dependence of the magnetron voltage during sputter cleaning of oxidized metal targets (monotonous e.g. for Al but non-monotonous e.g. for Ti).

2:50pm **TS4-5 First-principles Study of Adsorption and Diffusion of Oxygen on the Surface of TiN, ZrN, HfN and the Effect of Al on Oxidation Resistance of TiN Coatings**, ***Fangyu Guo,*** Central South University, China

Using first-principles calculations based on the density functional theory, we systematically study the adsorption and diffusion behaviors of single oxygen (O) atom on the (001) surface of nitride coating s of TiN, ZrN and HfN. When adsorbing at the top(N) site, the adsorption energy of TiN is much lower than the value of ZrN and HfN. The O atom is more likely to stabilize adsorbed on the ZrN and HfN surfaces. The diffusion behavior of O atom is investigated through determining the minimum energy pathways (MEP) and diffusion barrier on the (001) surface of these metal nitrides. O atom tends to diffuse on the (001) surface from one top(N) site to neighboring top(N) sites via the hollow site for all the three nitrides. It is also found that diffusion of O atom on the (001) surface of TiN is easier than that of ZrN and HfN. On the three nitrides surface, the adsorption of O on the TiN(001) surface is most unstable. This is a good explanation for a experimental phenomenon that the oxide thickness of TiN is smaller than that of ZrN under the same oxidation conditions.

In order to further increase oxidation resistance of TiN coating, the third elements are added to the TiN coating. TiAlN is widely used as protective coating for cutting and forming tools due to the high hardness combined with good oxidation and wear resistance. We used the special quasirandom structure (SQS) approach to represent the random Nacl structure TiAlN systems and address the effect of Al on the oxidation resistance of TiN by means of *ab initio* molecular dynamics simulations. The forming process of oxides of TiAlN coatings was investigated at 1123k and 773k.

3:10pm **TS4-6 Metastable Phase Formation of Pt-X (X= Ir, Au) Thin Films**, ***Aparna Saksena,*** *Y Chien, K Chang, P Kuemmerl, M Hans,* RWTH Aachen University, Germany*; B Völker,* Max-Planck-Institut für Eisenforschung GmbH, Austria*; J Schneider,* RWTH Aachen University, Germany

The dependence of phase formation and mechanical properties on the chemical composition has been investigated for Pt-Ir and Pt-Au combinatorial thin films. Composition spreads are deposited at substrate temperatures ranging from room temperature to 950°C and are subsequently characterized using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning transmission electron microscopy (STEM), atom probe tomography (APT) and nanoindentation. The formation of a single, metastable Pt-Ir solid solution phase has been observed for all experimentally probed compositions and growth temperatures. Upon Ir addition to Pt the experimentally determined changes in lattice parameter and Young's modulus display the expected rule of mixture behavior which is in very good agreement with our *ab initio* data. Whereas, in the Pt-Au system, the single metastable solid solution phase is seen to decompose into two solid solution phases as the growth temperature is raised to ≥ 600°C. The lattice parameters of the single metastable phase grown at temperatures < 600°C increase linearly as Au is added, showing rule of mixture behavior in good agreement with *ab initio* predictions. However, the lattice parameters of the phases in the dual phase region are independent of chemical composition displaying phase formation behavior consistent with the CALPHAD results. The substrate temperature and chemical composition dependent phase formation in Pt-Ir and Pt-Au thin films can be rationalized based on CALPHAD calculations combined with estimations of the activation energy required for surface diffusion: The metastable phase formation during film growth is caused by kinetic limitations, where Ir atoms (in Pt-Ir) need to overcome an up to factor 6 higher activation energy barrier than Au (in Pt-Au) to enable surface diffusion.

3:30pm **TS4-7 From Plasmas Towards Surfaces: How Plasma Simulation Supports Materials Development**, ***Mark J. Kushner,*** University of Michigan, USA **INVITED**

New materials development and fabrication often have the goals of new functionality or smaller dimensions. In many cases, thermal or equilibrium processes are challenged to achieve this functionality. The inherent non-equilibrium reactivity available from low-temperature plasma materials processing addresses both the prospect of new functionality, by enabling new structures to be fabricated, and smaller dimensions, due to the precision available to plasma produced fluxes to surfaces. An example of achieving both new functionality and finer precision is plasma enabled atomic layer deposition (ALD) and atomic layer etching (ALE). The broad parameter space available to plasma enhanced materials processing has motivated integrated plasma-materials modeling to help narrow the scope. In this talk, contributions of modeling of plasmas and plasma-surface-interactions to the development of new functionality and greater precision will be discussed. Examples will be shared from the low pressure, modeling enhanced development of new plasma excitation schemes with the goal of customizing fluxes; and feature scale modeling for ALE and high aspect ratio processes. Modeling enabled insights to atmospheric pressure plasma functionalization of surfaces will also be discussed.

4:10pm **TS4-9 Numerical Estimation of Intrinsic Stress in Physical Vapor Deposited Thin-Films**, ***Anurag Chakraborty,*** *R Anderson, J Ash,* South Dakota School of Mines and Technology, USA*; F Kustas,* Arbegast Materials Processing and Joining Laboratory (AMP), USA*; S Ahrenkiel,* South Dakota School of Mines and Technology, USA

A method of numerically quantifying the intrinsic stress estimates has been developed for physical vapor deposited thin-film coatings prepared at 250°C. This method involved constructing a prototype of a dedicated optical setup for measuring the curvatures of thinly coated samples with a film thickness ranging from 3-5 microns. A portable fixture was made which was clamped onto the translation stage of an optical microscope and this could be potentially usable with any commercial microscope that has 40 mm or more of vertical stage travel. Characterizations were performed on the optical instrument to enhance the sensitivity of detecting curvature changes over a given range of radii for the samples. The optical setup is compatible with reverse-mounted thin-film samples across a range of radii and it was modeled in Autodesk Inventor. A finite element model was developed in Abaqus where the deformation due to the residual stress in the thin-film sample was modeled as a pure thermal load. Subsequently, the initial stress state parameter was incorporated into the original model and systematically varied until the finite element model showed a deflection and a curvature which was in the range of 1-3% of the actual values obtained from the optical setup. The difference in the S11 and S22 principal stress values generated by the two models could be considered as equivalent to the actual intrinsic contribution to the eventual residual film stress in the coating responsible for the physical deflection. A test model with fixed constraints in Abaqus was also developed to capture the pre-deformed state of stress. Finally, this method was used to observe the intrinsic stress variations across 20 samples which were placed in a rectangular array formation over an 8" by 6" area of an aluminum supporting plate as a function of their separation distance from the target material. All 20 coatings were developed in a single deposition run to eliminate the process variables from having a non-uniform impact on the intrinsic stress development.

4:30pm **TS4-10 Modeling of UHMWPE Surface Texture for Reducing Wear on a Knee Prosthesis**, ***Tomas De la Mora Ramírez,*** Universidad Autónoma Metropolitana, Mexico*; I Hilerio Cruz,* Universidad Autónoma Metropolitana- Azcapotzalco, Mexico*; M Doñu Ruiz,* Universidad Politécnica del Valle de Mexico, Mexico*; N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico*; E García Bustos,* Universidad de Guadalajara, CUCEI, Mexico, México*; D Maldonado Onofre,* Tecnológico de Estudios Superiores de Jocotitlán, Mexico

The objective of the research is to improve tribological properties of UHMWPE through the morphological modification of its surface texture with the analysis of stress distribution, contact stress, volume loss and coefficient of friction. Test specimens were made through 3D printing to produce hexagonal geometric textures at depths of 18, 25, 36 and 50 micrometers at different geometric densities with respect to a uniform distribution on the surface of the specimen of 5, 10, 20 and 40%. Microabrasion tests were performed using a UHMWPE specimen and a ball of 52100 steel material one inch in diameter. Throughout 3D perfolometry the wear rate and the wear constant of the test specimens with and without texture were obtained. A dynamic simulation was performed by finite element analysis of the tribometer microabrasion test using a subroutine in fortran language linked to Abaqus V6.12 finite element software. With the simulation a rate of wear is obtained; comparing with the experimental results. With the experimental results and the simulation the subroutine was applied to predict its lifetime.

4:50pm **TS4-11 Perturbation Analysis Of Glassy Alloy Film Formation**, ***Rahul Basu,*** Adarsha Insitute of Technology, VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated incorporating surface convective effects. These equations which are non linear due to the moving interface are linearised and decoupled. Effects of the Biot, Fourier and Stefan numbers are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for

several alloys in various groups of the Periodic Table. Earlier work by Duwez (1) and Spaepen & Turnbull (2) is analysed in light of the present analysis.

References:

1) P. Duwez, Annual Review of Materials Science, 1976

2) F Spaepen and D Turnbull, Scripta Met, 8,563, 1974

5:10pm **TS4-12 First Principles Study of the Nb-Al Intermetallic System**, ***David Holec***, Montanuniversität Leoben, Austria; *N Koutna,* TU Wien, Institute of Materials Science and Technology, Austria; *K Preininger, S Zoehrer, R Franz,* Montanuniversität Leoben, Austria

Physical-vapour-deposited materials exhibit a variety of interesting and useful properties. Often, however, the actual behaviour strongly depends on the specific synthesis method and conditions. For revealing such synthesis-property relationships, understanding of the deposition process, which in turn is influenced by the target material used for the deposition, is critical.

In this contribution we will use first principles calculations to assess the stability of phases in a model binary intermetallic Nb-Al system. The convex hull constructed using the USPEX code yields Al_3Nb and $AlNb_2$ as the stable phases along with $AlNb_3$ being slightly metastable. These phases appear in published phase diagrams, in which the $AlNb_3$ is nevertheless a stable phase. Surprisingly, the reported compositional window for $AlNb_3$ does not contain the nominal x=0.75 composition.

Cohesive energies are calculated as representatives for the bonding strength and hence ease of the evaporation during an arc evaporation process. Additionally, we propose to use vacancy formation energies instead of cohesive energies as they provide species-specific information as well as their temperature dependence can be estimated. The vacancy formation energies are further on studied as a function of distance from the surface as well as the surface orientation. A correlation with experimental measurements of cathodic arc behaviour is attempted.

Topical Symposia
Room Royal Palm 1-3 - Session TS5
Anti- and De-icing Surface Engineering

Moderators: Alina Agüero Bruna, Instituto Nacional de Técnica Aeroespacial (INTA), Jolanta Klemberg-Sapieha, Polytechnique Montréal

1:30pm **TS5-1 Multi-step Modification of TI-Alloy and Stainless Steel Surfaces for Icephobic Applications**, ***Stephen Brown***, *J Lengaigne, A Riera, L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

In-flight component icing is a major issue in aerospace as it can lead to component failure or even cause aircraft to crash. While active solutions to icing such as heating and pneumatic boots do exist, a passive solution is desirable to avoid the additional weight and energy requirements of these systems. Superhydrophobic surfaces have been shown to reduce ice adhesion compared to bare metal surfaces; as such there is much interest in the modification of components to render them superhydrophobic.

In the present study, we look at a technique to modify the surfaces of Ti-6Al-4V and stainless steel substrates, to give them the hierarchical micro- and nano-scale roughness required for superhydrophobicity without invoking complex and costly processes such as photolithography. The desired morphology is obtained through a two-step process: samples are first sandblasted with alumina particles, and are subsequently etched in SF_6 plasma with a stainless-steel mesh placed directly on the sample to serve as a mask. The sandblast step induces a micro-scale roughness on the sample surface; the etching step adds more organized micro-scale features in the form of consistently sized and spaced pits, as well giving the surface nano-scale features. Mesh sizes as well as etching times are taken into consideration. Surface roughness remains relatively low after etching, with R_a < 5µm, and R_z < 30 µm. After coating with a fluorocarbon by thermal evaporation, the surfaces are rendered superhydrophobic with static water contact angles up to 170° and contact angle hysteresis as low as 6°.

1:50pm **TS5-2 Design and Characterization of Super-low Ice Adhesion Surfaces**, ***Zhiliang Zhang***, Norwegian University of Science and Technology (NTNU), Norway

Preventing the formation and accretion of ice on exposed surfaces is of great importance for Arctic operation, renewable energy, electrical transmission cables in air and shipping. While studies on suppressing ice nucleation by surface structuring and local confinement are highly desired, a realistic roadmap to icephobicity for many practical applications is perhaps to live with ice, but with the lowest possible ice adhesion. From the viewpoint of fracture mechanics, the key to lower ice adhesion is to maximize the ice-substrate interface-crack driving forces at multiple length scales. Herein, we present a novel macro-crack initiator mechanism in addition to the nano-crack and micro-crack initiator mechanisms, and demonstrate a new strategy to design super-low ice adhesion surfaces by introducing ordered sub-structures into smooth durable PDMS coatings to ultimately weaken ice-substrate interface [1]. Our results show that PDMS (weight ratio 10:10) thin films with 1 mm inner holes in two layers approach an ice adhesion strength of 5.7 kPa. The introduction of sub-structures into PDMS thin films promotes macro-crack initiators, and is able to further reduce ice adhesion strength by ~50% compared with that of PDMS thin films without sub-structures, regardless of layer thickness, curing temperature, weight ratio and the size of inner hole. Therefore, rationalizing the three crack-initiator mechanisms and their interactions at multi-length scales may provide an effective strategy towards designing super-low ice adhesion surfaces.

Reference:

[1] Zhiwei He, Senbo Xiao, Huajian Gao, Jianying He and Zhiliang Zhang, Multiscale crack initiator promoted super-low ice adhesion surfaces, *Soft Matter*, (2017) 13, 6562-6568.

2:10pm **TS5-3 Icephobic Nanocomposites for Aeronautics**, *F Martín,* ***Silvia Larumbe***, *M Monteserin, G Garcia Fuentes,* Asociación de Industria Navarra, Spain; *J Mora Nogues, P García Gallego, A Agüero Bruna, R Atienza,* INTA, Spain

Ice Protection Systems (IPS) are remarkable and essential parts of aircrafts since the formation of ice undergone in extremely hard conditions could give rise to the lack of the controllability of the aircraft. Traditional deicing systems suppose expensive and complicated systems that demand a very careful maintenance [1]. Moreover, the complexity of some of these systems makes them difficult to accommodate in small-medium aircraft. The need of seeking new systems with advantages like costs, low power consumption, reparability and lightness entails a relevant challenge.

In this regard, different coatings based on nanocomposites have been developed as passive systems against ice formation [2]. The basis of these coatings is the additivation of a hydrophobic matrix (silicones) with inorganic nanoparticles creating a controlled microroughness in the surface responsible of the icephobic behavior of the final coating. The main features to control during the process are on one side, the dispersion of the inorganic nanoparticles and on the second hand the final roughness. For the first aim, the inorganic particles were dispersed ultrasonically using high surface particles to improve the final dispersability in the organic matrix and also the final concentration was adjusted to obtain an enough microroughness for the accomplishment of a superhydrophobic coating keeping a good final adherence of the coating.

Several coatings based on nanocomposites with silicone and fluorosilicone reinforced with high surface alumina nanoparticles were prepared onto Al6061 substrates with different concentration of particles. The final adherence was optimized through different chemical and physical approaches obtaining as result a better adherence after the imprimation of the bare substrate and the subsequent use of an anchoring coating. The measurement of contact angle, roughness, ice formation, ice adherence and resistance to erosion were some of the characterization measurements carried out for the different coatings. Good adherence, contact angles within the range of 110-150° were obtained depending on the final additive concentration, improvement of the erosion resistance and lower ice formation comparing with other hydrophobic materials were some of the features of the developed materials, revealing these coatings as a promising alternative to other conventional IPS.

Acknowledgements

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References

F.T. Lynch et al, *Progress in Aerospace Sciences* **37,** 669 (2001).

H. Wang et al, *Applied Surface Science***349,** 724 (2015).

2:30pm **TS5-4 Development of Hydrophobic/icephobic Poly (Dimethylsiloxane) Based Composite Coating for Application in Ice Protection**, ***Junpeng Liu***, *J Wang,* University of Nottingham, UK*; H Memon,* University of nottingham, UK*; T Barman, B Turnbull, K Choi, X Hou,* University of Nottingham, UK

Accretion of ice on the surfaces of various engineering products under severe temperature condition is known to cause adverse socio-economic impacts and may lead to disasters. Development on hydrophobic/icephobic coatings has attracted increasing attention in many industrial areas, especially in aerospace. Aiming for reducing energy consumption for ice protection, poly(dimethylsiloxane) (PDMS) based composite coating had been developed. Particulate phase was integrated into the coating to improve the hydrophobicity and de-icing performance of the coating, and to reduce the overall energy consumption on ice protection. Ice adhesion tests were performed using a centrifuge method with a glaze ice block frozen on the studied coating in an environment chamber with temperature of -5 °C, with un-coated aluminium plates as references. The durability of the coatings was evaluated by erosion test under pressurized water droplet impinging. The composite coating demonstrated a typical water contact angle of 153° indicating good hydrophobicity. The ice adhesion test results showed an average ice adhesion strength of 5.8 kPa between the ice block and the coatings which is much lower than that of aluminium references (152.7 kPa). The de-icing test result indicated that PDMS-based composite coatings would effectively remove the ice and had great potential for application in ice protection.

Acknowledgement:

This work was supported by CleanSky II EU initiative GAINS (Grant Agreement No: 671398). The work forms a part of the project to develop a suitable hydrophobic and icephobic coating on aircraft wing surfaces.

2:50pm **TS5-5 Correlation Between Room Temperature Characteristics and Ice Adhesion**, ***Jianying He***, Norwegian University of Science and Technology (NTNU), Norway

Ice adhesion strength is dependent on the surface properties, and surface wettability is often correlated with ice adhesion strength. However, these established correlations are limited to high ice adhesion and become invalid when the ice adhesion strength is low. In this work we carried out an experimental study to explore the relationships between low ice adhesion strength and room temperature surface properties [1]. A variety of room temperature properties of hydrophilic and hydrophobic samples consisting of both low and high ice adhesion surfaces were analysed. The properties investigated include water adhesion force, water wettability, roughness, elastic modulus and hardness. Our results show that low ice adhesion strength does not correlate well with water contact angle and its variants, surface roughness and hardness. Low elastic modulus does not guarantee low ice adhesion though surfaces with low ice adhesion always show low elastic modulus. Low ice adhesion (below 60 kPa) of tested surfaces may be determinative of small water adhesion force (from 180 to 270 μN). Therefore, measurement of water adhesion force may provide an effective strategy for screening anti-icing or icephobic surfaces, and surfaces within specific values of water adhesion force will possibly lead to a low ice adhesion.

Reference:

[1] Zhiwei He, Elisabeth T. Vågenes, Chrisrosemarie Delabahan, Jianying He & Zhiliang Zhang, Room Temperature Characteristics of Polymer-Based Low Ice Adhesion Surfaces, *Scientific Reports* (2017) 7:42181.

3:10pm **TS5-6 Impact Dynamics and Icing Behavior of Supercooled Water Microdroplets on Surfaces of Different Wettabilities Ranging from Superhydrophilic to Superhydrophobic**, ***Jacques Lengaigne***, Polytechnique Montreal, Canada*; E Bousser,* Polytechnique Montreal, UK*; A Riera,* Polytechnique Montreal, Canada*; D Batory,* Lodz University of Technology, Poland*; S Brown,* Polytechnique Montreal, Canada*; A Dolatabadi,* Concordia University, Canada*; L Martinu, J Klemberg-Sapieha,* Polytechnique Montreal, Canada

Atmospheric icing on aircraft is a significant danger during flight and leads to high additional costs for operators. Icing occurs when supercooled micrometric water droplets (SWD), impact surfaces and freeze. Icephobic coatings based on superhydrophobic surfaces are the most promising avenue to replace current energy intensive techniques such as heaters and de-icing fluids. However, their wetting behavior under SWD icing is not well explored.

In this work, we investigate the influence of wettability on the impact dynamics of supercooled microdroplets. Four surface types with different wettabilities (characterized by their water contact angle, θ) were studied: superhydrophilic θ=10°, hydrophilic θ=70°, hydrophobic θ=107° and superhydrophobic θ=173° . Realistic atmospheric conditions, leading to supercooled microdroplet freezing, were simulated in an icing wind-tunnel with a wind speed of 10 m/s, subzero temperatures (down to minus 18° C) and a mean droplet diameter of 40 μm. High speed imaging was used to capture the impact sequence of droplets on the different surfaces.

Impact dynamics show transition from wetting to bouncing when the surface becomes hydrophobic. However, in icing conditions the repelling behavior is only maintained for the superhydrophobic coating whereas droplets freeze on the other surfaces. Limitations of superhydrophobic coatings under SWD icing are also explored.

3:30pm **TS5-7 Quasicrytalline Coatings by HVOF to Improve the Ice Accretion and Durability in Aerostructures Components**, *R Muelas Gamo,* ***Julio Mora Nogues***, *P García Gallego, A Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Weather hazards, in particular icing conditions, are an important contributing factor in aviation accidents and incidents world-wide. Further advancements in mitigation of in-flight performance degradation are necessary. This problem is being studied following two strategies: active systems or de-icing once the ice has formed, and passive or anti-icing systems to prevent or retard accretion. Many different anti-icing strategies are currently being explored to find suitable long-lasting solutions such as surface engineering which can provide a better alternative by reducing or eliminating ice accumulation.

Quasicrystals (QCs) are metallic materials in nature but with similar properties to those of ceramic materials, such as low thermal and electrical conductivities, and high hardness. These materials exhibit five and seven fold rotational symmetries, which were forbidden according to the rules of classical crystallography. In particular, those that have low surface energy are good candidates to be employed as icephobic coatings. These types of coatings are used commercially instead of Teflon on frying pans as they do not scratch easily.

Al based QCs have been applied by High Velocity Oxyfuel (HVOF) thermal spray on typically used aeronautic materials such as Ti and Al alloys as well as steels. The coatings have been characterized and evaluated (adhesion, hardness, wetting angle and ice accretion in an Icing Wind Tunnel. Moreover surface modifications of the coating have been carried out by laser and machining in order to study the effect of the surface roughness and morphology on the ice accretion properties. The QC coating has been compared with an anti-icing commercial paint, and the result indicate a significant reduction of the ice accretion behaviour. Since the coatings are hard ($HV_{0.3}$: 550), a durable behaviour is expected.

The proposed solution is and will help eliminate the need for frequent on-ground de-icing procedures. This in turn will contribute to the reduction of cost, pollution and flight delay.

Special Interest Talk
Room San Diego - Session SIT

Special Interest Talk

5:45pm **SIT-1 Tracing the Recorded History of Thin-Film Sputter Deposition: from the 1800s to 2018***, Joe Greene,* University of Illinois at Urbana-Champaign, USA

Thin films, ubiquitous in today's world, have a documented history of more than 5000 years. However, thin-film growth by sputter deposition, which required the development of vacuum pumps and electrical power in the 1600s and 1700s, is a much more recent phenomenon. First reported in the early 1800s, sputter deposition already dominated the optical-coating market by 1880. Preferential sputtering of alloys, sputtering of liquids, multi-target sputtering, and optical spectroscopy for process characterization were all described in the 1800s. Measurements of threshold energies and yields were carried out in the late 1800s, and results in reasonable agreement with modern data were reported in the 1930s. Roll-to-roll sputter coating on flexible substrates was introduced in the mid-1930s and the earliest demonstration of sustained self-sputtering (i.e., sputtering without the introduction of gas) occurred in 1970.

The term magnetron dates to 1921 and the results of the first magnetron sputtering experiments were published in the late 1930s. The earliest descriptions of a parallel-plate magnetron were provided in a patent filed in 1962, rotatable magnetrons appeared in the early 1980s, and tunable "unbalanced" magnetron sputtering was developed in 1992. Two additional forms of magnetron sputtering evolved during the 1990s, both with the goal of efficiently ionizing sputter-ejected metal atoms: ionized-magnetron sputtering and HIPIMS, the later now available in several variants.

rf glow discharges were reported in 1891, with the first results from rf deposition and etching experiments published in the 1930s. Modern capacitively-coupled rf sputtering systems were developed and modeled in the early 1960s and a patent was filed in 1975 that led to pulsed-dc and mid-frequency-ac sputtering.

The purposeful synthesis of metal-oxide films goes back to at least 1907, leading to early metal-oxide and nitride sputtering experiments in 1933, although the term "reactive sputtering" was not used in the literature until 1953. The effect of target oxidation on secondary-electron yields and sputtering rates was reported in 1940. The first kinetic models of reactive sputtering appeared in the 1960s; high-rate reactive sputtering, based on partial-pressure control, was developed in the early 1980s.

While abundant experimental and theoretical evidence already existed in the late 1800s to early 1900s demonstrating that the sputtering process is due to momentum transfer through near-surface collision cascades, the concept of sputtering due to local "impact evaporation" continued in the literature into the 1960s. Modern sputtering theory is based upon a linear-transport model published in 1969.

No less than eight Nobel Laureates in Physics and Chemistry played major roles in the evolution of modern sputter deposition.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-1

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Qi Yang, National Research Council of Canada, Jyh-Ming Ting, National Cheng Kung University

8:00am **B1-1-1 Boon and Bane of Internal Interfaces and Microstructure Defects**, ***David Rafaja,*** TU Bergakademie Freiberg, Germany **INVITED**

The highest priority in materials technology is avoiding the material defects during the materials production. On the other hand, a targeted integration of microstructure defects into the materials structure can be as a very efficient tool for improving the materials properties. Still, when considering the defect engineering as a possible instrument of materials design, one should always distinguish between 'good' and 'bad' microstructure defects. In this contribution, several examples of microstructure defects and their impact on the properties of the thin films of nitrides and oxides of transition metals will be given with the emphasis on the production of metastable phases and on their stabilization at elevated temperatures by utilizing particular microstructure defects.

For titanium nitride coatings alloyed with aluminum it will be shown, how the partially coherent interfaces between adjacent crystallites can be formed in a deposition process and how the presence of such interfaces influences the hardness of the cathodic arc evaporated (Ti,Al)N coatings and the stability of metastable (Ti,Al)N having the rock-salt crystal structure. In this context, the role of the lattice misfit and the role of the microstructure defects like dislocations and stacking faults will be discussed. On the example of the (Ti,Al)N/(Al,Ti)N multilayers with partially coherent interfaces, the competition between the Gibbs energy and the strain energy will be illustrated.

As examples of metastable transition metal oxides, the $(Cr,Zr)_2O_{3+x}$ coatings deposited using reactive ion beam sputtering and the thin films of $(Zr,Ta)O_{2+x}$ deposited using radiofrequency magnetron sputtering will be addressed. For the first system, the solubility of zirconia in chromia driven by the microstructure defects and in particular the mechanisms of the incorporation of zirconium into the crystal structure of Cr_2O_3 will be discussed. For the second system, the deposition of oversaturated $(Zr,Ta)O_{2+x}$ having an orthorhombic crystal structure will be reported. For both oxide systems, it will also be shown, how the formation of nanocomposites and the presence of internal interfaces influence the thin films properties.

8:40am **B1-1-3 The Material (in) Dependency of Impurity Affected Thin Film Growth**, *F Cougnon, D Altangerel, R Dedoncker,* ***Diederik Depla,*** Ghent University, Belgium

It is a well-known fact that the growth of metal thin films by physical vapour deposition is affected by the presence of contaminants or impurities. This is understandable due to the high chemical reactivity of metal thin films. First results have already been reported in the earlier seventies of previous century. A surprising point when analysing this older work is the presence of a power law between the domain size and the impurity-to-metal impingement flux ratio. In this paper the correlation between the domain size on the one hand, and the impurity-to-metal impingement flux ratio was studied in more detail for different materials for metals (Cu, Cr, Al), binary alloys (NiCr, CuNi) and complex alloys (CoCrCuFeNi). The thin films were deposited by DC magnetron sputtering, and the impurity flux was controlled by leaking air in the vacuum chamber. The domain size was determined by XRD which permits also to study the thin film texture and the behaviour of the lattice parameter. The analysis revealed that a power law behaviour between domain size and the impurity-to-metal impingement flux ratio was valid for all studied materials. Further, the materials could be separated in two groups depending on the power law exponent, and some interesting textural changes could be observed. Moreover, a linear correlation between the lattice parameter and the impurity-to-metal impingement flux ratio was observed for most materials. This material (in)dependency is intriguing which asks for a rather general valid explanation. Some of the possible reasons for this behaviour will be discussed in this paper.

9:00am **B1-1-4 Stress in Sputtered Metal Thin Films: Dependence on Growth Rate and Pressure**, *T Kaub,* University of Alabama, USA*; Z Rao,* Brown University, USA*; G Thompson,* University of Alabama, USA*;* ***Eric Chason,*** Brown University, USA

Stress in sputtered films is a critical issue that affects the performance and lifetime of coatings. Many parameters play a role in stress evolution such as the growth rate, temperature, grain size and gas pressure. Therefore, a deeper understanding requires systematic studies combined with control and characterization of the microstructure. To address this, we have performed measurements of stress evolution in sputtered metal films at different growth rates and gas pressure. Metals with relatively high atomic mobility (Cu and Ni) were studied so that the effects of thin film growth and energetic particle bombardment could both be seen. This leads to a change in the dependence on growth rate at high and low gas pressures. The results are analyzed in terms of a model for stress evolution that includes both non-energetic and energetic processes.

9:20am **B1-1-5 Improved Ionization Fraction and Film Quality Using a Serpentine Linear Magnetron and a Modified HiPIMS Waveform**, ***Ian Haehnlein,*** *B Wu, I Schelkanov,* University of Illinois at Urbana-Champaign, USA*; J McLain,* Starfire Industries LLC, USA*; D Patel,* University of Illinois at Urbana-Champaign, USA*; B Jurczyk,* Starfire Industries LLC, USA*; D Ruzic,* University of Illinois at Urbana-Champaign, USA

High Power Impulse Magnetron Sputtering (HiPIMS) produces film qualities superior to that of Direct Current Magnetron Sputtering (DCMS) at the cost of deposition rate attributed to returned ions to the target surface. By altering the magnetic field strength over multiple magnetic confinement regions, or multiple effective regions, the magnetic field strength can be made to drop off by 90% within 5cm of the target surface. This allows for controlled electron loss producing escape paths for ionized target material by ambipolar diffusion. Introducing a timed lower potential positive polarity pulse following the main negative polarity high power pulse while operating in HiPIMS utilizes the escaped ions by further accelerating the ionized target material away from the target surface that would otherwise be trapped within the magnetic field.

Through modification of the magnetic field in a 12.7cm by 25.4cm linear magnetron, a decrease in the confinement parameter of the magnetron allows for an increase in deposition rate for Cu yielding average deposition rates for HiPIMS of approximately 5.6nm/s +/- 0.1nm/s. For the same power DCMS using a standard magnetic field configuration, deposition rate was 5.5nm/s +/- 0.1nm/s. An increase in ion to total particle flux fraction from 13% +/- 2% to 35% +/- 3% at the substrate surface was measured using deposition rate in a gridded energy analyzer (GEA) with the same discharge conditions in HiPIMS. Introducing a positive polarity kick pulse following the high power pulse showed an even further increase in deposition rate (~15%) attributed to the increased repulsion of ions following the pulse. The positive kick induces a potential that increases the flux and energy of ions. This resulted in a decrease in residual tensile stress to from 1000 MPa +/- ~150 MPa with standard HiPIMS to 350 MPa +/- ~50 MPa using modified HiPIMS. This work presents the effects of various magnetic field configurations along with the plasma density and deposition rate effects of a positive polarity pulse modified HiPIMS.

9:40am **B1-1-6 Microstructural, Mechanical and Erosion Properties of Cylindrical Magnetrons Sputter Deposited TiSiCN, TiAlVN and TiAlVSiCN Coatings on Inner Surface of Cylinder**, ***Ronghua Wei,*** *E Langa, J Lin,* Southwest Research Institute, USA*; W Zhao, L Li,* Beijing Sanju Enviro. Protect. & New Matls., China

In order to improve the erosion resistance of plunger valve expander, cylindrical magnetron sputtering (CMS) was used to deposit nanocomposite coatings. Three coatings of TiSiCN, TiAlVN and TiAlVSiCN were deposited via sputtering a tubular target made of either pure Ti or Ti-6Al-4V in a gas mixture of Ar+N2 with or without TMS (trimethylsilane, (CH3)3SiH). The TiSiCN coating was selected because it has been studied extensively in planar magnetron systems and it shows excellent erosion resistance, while TiAlVN and TiAlVSiCN, though less studied, also show good wear resistance. The coatings were initially deposited on stainless steel coupon samples that were mounted on the inner surface of carbon steel tubes that simulated the expander made of tungsten carbide (WC). After the depositions, the coating on the coupon samples were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD), nano-indentation, micro-indentation, RC indentation for the coating thickness, morphology, microstructure, hardness and adhesion. Then the coupons were erosion tested using 50 µm alumina at two incident angles of 30° and 90°. The microstructural analyses indicate that the coatings have a

nanocomposite structure consisting of nanocrystalline TiCN or Ti(AlV)CN with the grain size of 4-10 nm in a matrix of amorphous Si-C-N. These coatings are fairly hard in the range 20-30GPa. They also showed excellent erosion resistance. Based on the test results, two actual WC valve expanders were deposited with TiSiCN and TiAlVSiCN that will be tested in actual service. In this paper, we will discuss the design and characteristics of the cylindrical magnetron, the deposition process of the TiSiCN, TiAlVN and TiAlVSiCN coatings, and the microstructure and the erosion resistance of the coatings.

10:00am **B1-1-7 Template Effect on Texture Evolution of VN Thin Films Deposited by Unbalanced Magnetron Sputtering**, ***Po-Chi Su***, *J Huang, G Yu,* National Tsing Hua University, Taiwan

The purpose of this study was to investigate the texture evolution of VN films deposited under the influence of Ti or V templates. Texture is a crucial factor in film mechanical properties, such as hardness and residual stress. Previous studies indicated that the texture of VN thin films can be controlled by nitrogen flow rate, substrate temperature, and substrate bias. At low temperature and high nitrogen flow rate (or low energy conditions), VN films showed loose-packed zone 1 columnar structure with (111) preferred orientation, while at high temperature and low nitrogen flow rate, the structure of VN films changed to zone T with dense columnar structure, and the texture became (200) prevailed. Since the atomic configuration of Ti (0002) is similar to VN(111), a Ti template layer with (0002) orientation was used to enhance the growth of VN(111). The goal is to change the microstructure of VN films with (111) texture from zone 1 to zone T, and further improving the mechanical properties of the VN thin films. On the other hand, the atomic configuration of V(110) is similar to VN(200), which may facilitate the formation of VN(200) texture. Thus, V template with strong (110) texture was applied to examine the texture evolution for the VN films deposited at conditions favoring the growth of (111) texture. By this way, the effect of template on the texture evolution of VN thin films can be evaluated. After deposition, the crystal structure and texture of the VN thin films were characterized using X-ray diffraction. The residual stress of the films was determined using laser curvature method. Film hardness and roughness were measured by nanoindentation and atomic force microscopy, respectively. The results showed that the Ti(0002) template may enhance the VN(111) texture, while V(110) template can facilitate the VN(200) preferred orientation. Based on the experimental results, the correlations between texture and different templates were explored.

10:20am **B1-1-8** ***IN SITU*** **High Resolution Stress Measurement Coupled with Interrupted Deposition in Case of Völmer-Weber Thin Film Growth**, ***Quentin Herault***, *S Grachev, J Wang, I Gozhyk,* Saint-Gobain Recherche, France*; R Lazzari,* Université Pierre et Marie Curie, France

Low melting point materials (Au, Ag, Cu) exhibit Compressive-Tensile-Compressive (CTC) stress behavior during deposition. A new high resolution *in situ* stress measurement approach allowed us to observe such a behavior during sputter-deposition of Ag in greater detail . With a help of periodic interruptions, we observed stress relaxation at different stages of growth and interpreted it by thermal effects and adatom diffusion. Thermal heating during deposition was estimated by direct measurements and appeared to be an important part of relaxation curve at most of the conditions. Due to interruptions, the tensile and compressive peaks shifted considerably indicating an impact on the percolation threshold. Interruption frequency and deposition parameters such as substrate bias, working pressure and magnetron power were varied in order to modify particles kinetic energy and surface phenomena in general. This novel approach in combination with high resolution of the curvature measurement provided a more detailed view on the nucleation of film and on the stress generation phenomena.

10:40am **B1-1-9 High-Frequency Properties of Soft Ferromagnetic Films on Cemented Carbide Substrates an Approach for Sensor Applications**, ***Stefan Beirle***, *K Seemann, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

The thermal and mechanical induced high frequency property changes of soft ferromagnetic Fe-Co-Hf-N films with an in-plane uniaxial anisotropy are promising for the application for sensor systems. For example, one can use the sensor signal to measure the cutting tool temperature during metal processing. Consequently, it is necessary to investigate how the soft ferromagnetic Fe-Co-Hf-N film interacts with a cemented carbide substrate, which is typically used for cutting tools, but consists itself of an approximate 10 wt% hard ferromagnetic Co phase.

In order to overcome the exchange interactions between the substrate and the ferromagnetic film, it is possible to predeposit a non-ferromagnetic buffer layer by varying the thickness from 0.5 µm up to 5 µm on the WC-Co substrate. For this purpose different hard coatings like Ti-N and Ti-Al-N and an electrically insulating Si-O buffer layer were investigated. The buffer layers were deposited by D.C. and r.f. magnetron sputtering. On top of the layers a 200 nm thick Fe-Co-Hf-N film was deposited. After film deposition the samples were annealed in a static magnetic field to induce a uniaxial anisotropy in the ferromagnetic film plane. In order to determine the static and dynamic magnetic properties of the film, MOKE measurements were carried out as well as the complex permeability was determined by a strip-line permeameter setup. The buffer materials show a different decoupling behaviour regarding the high frequency permeability due to different electrical and microstructural properties. The decoupled ferromagnetic films exhibited an in-plane uniaxial anisotropy of about 4.5 mT and a saturation polarization of 1.4 T which results into a measurable ferromagnetic resonance absorbance at a frequency of 2.2 GHz. The FWHM of the resonance line can be tuned by increasing the buffer layer thickness, but only in the case of the electrically insulating Si-O buffer layer material. This can be explained by the formation of eddy-currents in the electrically conductive substrate or Ti-N / Ti-Al-N buffer material. So, the high-frequency properties of the decoupled film system can be exploited for a mechanical stress and/or thermal sensor system.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B2-1

CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

8:00am **B2-1-1 Microstructure Investigation on CVD $Ti_{1-x}Al_xN$ Hard Coatings**, ***Ren Qiu***, *O Bäcke, M Hassine, M Halvarsson,* Chalmers University of Technology, Sweden*; D Stiens, T Manns, J Kümmel, V Janssen,* Walter AG, Germany

TiN with NaCl crystal structure has been widely used in hard coatings for cutting tool materials. By replacing the Ti atoms partially with Al, cubic $Ti_{1-x}Al_xN$ is formed which has attracted significant attention in the latest years due to its outstanding oxidation and wear resistances. In recent years, CVD (Chemical Vapour Deposition) has been used for the deposition of the $Ti_{1-x}Al_xN$ coatings which used to be produced by PVD (Physical Vapour Deposition). In this work, CVD $Ti_{1-x}Al_xN$ hard coating is grown on cemented carbide substrate pre-coated with TiN. Lift-out samples at different interesting areas are prepared by focused ion beam (FIB) microscopy. Local variation of the coating structures is studied by electron diffraction and high resolution (scanning) transmission electron microscopy (S)TEM imaging. Local variation of the chemical composition is investigated by the energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS). It is found that the content of the coatings varied periodically with high (~90 at.%) and low (~50 at.%) regions of Al. Both regions exhibit the fcc structure, which is the desired phase for hard coatings. The general microstructure appeared as a “fish-bone” structure with a 111 texture, with growth occurring on 001 faces, leading to a pyramidal surface morphology. The microstructural differences for varying growth conditions will be described.

8:20am **B2-1-2 Elaboration and Characterization of (TI,AL)N Coatings Deposited by Thermal CVD for Protection in Severe In-service Conditions**, ***Florent Uny***, *S Achache, S Lamri, G Raine,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France*; Z Dong,* Nanyang Technological University, Singapore*; M Pons, E Blanquet,* Université Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France*; F Schuster,* Commisariat à l'Energie Atomique et aux énergies alternatives (CEA) Saclay - Nogent International Center for CVD Innovation, France*; F Sanchette,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France

Ceramic hard coatings, especially TiAlN thin films received a good interest for several decades for protection of cutting tools owing to their high hardness and oxidation resistance [1]. While PVD deposition was widely investigated, only few literature are available on thermal CVD deposition of TiAlN coatings. Recent advances in CVD deposition showed the formation of nanocomposite coatings in an industrial deposition unit at pressure below 30mbar. These coatings, consisting of an arrangement of TiN and AlN lamellae, combine high hardness and good oxidation resistance [2], [3].

In this work, TiAlN coatings with varied Al-contents were deposited in an industrial CVD scale unit by means of ammonia and aluminum and titanium chlorides. Morphological and microstructural evolutions were characterized regarding the Al-content in the coating. A change in morphology, from globular grains to "cubic" grains was observed by increasing the amount of Aluminum in the film. This modification seems to be related to the appearance of the hcp-AlN structure. The influence of these morphological and microstructural changes on the mechanical properties and oxidation resistance was also characterized.

References:

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[2] J. Todt *et al.*, « Superior oxidation resistance, mechanical properties and residual stresses of an Al-rich nanolamellar Ti0.05Al0.95N coating prepared by CVD », *Surf. Coat. Technol.*, vol. 258, p. 1119–1127, nov. 2014.

[3] J. Todt *et al.*, « Al-rich cubic Al0.8Ti0.2N coating with self-organized nano-lamellar microstructure: Thermal and mechanical properties », *Surf. Coat. Technol.*, vol. 291, p. 89–93, avr. 2016.

8:40am **B2-1-3 Investigation of CVD-AlTiN Films with High Al Content**, ***Kenichi Sato**, S Tatsuoka, K Yanagisawa, T Ishigaki, K Yamaguchi,* Mitsubishi Materials Corporation, Japan **INVITED**

Recently, Aluminum Titanium Nitride (AlTiN) films deposited by thermal CVD method (CVD-AlTiN) has attracted cutting tools suppliers because some research groups have reported their good results in milling tests of alloy steels and cast irons. In this deposition method, ammonia gas is used as nitrogen source. One of the most interesting characteristics of CVD-AlTiN films is the amount of Al. It is higher than that of AlTiN films deposited by PVD method. It is well-known that conventional AlTiN films deposited by PVD method have cubic structure in the range of Al content lower than about 0.7, while they obtain hexagonal structure in the range of Al content higher than 0.7. However, CVD-AlTiN films keep cubic structure in Al content higher than 0.7, which prevents their cutting properties from getting worse. The amount of Al of AlTiN films is one of the most important factors which determine cutting properties, because it affects mechanical properties. For the last several years, the research on CVD-AlTiN films has made some progress, and some cutting tools suppliers have launched CVD-AlTiN films inserts which showed good cutting performance.

In this presentation, our works on CVD-AlTiN films with high Al content will be shown. We have focused on the influence of Al content on the characteristics of CVD-AlTiN films and the change of their structure and characteristics. As a result, we obtained CVD-AlTiN films with high Al content, about 0.85, which showed high hardness and interesting structure. From the result of Electron Backscattering Scanning Microscopy (EBSD), mis-orientation in grains was observed and the average value of Grain Orientation Spread (GOS) is bigger than that of conventional hard coatings. Also, nano-lamellae structure was observed by Scanning Electron Microscopy. We are going to discuss the growth mechanism of CVD-AlTiN films from our results. CVD-AlTiN films with these interesting characteristics showed better cutting performance than conventional CVD-inserts and PVD-inserts in our milling tests of ductile cast irons.

9:20am **B2-1-5 Microstructural Investigation of CVD Titanium Aluminium Nitride – Kappa Alumina Coatings**, ***Olof Bäcke**, M Halvarsson, H Petersson,* Chalmers University of Technology, Sweden*; D Stiens, T Manns, J Kümmel,* Walter AG, Germany

TiAlN is today a common choice for wear-resistant coatings on cutting tools used for metal machining due to its high hardness and excellent oxidation resistance. For long, physical vapour deposition (PVD) has been the standard method for producing commercial available TiAlN coatings. Using PVD it has been impossible to reach $Ti_{(1-x)}Al_xN$ coatings with a higher Al content than x = 0.65. A few years ago however a new low pressure chemical vapour deposition (CVD) technique was developed that makes it possible to deposit $Ti_{(1-x)}Al_xN$ coatings with a very high Al content, x = 0.9. These high Al content TiAlN coatings show improved hardness compared to other TiAlN coatings and commercially available CVD grown TiAlN coatings are just reaching the market. However, wear-resistant coatings often combine layers of different materials to improve properties, where one common candidate is alumina. It is thus of interest to investigate if CVD grown TiAlN can be combined with other materials in multilayered coatings. In this work, the focus has been on investigating the possibility of growing kappa alumina on CVD grown TiAlN. TiAlN multilayer coatings were produced on standard WC/Co cemented carbide substrates, where kappa alumina layers were grown on top of TiAlN layers with different texture. The coatings were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy (STEM and TEM), and energy dispersive X-ray analysis (EDX). Focus were on how the microstructure of the different textured TiAlN layers, which are metastable, changed when exposed to temperatures necessary for growing kappa alumina, and the texture of the grown kappa alumina. The results show that hexagonal AlN and cubic TiN can be found precipitated along grain boundaries in the TiAlN layers. The orientation relationships between TiAlN and kappa alumina layers were also described and a model for how the kappa alumina grains are growing on the TiAlN grains suggested.

9:40am **B2-1-6 Deep Electron Microscopy Investigation of $Ti_{1-x}Al_xN$/TiCN Multilayer CVD Coatings**, ***Mohamed Ben Hassine**, O Bäcke,* Chalmers University of Technology, Sweden*; D Stiens, T Manns, J Kümmel, W Janssen,* Walter AG, Germany*; M Halvarsson,* Chalmers University of Technology, Sweden

$Ti_{1-x}Al_xN$ is a well-established material for cutting tool applications exhibiting high hardness and excellent oxidation resistance. Recently, CVD has been used for the deposition of TiAlN coatings. The desired fcc phase of TiAlN is metastable and can be produced by CVD processes using ammonia (NH3) as a precursor. The Al/Al+Ti ratio in TiAlN is around 0.9 by CVD. This is thought to be beneficial for the oxidation resistance and performance of such coatings in metal cutting applications. Moreover, the combination of $Ti_{1-x}Al_xN$ with TiCN has attracted significant attention in the latest years due to its outstanding oxidation and wear resistances.

In this work, hard CVD coating of multilayer of $Ti_{1-x}Al_xN$ and TiCN is grown on cemented carbide substrate pre-coated with TiN. The microstructural development of $Ti_{1-x}Al_xN$ growing on TiCN is compared with TiCN growing on $Ti_{1-x}Al_xN$. A suite of electron microscopy and spectroscopy techniques was used to carefully examine the structure and chemical composition of the multilayer at different scales including grain size, texture and atomic resolution imaging. Aberration corrected scanning transmission electron microscopy (STEM) revels the presence of interfacial dislocations, twins, stacking faults and the formation of new interfacial phases. These results explain the different growth modes observed in the two multilayer systems.

10:00am **B2-1-7 Some Guidelines for the Determination of Texture Coefficients in CVD α-Al_2O_3 Coatings**, ***Rafael Stylianou**, M Tkadletz,* Montanuniversität Leoben, Austria*; M Penoy,* CERATIZIT Luxembourg S.à r.l., Luxembourg*; C Czettl,* CERATIZIT Austria GmbH, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

α-Al_2O_3 coatings deposited onto cemented carbide tools by chemical vapor deposition (CVD) are widely employed in cutting applications due to their excellent wear resistance, thermal stability and chemical inertness. Recent advances have allowed the control of their crystallographic texture, enabling α-Al_2O_3 coatings to benefit from the anisotropy in wear resistance across various orientations. Within this study, a comprehensive microstructure characterization of CVD α-Al_2O_3 coatings is presented, with the goal to provide useful guidelines for the determination of their crystallographic texture in the growth direction using texture coefficients determined by X-ray diffraction, as well as pole figures derived from X-ray diffraction and electron back-scatter diffraction. Texture coefficient calculations require the X-ray diffraction intensities from a θ/2θ scan of texturized coatings and non-texturized powder standards. Within this work, texturized coating intensities were determined for a representative sample (i.e. a CVD α-Al_2O_3 coating). Non-texturized intensities were retrieved, firstly from an equivalent coating turned into powder by chemically etching the substrate with HNO_3, and secondly from a corundum standard sample provided by NIST. Synchrotron intensity measurements have been performed for the non-texturized powder samples, and are used as a reference. In a next step, intensity data has been collected from four different X-ray diffractometers in parallel beam and Bragg-Brentano configurations, for both coating and powder samples. The calculated texture coefficients indicate a (001) growth texture, which was confirmed by pole figure measurements of the α-Al_2O_3 coating surface. Based on the results obtained, a simple set of guidelines is advised for the determination of texture coefficients: (a) X-ray intensity acquisition only for symmetric θ/2θ scans, (b) removal of X-ray background intensity, (c) introduce intensity corrections, that take into account the irradiated α-Al_2O_3 volume, corresponding to each diffraction angle value, (d) use of reflections that have a high peak to background X-ray intensity ratio, (e) exclusion of second order reflections at the presence of first order reflections, (f) texture coefficients provided should be accompanied by the respective

coating thickness due to its dependency, and (g) use of appropriate powder standards.

10:20am **B2-1-8 Hot Filament CVD Diamond and HIPIMS-Diamond Coating Technology on Cemented Carbide Substrates for Cutting Tool Applications**, ***Michael Woda***, *W Puetz, M Frank, S Bolz, W Koelker, O Lemmer, T Leyendecker,* CemeCon AG, Germany

Polycrystalline CVD diamond thin films are mainly deposited by means of either microwave or hot filament assisted CVD coating techniques. The later one being discussed here is a suitable coating method for cutting tools with complex geometries and is well established on an industrial scale. Besides addressing the basics of the coating equipment and deposition technology, this presentation discusses the results of case studies dealing with cutting applications on machining of various classes of highly abrasive materials with pure CVD Diamond thin films. These case studies include applications with Carbon fiber reinforced plastics (CFRP) systems for aerospace industry, zirconium oxides systems for dental applications up to direct milling of cemented carbide. In addition a novel class of coating materials which combines thin film HIPIMS and CVD Diamond is introduced. This merging of ultra-hard CVD diamond coatings and extremely dense and extraordinary smooth HIPIMS coatings creates the possibility of completely new cutting tool performance. The extreme hardness and excellent thermal properties of diamond is a clear benefit for the overall tool performance. The HIPIMS contribution provides excellent heat flow properties into the chips, serves as a well-suited protection mechanism at high cutting temperatures and improves the reduction of friction. Coating technology, film properties and application results for HIPIMS-Diamond coatings will be discussed in the scope of this work.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D2

Bio-corrosion, Bio-tribology, and Bio-tribocorrosion

Moderators: Anna Igual Munoz, Universitat Politècnica de València UPV, Steve Bull, Newcastle University, Nuria Espallargas, Norwegian University of Science and Technology (NTNU)

8:00am **D2-1 Magnetic Abrasive Finishing of Additively Manufactured Components for Biomedical Applications**, ***Hitomi Yamaguchi,*** University of Florida, USA **INVITED**

Additive manufacturing (AM), which produces components by depositing material, attracts attention in various fields, including medical device manufacturing. AM technologies have broken out of the traditional manufacturing paradigm, especially the manufacturing of complex components in small batches. Selective laser melting (SLM) is one of the most versatile AM processes, and it enables the production of components by binding powders. Components made using SLM have applications in a wide variety of industrial areas including aerospace, biomedical engineering, etc. However, the powder-consolidation mechanism in SLM influences the mechanical properties, surface morphology, and surface integrity (e.g., hardness and residual stress) of products and the corresponding product functions. Therefore, choice d of post-SLM processes, such as heat treatment and surface finishing processes, plays an important role in minimizing these defects and maximizing the component performance. This presentation describes the effects of these defects on surface geometry (roughness), surface integrity (residual stress), tribocorrosive behavior, and wear characteristics of the SLM-produced 316L stainless steel samples. Tribocorrosive behavior and wear characteristics investigated with 0.9% NaCl solutions and SLM-produced 316L stainless steel samples will be introduced.

A manufacturing technology called *Magnetic Abrasive Finishing* (MAF) has been applied for surface finishing of the 316L stainless steel SML-produced components. In MAF, ferrous particles are suspended by magnetic force and link together along the lines of magnetic flux in a magnetic field. The ferrous particle chains, connected by magnetic force, enable a flexible configuration. This unique behavior of the ferrous particles allows the application of the finishing operation not only to easily accessible surfaces but also to areas that are hard to reach by conventional mechanical techniques, such as freeform components (e.g., knee prostheses) and the interiors of capillary tubes (e.g., needles) and flexible tubes (e.g., catheter shafts). The ability of MAF to alter the surface roughness and change the residual stress from tensile to compressive was demonstrated. This presentation describes the fundamentals of MAF and its processing characteristics and mechanisms.

8:40am **D2-3 Investigating Some New Coatings to Improve the Modular Junction of Total Hip Prostheses**, *S Ehsani-Majd,* Mines Saint-Etienne, France*; V Fridrici,* Ecole centrale de Lyon, LTDS, France*; C Desrayaud,* Mines Saint-Etienne, France*; P Kapsa,* Ecole centrale de Lyon, LTDS, France*; A Boyer,* ***Jean Geringer,*** Mines Saint-Etienne, France

Hip replacement surgeries affect approximately 160'000 patients a year in France, 600'000 in the US and more than 1 million all over the world [1]. The main concern for both patients' health/quality of life and economical reasons is the lifetime of the implants. Due to mechanical restrictions hip stem, femoral neck and metal back are made of metallic alloys. The main aim of the current work is to study the Ti-6Al-4V—Ti-6Al-4V contact under fretting-corrosion conditions to understand the modular junction behavior and to improve it. To do so, an in-house made device was used and the experiments were performed in bovine serum. Open circuit potential data, coefficient of friction (COF) and total dissipated energy data were obtained from electrochemical and mechanical results. The second aim is to investigate/introduce new surface coatings (diamond-like carbon (DLC) coating) to improve the durability of the modular junction material. The hard surface on hard surface junctions are very difficult to control while assembling the prosthesis during the surgical operations. Therefore, to avoid this hard-on-hard contact, new surface coatings are under investigation. Finding the right coating will considerably promote the lifetime of the implants.

The initial results, corresponding to Ti-6Al-4V—Ti-6Al-4V contact, highlight both tribological behaviors. The friction coefficient, the dissipated energy and the related A ratio (dissipated energy over total dissipated energy) emphasize both tribological behaviors. The A-ratio lower than 0.2 represents partial slip phenomenon, while the A-ratio greater than 0.2 represents gross slip regime. The goal is to define a transition map between partial and gross slip regimes about this typical contact. Some results are in progress related to Ti-6Al-4V—Ti-6Al-4V/DLC coating. The results highlight that the DLC1—Ti-6Al-4V or DLC5—Ti-6Al-4V contacts result in better tribological properties as compared to Ti-6Al-4V—Ti-6Al-4V contacts, hopefully. Although all the experiments were cautiously investigated in the similar experimental conditions, controlling the stick or slip regimes is unreachable to get some statements about gross slip or partial slip regimes. The ongoing results seem to emphasize that DLC5 involves lower total wear volume than the one related to DLC1 coating. Some additional investigations are in progress in order to assess this first tendency.

References

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9:00am **D2-4 Tribological Coatings on Titanium Alloy (Ti6Al4V) for Orthopedic Applications.**, ***Kai-yuan Cheng,*** University of Illinois at Chicago, USA*; N Pagan,* Auburn High School, USA*; M McNallan,* University of Illinois at Chicago, USA*; D Bijukumar, M Mathew,* University of Illinois College of Medicine, USA

Problems, including release of metal ions and inflammatory effects of wear debris, from Metal-on-Metal (MoM) artificial hip implants caused a major decline of this design in the market. After several recalls of commercial hip implant products, FDA issued warnings on MoM arthroplasty in 2010 and 2011. Since then, use of MoM implants in surgery have been rare. In this study, two proposed materials: solid state-carburized titanium and carbide-derived carbon(CDC), were synthesized on Ti6Al4V and examined for their corrosion, tribocorrosion, and biocompatibility properties. A preliminary conclusion is drawn for their use for this application.

In this study, there are four stages of experiments. **(1) synthesis:** Two carburization processes have been employed to produce specimens. For solid-carburized titanium, titanium alloy was buried in carburizing materials in a stainless steel crucible.The whole package was heated to 925°C in a box furnace for 48 hours. For CDC production, the titanium alloy pins were covered by graphite powder in an alumina crucible and heated to 1000℃ for 20 hours under flowing argon gas. Then, the carburized samples were chlorinated at 700°C for 5 minutes. After all production processes, specimens were characterized by x-ray diffraction and Raman spectroscopy. **(2) corrosion:** The electrochemical cells for corrosion and tribocorrosion experiments were similar. They contain a counter electrode, a reference electrode and the sample is the working electrode in bovine calf serum (BCS, 30 g/L) solution. **(3) Tribocorrosion:** The experimental set-

up is a combined hip simulator and electrochemical cell. The electrochemical tests were performed at open circuit potential and potentiostatic at -0.2 (V) condition. The experiment was performed for 3600 (s) with 16 (N) of applied normal force and 1(Hz) sliding frequency. **(4) Biocompatibility:** The biocompatibility test was performed with osteoblast cells (MG-63). Cell proliferation and cellular growth after 1, 3, and 6 days were analyzed using alamarBlue assay and Rhodamine phalloidine/DAPI staining.

Both treated samples experience more severe corrosion than untreated titanium alloy, which may result from crevice corrosion. However, results on both samples from the tribocorrosion experiments shows less wear-induced corrosion, and a lower wear rate and friction coefficient. Similar cell proliferation and confocal images indicate that biocompatibility is not affected by the treatment. The preliminary data shows that solid-carburized titanium and CDC have excellent potential for orthopedic applications. Further investigation of these materials is justified.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D3

Medical Devices, Biosensors, and Biodegradation

Moderators: Jessica Jennings, University of Memphis, USA, Robin Pourzal, Rush University Medical Center

9:20am **D3-5 Osteochondral Tissue Regeneration into Porous PCL Scaffolds With and Without Chitosan Coatings of 98% or 80% Degree of Deacetylation**, ***Caroline Hoemann***, George Mason University, USA; *J Guzmán-Morales, G Chen, J Rodriguez-Gonzales, E Jalali Dil, B Favis,* Ecole Polytechnique de Montreal, Canada; *J Henderson,* McGill University, Canada **INVITED**

Polycaprolactone (PCL) is a bioplastic currently under development as a bone void filler. According to 3-dimensional *in vitro* osteogenesis assays, porous PCL scaffolds are hydrophobic and non-osteogenic, but the inner pore surfaces can become osteoconductive when coated with chitosan, a linear cationic polysaccharide composed of 98% glucosamine and 2% N-acetyl glucosamine (98% degree of deacetylation, DDA). In this study we tested the hypothesis that osteochondral bone regeneration is accelerated *in vivo* inside porous PCL scaffolds when the surfaces are coated with 80% or 98% DDA chitosan. Experiments were carried out under ARRIVE guidelines and institutional ethics-approved protocols. Sterile cylindrical PCL scaffolds with 155 µm average pore diameter were created, and coated or not with Layer-by-Layer polyelectrolytes followed by a surface coating of 98% DDA chitosan (PCL-98); half of the PCL-98 scaffolds were additionally coated with 80% DDA chitosan (PCL-80). New Zealand White rabbits (N=7) were submitted to small sequential knee arthrotomies to create two 3 mm diameter, 2 mm deep drill holes per trochlea, that were press-fit with PCL, PCL-80 or PCL-98 scaffolds just below the bone surface, or left to bleed as surgical controls. Distal femurs were collected at 1 day (N=1) or 6 weeks (N=6) post-operative and analyzed by micro-computed tomography and by non-decalcified plastic histology for repair tissue characteristics. At day 1, blood clot filled all PCL scaffold pores and drill-only defects. At 6 weeks, micro-CT measures and histological scores showed significant bone repair in drill-only defects compared to initial defects. Both PCL and PCL-98 scaffolds showed a minor and similar degree of bone ingrowth into the pores at the bottom of the scaffold, and PCL-80 scaffolds induced a slight bone resorption at the edges. PCL-98 scaffolds specifically promoted cartilage repair resurfacing, with around 80% repair tissue covering the scaffold surface compared to ≤20% resurfacing of PCL-only and PCL-80. These data revealed that *in vitro* osteogenesis assays do not necessarily predict *in vivo* osteogenesis where complex factors (biofactor deposits, innate immune responses, multiple cell types, angiogenic and mechanical cues) all influence the regenerative response. This study generated new knowledge that PCL-only scaffolds have a similar capacity as PCL-98 scaffolds to allow vascular bone ingrowth in a trabecular bone environment, but have a significantly lower ability to support cartilage resurfacing of the scaffold in the synovial cavity environment. 98% DDA chitosan coatings improved chondroinductive properties of subchondral porous PCL scaffolds.

10:00am **D3-7 Vancomycin-Phosphatidylcholine Spray Coatings for Delivery of Antimicrobials from Implants**, ***Rukhsana Awais***, *B Barr, R Gopalakrishnan, J Jennings,* University of Memphis, USA

Research on point-of-care coatings applied to implant materials has shown that manually applied coatings can be loaded with antibiotics for infection control and control of biofilm formation at the surface of implant. While release of antimicrobials has been shown to be effective at preventing infection in vitro and in vivo, manually-applied coatings are difficult to apply uniformly. In this study spray coatings were deposited on stainless steel coupons at flow rate of 45 and 60 liters per minute with a capillary of inner diameter of 25 micrometers using an aerosol spray device. The objective of the study was to compare the elution rate of the antibiotic deposited as a spray coating with the manually applied coating. Vancomycin mixed with phosphatidylcholine was mixed with deionized water to form a uniform mixture. Coatings loaded with water-insoluble dye Oil-Red O dye was also used to visually inspect the homogeneity of coatings. Control coatings consisted of vancomycin mixed with phosphatidylcholine which were then manually applied to the surface of coupons. An elution study in phosphate buffered saline was conducted for seven days and vancomycin concentrations were determined using HPLC. . Evaluation of the results showed that there was a continuous release of the drug in PBS (phosphate buffered saline) over seven days compared to three day release from manually-applied coatings. A large burst of antibiotic was observed for manually-applied coatings, which was not present in spray-applied coatings. Spray coatings had a uniform distribution over the entire surface of interest, compared to manually applied coatings with varying thickness of deposition observed visually. Coatings remained on the surface for seven days when elution studies were performed with the addition of dye Oil Red O to Phosphatidylcholine in the absence of antibiotic. Our studies suggest that a spray coating method for antibiotic release may be more effective in the application of local antibiotic therapy as prevention for infection in orthopedic surgery. In future studies, methods to increase the amount of coating will be sought, as well as design of a portable hand-held unit.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Royal Palm 4-6 - Session E1-1

Friction, Wear, Lubrication Effects, and Modeling

Moderators: Albano Cavaleiro, University of Coimbra, Carsten Gachot, Vienna University of Technology, Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

8:00am **E1-1-1 Tribologically Induced Oxidation of High-purity Copper as a Function of Sliding Distance**, *C Greiner, S Becker,* ***Christian Haug***, Karlsruhe Institute of Technology (KIT), Germany

Tailoring the surface properties of a material for low friction and little wear has long been a goal of tribological research. Since the microstructure of the material under the contact strongly influences tribological performance, the ability to control this microstructure is thereby of key importance. However, there is a significant lack of

knowledge about the elementary mechanisms of microstructure evolution under tribological load.

In order to under how different elastic and plastic strains influence this microstructure evolution, both were systematically varied in high-purity copper samples. Scanning electron (SEM) and focused ion beam (FIB), electron back scatter diffraction (EBSD) and transmission electron microscopy (TEM) are applied to monitor the resulting microstructure changes.

Our results demonstrate that with increasing strain, the tribologically deformed layer grows deeper into the material. Also an influence on grain rotation and refinement mechanisms will be discussed in the talk.

These results strongly suggest that the amount of tribologically induced strain is a key elementary that needs to be addressed in future modelling of the microstructure evolution in tribological contacts.

8:20am **E1-1-2 Investigation on the Reason for Low Friction between Diamond-like Carbon Coating and Ti-6Al-4V under Fretting Conditions**, ***Haohao Ding***, *V Fridrici, P Kapsa,* Ecole centrale de Lyon, LTDS, France

Ti-6Al-4V / Ti-6Al-4V contacts submitted to fretting (for instance, in the contact between femoral stem and neck adapter in hip joints) present high adhesive wear and very high friction coefficient (around 1.0 – 1.2). Diamond-like carbon (DLC) coatings can be deposited on one of the contacting bodies to decrease friction and wear between two metallic parts in contact.

The objective of this paper is to investigate the reason for the low friction between the DLC coating and Ti-6Al-4V under fretting conditions with a

cylinder-on-flat geometry contact. Flats (rough and smooth) and the cylinder (rough) are made of Ti-6Al-4V. Flats were coated with DLC coating using PACVD. The coating thickness is around 2.0 µm. The nano-hardness and the elastic modulus reach 29 ± 4.5 GPa and 236 ± 24 GPa, respectively. Tests were carried out with the normal force of 250 N and the displacement of 20 µm. The evolution of surfaces of both the DLC coating and the Ti-6Al-4V counterbody was explored.

The results indicate that the friction coefficient decreases from around 0.5 to a lower value (around 0.1) during the running-in period, corresponding approximately to the first 100 cycles. After 100 cycles, rotating the cylinder (i.e., putting in contact a new surface from the Ti-6Al-4V counterbody with the already rubbed DLC coating) leads to a new running-in period. Moving the flat (i.e. putting in contact a new surface from the DLC coating with the already rubbed Ti-6Al-4V counterbody surface) results in a continuous low friction coefficient. Those mean that the surface state of Ti-6Al-4V after running-in is the key factor to the low friction. When the DLC coating and Ti-6Al-4V are put into contact, Ti-6Al-4V is adhered to the DLC surface. When the DLC coating starts to slide, more Ti-6Al-4V is abraded and adhered to the DLC. The energy required to break the metallic bonds in Ti-6Al-4V results in the high friction. During the running-in period, the worn surface of Ti-6Al-4V is gradually covered by a tribofilm, which is mainly composed of the worn-off Ti-6Al-4V with oxidization. Carbonaceous material is also observed on the tribofilm. The tribofilm and carbonaceous material separate the Ti-6Al-4V and DLC (impeding direct contact between the 2 counterbodies) and lead to the low friction. Furthermore, the coefficient of friction is higher when the roughness of the coated flat is higher. Cracks of DLC coating are observed on rough flat, but no cracks are observed on smooth flat, because the local contact pressure between asperities from rough flat surface and rough cylinder surface is higher than that between smooth flat surface and asperity from rough cylinder surface.

8:40am **E1-1-3 Tribological and Wettability Evaluation of Magnetron Sputtered WS-C/F Coatings**, ***Simone Pereira Rodrigues***, University of Coimbra, Portugal; *S Carvalho,* University of Minho, Portugal; *A Cavaleiro,* University of Coimbra, Portugal

The automotive industry produces a huge amount of mechanical components daily. Namely, the ignition systems need lubrication on their assemblage step, which their excessive use is nowadays a concern because of environmental/human risks. The lubrication tools in use are often stopped for maintenance due to either deficient distribution of the lubricant or high friction phenomena. The solution for these issues is the development of functionalized surfaces addressing both low friction/longer lifetime, due to an improvement of the wear resistance, and further special water/oil wettability properties to improve the lubricant application homogeneity. Two possible surface modification approaches can be used, separately or in synergy, as solutions for those problems: (i) surface structuring by anodization processes and/or (ii) deposition of self-lubricating coatings. In this work, the latter was explored by the optimization of the deposition of self-lubricant coatings based on TMDs, alloyed with carbon and fluorine (W-S-C/F).

WS-C/F coatings were deposited by magnetron sputtering in a reactive Ar/CF_4 gas mixture, from a WS_2 target. Different F contents up to 20 at.% were achieved by varying the CF_4 flow rate. The top-view/cross-section morphologies, the chemical composition/bonding, structure and wettability of the coatings were characterized by SEM, XPS, XRD techniques and water/oil contact angle measurements, respectively. The mechanical properties such as hardness, elastic modulus were as well performed through nanoindentation procedure and the adhesion by scratch testing. The tribological performance was evaluated at room temperature (RT) and at 200 ºC at 20N load against a 100Cr6 steel ball.

The F incorporation led to higher surface hydrophilicity of the coatings, with no effect on the oil wettability, behaviour which could be related to the decrease on the surface roughness. RT tribological tests showed that averagely all tested coatings have similar friction coefficient (COF mean value=0.06), however, both pure WS_2 and the highest F-containing coatings showed a very irregular friction curve at the first 5000 running cycles. Sudden increases of COF, followed by its progressive decrease down to very low values, were observed (0.04 for pure WS_2 and 0.02 for WS-C/F coating). Tribological testing at 200 ºC (dry conditions) showed the same trend, i.e. high F-doped coating reached a COF mean value of 0.016 compared to 0.030 for WS_2 coating. This was interpreted as a beneficial effect of F on increasing the interplanar basal distance of the hexagonal WS_2 tribolayer formed in the contact, decreasing the van der Waals bonding, with the consequent COF decrease.

9:00am **E1-1-4 Tribological Properties and Oxidation Resistance of WN_x Thin Films at High Temperatures up to 500°C**, ***Daniel Javdošňák***, *J Musil, Z Soukup, R Čerstvý, S Haviar, J Houska,* University of West Bohemia, Czech Republic

The paper reports on the structure, microstructure, mechanical properties, friction coefficient µ, wear rate k and oxidation resistance of the WN_x films; here x=N/W is the stoichiometry of nitride films. The films were reactively sputtered from a W target of diameter of 100 mm on Si(100) and Steel 15330 substrates in a mixture of $Ar+N_2$ gases using an unbalanced magnetron powered by the AC pulsed power supply. The properties of sputtered WN_x films were characterized by (i) X-ray diffraction (XRD), (ii) Scanning Electron Microscope (SEM), (iii) micro–indentation testing, (iv) pin–on–disk tribometry in wide range of temperatures T from room temperature (RT) up to 500°C and (v) ellipsometry. It was found that sputtered WN_x films are polycrystalline nanocomposites composed of either a mixture of low–T α-W and high–T β-W_2N the phases at x≤0.5 or high–T β-W_2N and low–T δ-WN the phase and exhibit: (1) high values of the hardness H, effective Young's modulus E^*, elastic recovery W_e increasing with increasing x up to 34 GPa, 0.13 and 88%, respectively, (2) the friction with Al_2O_3 ball (i) increases from 0.3÷0.4 at RT to 0.8÷1.2 at 200°C and (ii) decreases to 0.5÷0.6 at 400°C and sliding distance of 1000 m, (3) the wear with Al_2O_3 ball increases from 10^{-8} mm^3/Nm at T≤200°C up to ~2.5×10^{-6} mm^3/Nm at T ranging from 200 to 400°C. The WN_x films are completely removed from the substrate at T=500°C already at sliding distances of about 350 to 600 m due to formation of the WO_x scale on the coating surface.

9:20am **E1-1-5 Correlation between Evolution of Roughness Parameters and Micropitting of Carburized Steel Surfaces under Boundary Lubrication Condition**, ***Sougata Roy***, *D White, S Sundararajan,* Iowa State University, USA

This paper investigates the correlation between the evolution of the amplitude (R_a, R_{RMS}, R_{sk} and R_{ku}) and spatial (autocorrelation length) roughness parameters and micropit initiation and propagation during rolling contact fatigue (RCF) of carburized steel samples under boundary lubrication conditions. Steel samples with three levels of retained austenite or RA (~0%, 15% and 70% as measured by micro X-ray diffraction) were prepared for the RCF study which was conducted with a rolling-sliding contact in a micropitting rig. It was observed that run-in happened within an order of 10^4 cycles for all samples and during this period, a significant decrease in R_a and R_{RMS} occurred while the correlation length increased and stabilized. The low RA samples failed due to early crack initiation and rapid crack propagation. The medium and high RA samples showed initiation and propagation of micropitting during RCF life. Micropitting initiation and propagation were captured for the mid and high RA samples using an optical profilometer which utilizes a non-contact white light interferometry technique. Micropitting trends were then correlated with different surface roughness parameters. It was observed that, if surface change due to mechanisms other than micropitting is controlled, then R_a and R_{RMS} follow the same trend with the propagation of micropitting. Skewness can be used as a parameter to predict the initiation and propagation of micropitting; significant propagation resulted in a decreasing trend of skewness (negative) and increasing trend of kurtosis. Transverse directional correlation length also was found to be in agreement with the propagation of micropitting. It was observed that the correlation length decreased as micropitting progressed. The present study shows that drivetrain industries can track correlations with surface roughness parameters to predict the long-term performance of the components under the boundary lubrication regime.

9:40am **E1-1-6 The Influence of Temperature on the Wear Mechanisms of a Cobalt-based Alloy Contact Subjected to Fretting: from an Abrasive Tribo-oxydation Process to the Glaze Layer Response**, ***Alixe Dreano***, *S Fouvry, G Guillonneau,* LTDS - Ecole Centrale de Lyon, France

Cobalt-based alloys are widely used in the aeronautical industry for their good mechanical properties and corrosion resistance at high temperature. Vibrations, or other micro-displacements, of mechanical pieces initiate fretting and then lead to wear. Wear mechanisms of cobalt-based alloys are commonly known to be dependent on temperature. Above a transition temperature TGL, wear rate decreases and becomes very low given that a compacted and oxidized layer is spontaneously created in the contact ("glaze layer"). Below TGL, wear is severe and the tribolayer is not generated. The high-temperature layer has been thoroughly studied by many authors who associated its formation to the capacity of oxidized debris to sinter and adhere to the bulk metal.

The present study was focused on the change of wear mechanisms occurring through a range of temperatures (from ambient to 600°C). A cross-cylinders cobalt-based alloy against alumina contact was subjected to gross-slip fretting. The study showed that wear, before severe-to-mild wear transition, TGL, is controlled by the continuous oxidation of the interface and is therefore strongly influenced by the operating temperature and frequency of solicitation. An analytical wear law was developed in order to describe the wear mechanism below TGL. The dependence of TGL on frequency was also outlined and associated to the capacity of debris to sinter. Finally, to completely describe the behavior of the tribocouple, the mechanical response of the glaze layer is discussed in the light of the results of in-situ compression of micro-pillars cut into the glaze layer.

10:00am **E1-1-7 Coated Surface Wear Resistance Design by Comutational Modelling**, ***Kenneth Holmberg***, *A Laukkanen, T Hakala,* VTT Technical Research Centre of Finland Ltd, Finland **INVITED**

The presentation gives an overview of Integrated Computational Materials Engineering (ICME) and the approach and techniques we have used for computational materials modelling and simulation. The focus is on meso- and microscale modelling, integrated approaches and wear related applications. The FEM modelling technique has been stretched to observe stress and fracture phenomena on microscale in thin hard diamond-like carbon (DLC) and titanium nitride (TiN) physical vapour deposited coatings and an equation was developed to show the dominating effects on potential wear failure.

A novel multiscale numerical finite element method (FEM) model was developed to integrate the layered and microstructural material features with the orientation of surface topographical features. A fractal geometry and surface voxelisation based approach were utilised to derive representative 3D topography. The simulations show the details of the main topographical orientation effects on local stresses affecting wear as they appear at a single scratch by a diamond ball and in a self-mated sliding contact between two rough surfaces. The 45º sliding direction to the grooves resulted in a mixed state of surface loading in contact during the scratch test. The complex state of stress-strain within the roughness peaks decreased the overall tensile stress state and resulted in a greater surface resistance to cracking compared to 0º and 90º directions. Model based calculations showed that the surface structure was about four times more rigid in the direction of grooving compared to the more flexible behaviour in the direction perpendicular to the grooving. This behaviour was confirmed experimentally. Modelling and simulation of a tribocontact help to understand the mechanisms that result in surface cracking, wear particle formation and wear evolution and to work out guidelines for optimal contact and surface design for best friction and wear performance tailored for specific applications. Numerical simulations can be carried out on several spatial scale levels, from nano size to macro size, by using software representing the material structure from atomic and even sub-atomic to continuum macro and component level. VTT has introduced the *VTT Propertune* approach and software to find optimal solutions to industrial material challenges worldwide (http://www.vttresearch.com/propertune).

10:40am **E1-1-9 Room and Elevated Temperature Sliding Wear Behavior and Mechanisms of a Cold Sprayed Ni-WC Composite Coating**, ***Tyler Torgerson***, *M Harris,* University of North Texas, USA*; S Alidokht,* McGill University, Canada*; T Scharf, S Aouadi,* University of North Texas, USA*; R Chromik,* McGill University, Canada*; J Zabinski,* Army Research Laboratory, USA*; A Voevodin,* University of North Texas, USA

Cold sprayed Ni-WC metal matrix composite coatings have advantageous tribological properties that have only been investigated in the literature at room temperature. This study sought to identify their elevated temperature dry sliding behavior from room temperature up to 400 °C as well as during thermal cycling with a sliding speed of 2 cm/s and a load of 2.45 N. Further characterization included the use of SEM, EDS, XRD, XPS, Raman spectroscopy, interferometry, and hardness measurements. Results indicate that an increasing temperature leads to a decrease in friction and an increase in wear. The coefficient of friction decreased from 0.41 at 23 °C to 0.32 at 400 °C, while the wear rate increased from 0.47×10^{-4} mm^3 N^{-1} m^{-1} at 23 °C to 3.67×10^{-4} mm^3 N^{-1} m^{-1} at 400 °C. This lowering of friction is attributed to the formation of a lubricious tribochemical phase in the wear track. The increase in wear is due to a combination of thermal softening and a change in the wear mechanism from adhesive to abrasive. During thermal cycling, the coating exhibited self-adaptive behavior from the high to low friction regime. The results revealed that thermal softening and tribochemical reactions that occurred at elevated temperatures slightly compromised the wear resistance while producing a lubricious tribofilm. Therefore, WC-Ni cold spray coatings are potential candidates for elevated temperature sliding wear applications.

New Horizons in Coatings and Thin Films
Room San Diego - Session F2-3

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Jon Tomas Gudmundsson, University of Iceland

8:00am **F2-3-1 Ultra-thick CrN/AlN Superlattice Coatings Deposited by a Combination of Plasma Enhanced Magnetron Sputtering and High Power Impulse Magnetron Sputtering**, ***Jianliang Lin***, *R Wei,* Southwest Research Institute, USA

Plasma enhanced magnetron sputtering (PEMS) is an advanced version of conventional magnetron sputtering by generating a global plasma, in addition to the magnetron plasma, in the entire deposition system using hot filament thermionic emission to enhance the ionization and bombardment. As one version of high power impulse magnetron sputtering (HiPIMS) technique, deep oscillation magnetron sputtering (DOMS) generates large oscillation high power pulses to achieve a high ionization fraction of target species for reactive HiPIMS sputtering. Both DOMS and PEMS aim at utilizing a highly ionized plasma to improve the structure and properties of the coatings. In this paper, ultra-thick CrN/AlN superlattice coatings (20 µm) were deposited on steel substrates by reactive sputtering using a combination of PEMS and DOMS techniques. These coatings were deposited at different PEMS plasma discharge currents (0 to 4 A) which represent different levels of low energy ion bombardment. The bilayer thickness of the nanolayers was controlled in the range of 4 to 7 nm. The microstructure of the coatings gradually changes from long columnar grains to extremely dense structure with an increase in the PEMS discharge current. These thick CrN/AlN coatings show very high hardness and excellent adhesion . The high temperature wear resistance of selected coatings was measured using a high temperature pin-on-disc tribometer in the ambient air from 600 °C to 900 °C. The solid particle erosion resistance of these ultra-thick CrN/AlN coating was evaluated and compared with other thick hard coatings, e.g. CrN, TiN, TiSiCN, etc., using an air jet sand erosion tester.

8:20am **F2-3-2 Deposition of DLC Coatings by HIPIMS to Arc Mixed Mode**, ***Holger Gerdes***, *R Bandorf, J Rösler, M Vergöhl, G Braeuer,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

The deposition of hard carbon or diamond-like carbon (DLC) films is still of high interest, especially in combination with high power impulse magnetron sputtering (HIPMS). In automotive applications, the use of hydrogen-free, so-called ta-C coatings is well established. The ta-C are mainly deposited by arc processes, suffering increased roughness due to high energetic macro-particles. Introducing a HIPIMS to Arc mixed mode by M. Lattemann et al. opened the scene for combining the high density sputtering of smooth coatings with the high energy processing by arc. In 2015 Ganesan et al. reported on the deposition of ta-C films with high sp3-content from a 3 inch target.

This presentation will show an approach for upscaling a HIPIMS-Arc mixed mode to an industrial sized cathode (0.5 m). The process parameters and basic aspects on how to design a pulse for transitioning into an arc will be discussed. The investigations by optical emission spectroscopy (OES) showed clearly an indication on generating carbon-ions. The Vickers hardness of prepared films were measured and showed first results with a hardness of up to 3500 HV.

8:40am **F2-3-3 Performance Improvements of Tungsten and Zinc Doped Indium Oxide Thin Film Transistor by Fluorine Based Mixing Plasma Treatment with a High-K Gate Dielectric**, ***Yu-Chuan Chiu***, *P Liu, D Ruan, M Yu, K Gan, T Chien, Y Chen, P Kuo, S Sze,* National Chiao Tung University, Taiwan

This study investigates the physical analysis and electrical characteristics for amorphous tungsten and zinc doped indium oxide thin film transistor (a-InWZnO TFT) with a high-k gate insulator, which is applied by fluorine based mixing plasma treatment. Compared with the traditional InGaZnO TFT, the tungsten dopant was proposed as excellent carrier suppressor, which may improve the reliability significantly. However, the carrier mobility was also slightly inhibited by the dopant. In order to achieve good stability and high carrier concentration simultaneously, the fluorine based mixing plasma treatment was introduced in the device process. The fluorine plasma is used as a method to passivate carrier traps within the

channel or at the channel/dielectric interface, which can effectively improve the channel conductivity. In addition to that, the oxygen vacancies are also increased in the back channel region by only fluorine plasma treatment. This may result that a extreme high carrier mobility at the back channel surface which can't be control by a reasonable gate bias. With a mixing plasma process, this phenomenon can be suppressed. Furthermore, a high-k gate insulator is applied for improving the ability of gate control. In this report, the devices with CF_4 + N_2O plasma treatment show a high field-effect mobility of ~ 25 cm^2/V.s, a high On/Off current ratio of ~ 6×10^6 and a small subthreshold swing of 0.1 V/decade for a best interface quality for all samples. This research proposes that the fluorine based mixing plasma treatment may be an effective approach to improve the interface quality for novel metal oxide TFT fabrication.

9:00am **F2-3-4 Effect Of Craters Formation On Deep Hardening Under Pulsed Electron Beam Treatment**, ***Thierry Grosdidier,*** LABoratoied'ExcellenceDesign des Alliages Métalliques pour Allègement de Structures (Labex DAMAS), France*; Y Samih,* Laboratoire d'Etude des Microstructures et de Mécanique des Matériaux (LEM3), France*; C Dong,* Key Laboratory of Materials Modification, Dalian University of Technology, China

Techniques like the intense pulsed electron beams (IPEB) or intense pulsed ion beams (IPIB) generally induce surface melting, evaporation followed by rapid solidification and quenching which are accompanied by the formation of stress waves. As a result, surface/near surface properties such as corrosion and wear resistances can be improved while the generation of structural defects such as vacancies and dislocation loops also affect the depth of the samples and can lead to sub-surface hardening. While the improved wear resistance and corrosion resistance have been attributed to several complementary factors (surface hardening, nanostructure formation) the mechanisms responsible for the deep hardening are much less understood.

In the case of IPEB, the large pulse duration (about 800 ns under High Current Pulsed Electron Beam) and, accordingly, the low rate of energy input, does not provide with the formation of the dynamic stress wave and the increase in dislocation density was entirely provided by the action of the quasi-static thermal stresses. In their modelling approach, Quin et al. [1] suggested that the subsurface initial melting that is associated with the specific energy distribution of the electron beam could create an additional source of plastic deformation via the recoil impulses that are generated as a consequence of crater eruptions.

To the authors knowledge however, there is no experimental work that has been carried so far to undoubtedly verify the electiveness of the formation of craters on hardening the surface and subsurface of HCPEB treated samples. The aim of the present paper is to investigate experimentally the contribution of the potential crater bursts on modifying the deep hardening phenomena. To this end, the HCPEB technique has been applied under similar processing conditions on two stainless steels of very close chemistry but having different potential for crater formation.

[1] Qin, Y ; Dong, C ; Song, ZF; Hao, SZ; Me XX; Li, JA; Wang, XG; Zou, JX; Grosdidier, T, JOURNAL OF VACUUM SCIENCE & TECHNOLOGY A, 27, Pages: 430-435, MAY 2009

9:20am **F2-3-5 Mechanical Property Evaluation of ZrCN Films Deposited by a Hybrid Superimposed High Power Impulse- Middle Frequency Sputtering System***, Q Tang, Y Wu,* National Taipei University of Technology, Taiwan*; **Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

High power impulse magnetron sputtering (HiPIMS) is a relatively new physical vapor deposition technology, which is characterized by its ultra-high peak current, peak power density and high-density plasma to achieve unique thin film mechanical properties, such as high hardness, good adhesion and good wear resistance. Recently, a superimposed HiPIMS-middle frequency (MF) power system has been proved to increase the deposition rate of HiPIMS technique effectively. In this study, a superimposed HiPIMS-MF power system was used to deposit the ZrCN films with different carbon content on hardened tool steel disks and silicon wafer substrates. The phase of each coating was studied by means of the X-ray diffractometer. The microstructures of thin films were examined by a field-emission scanning electron microscopy. Atomic force microscopy was used to characterize the surface morphology and roughness. The nanoindentation and scratch tests were used to evaluate the hardness and adhesion properties of thin films, respectively. The pin-on-disk wear test was employed to study the tribological property of coating. Effects of carbon content on the microstructure, mechanical and tribological properties of ZrCN coatings were further discussed in this work.

Surface Engineering - Applied Research and Industrial Applications

Room Sunset - Session G2

Component Coatings for Automotive, Aerospace, Medical, and Manufacturing Applications

Moderators: Osman Levent Eryilmaz, Argonne National Laboratory, USA, Jolanta Klemberg-Sapieha, Polytechnique Montréal

8:00am **G2-1 The Effects of Temperature and Gas Mixture Composition on the Microstructure and Tribological Properties of the Plasma Nitrocarburized DIN 100 CR6 Steel***, M Fontes,* Federal University of Sao Carlos, Brazil*; V Baggio-Scheid,* Sao Jose dos Campos, Brazil*; D Machado,* Tecumseh Products Company, Brazil*; L Casteletti,* University of Sao Paulo, Brazil*; **Pedro Nascente,*** Federal University of Sao Carlos, Brazil

Nitrocarburizing is considered one of the most important thermochemical treatments for surface modification of metallic materials, and involves the simultaneous diffusion of nitrogen and carbon onto the surface. Understanding and controlling the formation of the nitrocarburized layer have considerable industrial interest due to the improvements regarding wear, fatigue, and corrosion resistances. In this study, the DIN 100Cr6 steel was chosen due to its use as raw material in the manufacture of a mechanical component applied in hermetic compressors for refrigeration. The DIN 100Cr6 steel samples were treated by plasma nitrocarburizing for two hours, with two treatment temperature (550°C and 600°C) and four methane concentrations in the gas mixture composition (0%, 1.0%, 1.5%, and 2.0%) as variables. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) analyses, as well as wear resistance and micro-hardness tests, were used to characterize the modified samples. The results showed that the treatment temperature and atmosphere composition had considerable influence on the compound layer composition and morphology. The presence of carbon in the gas mixture contributed to the formation of the ε-$Fe_{2-3}N$ phase, which has a HCP crystalline structure, and elevated temperatures caused an increase in the thickness of the compound layer, diffusion zone, and micro-porosity layer. The nitrided samples had a compound layer composed only by the γ'-Fe_4N phase having a FCC structure. For the nitrocarburized samples, the compound layer was a mixture of ε-$Fe_{2-3}N$ and γ'-Fe_4N phases, with a columnar-like microstructure; the amount of each one of these phases was a function of the CH_4 percentage present in the treatment atmosphere. A micro-porosity layer was formed for all produced surface layers. A larger micro-porosity layer thickness was observed for samples nitrocarburized without CH_4. Higher nitrogen concentrations in the atmosphere resulted in more pores in the compound layer.

8:20am **G2-2 Selected Aspects of Industrial Applications of Hydrogen Free DLC Coatings Deposited by CVAE***, **Joerg Vetter,*** Oerlikon Balzers Coating Germany GmbH, Germany*; J Karner,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; J Becker, M Markus,* Oerlikon Balzers Coating Germany GmbH, Germany*; N Beganovic,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; E Billot,* Oerlikon Balzers Coating Germany GmbH, Germany*; H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, Switzerland

The number of industrial applications of hydrogen free ta-C and a-C coatings continues to increase, primarily for tribological coatings to reduce wear and friction. Tetrahedrally-bonded hydrogen-free coatings (ta-C) provide the highest hardness, and are successfully applied in many cutting and forming applications, while various softer a-C coatings are also useful in various tribological applications. Recent research and industrial solutions for generating carbon-based coatings by CVAE (cathodic vacuum arc evaporation) are described. The performance of the coatings are influenced both by process parameters (coating architecture) and by topographical effects. Laboratory scale tribological investigations will be presented. Selected aspects of basic prerequisites for industrial applications are highlighted.

8:40am **G2-3 Erosion Resistant PVD Coatings for Gas Turbine Compressor Blades***, **Lin Shang,*** *C Acikgoz,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Moser, G Szyndelman,* Oerlikon Metco AG, Switzerland*; O Jarry,* Oerlikon Balzers, Oerlikon Balzers Coating Germany GmbH, Germany*; M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Although advancements in turbine materials have contributed to enhancing engine power ratings and efficiency levels, solid particle erosion (SPE) which occurs most prominently in the compressor section of aircraft engines during taking-off and landing still remains as a critical issue since

the consequence removal of the turbine blade material degrades the aerodynamic performance, inducing reduced engine efficiency. Hence protecting turbine blades against erosion by applying PVD coatings can be a solution to maintain high level engine performance and lower maintenance costs.

In this work, TiAlN based coatings deposited by cathodic arc were applied on IN718, TiAl6V4 and stainless steel substrate materials. The influence of thermal exposure, coating thickness, hardness and residual stress on the SPE resistance of the coatings have been studied. SPE tests have been performed at 20° and 90° impact angles. Furthermore, the salt spray corrosion, SPE by water jet and cavitation resistance and fatigue behaviour of these coatings have been tested. The water jet erosion test was performed at different angles and also compared to HVOF sprayed WC-CoCr based coating. Compared to the uncoated substrate materials, the PVD coated substrates have been proven to have much higher erosion resistance.

9:00am **G2-4 Synthesis and Characterization of Ta-C, Hf-C and Ta-Hf-C Coatings Obtained by Cathodic Magnetron Sputtering in Reactive Conditions**, ***Alexis de Monteynard,*** Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France*; A Billard,* Institut FEMTO-ST, CNRS, UTBM, Univ. Bourgogne Franche-Comté, Site de Montbéliard, France*; F Sanchette,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France

Ultra-high temperature ceramics (UHTCs) have received a particular interest due to their high melting point leading to a well thermal protection for structures in extreme conditions [1]. The Ta-Hf-C system offers the possibility to create binary or ternary alloys having a melting point above 4000 K. Structural and thermal properties of bulk materials (TaC, HfC and Ta-Hf-C with a wide range composition) have already been investigated [2]. Influence of non-reactively magnetron-sputtering deposition parameters on Ta-C and Hf-C coatings properties has been studied, showing a strong impact of carbon content on structure, morphology, mechanical properties as well as thermal stability [3].

Ta-C, Hf-C and Ta-Hf-C thin films were deposited by cathodic magnetron sputtering of pure Ta and Hf targets in reactive condition (CH_4 being the reactive gas). Structural, morphological and mechanical properties have been studied. The influence of carbon content on coatings properties is discussed.

[1] W. G. Fahrenholtz, E. J. Wuchina, W. E. Lee, and Y. Zhou, Eds., Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications. Hoboken, NJ: John Wiley & Sons, Inc, 2014.

[2] O. Cedillos-Barraza et al., "Investigating the highest melting temperature materials: A laser melting study of the TaC-HfC system," Sci. Rep., vol. 6, p. 37962, Dec. 2016.

[3] H. Lasfargues et al., "Non-reactively sputtered ultra-high temperature Hf-C and Ta-C coatings," Surf. Coat. Technol., vol. 309, pp. 436–444, Jan. 2017.

9:20am **G2-5 Thin and Thick Coatings and Applications in Aerospace Industry**, ***Satish Dixit,*** Plasma Technology Inc., USA **INVITED**

Coatings for wear, erosion, corrosion etc. have been implemented on over 500 different applications in aerospace industry. This includes, aircraft's used for commercial as well as military purposes along with critical components used in the Space exploration applications. In this talk I will be primarily focusing on thin and thick film coatings particularly applicable to functional aerospace components that are subjected to severe wear, corrosion, erosion etc. Thin films are critical where post processing is not an option and thick films are essential on more robust applications where endurance and strength is desired. I will be highlighting some of the applications developed in house as well as the applications prevalent predominantly within the industry at large.

10:00am **G2-7 HNT-Containing Ceramic PEO Coatings for Active Corrosion Protection of Magnesium Alloys**, *B Mingo,* ***Yue Guo,*** *A Matthews, A Yerokhin,* The University of Manchester, UK

The growing interest for magnesium in weight-sensitive applications has triggered the development of surface modifications techniques capable of improving its properties mainly, its corrosion resistance. Amongst them stand out Plasma Electrolytic Oxidation (PEO), which is a high voltage electrolytic-plasma surface treatment capable of obtaining highly stable ceramic coatings with excellent hardness, adhesion, corrosion and wear resistance. However, these coatings only provide passive protection, i.e. act only as a physical barrier between the metallic substrate and the aggressive environment.

The aim of this study is to develop a functional ceramic coating on a commercial magnesium alloy capable of interacting with its surrounding by responding selectively to specific triggers. For that, halloysite nanotubes (HNT) are incorporated into the coating, which can be loaded with different active agents such as corrosion inhibitors, lubricants or drugs.

Halloysite nanotubes are biocompatible natural clays composed by two layers of aluminosilicates arranged in a hollow tubular shape. These nanotubes can be loaded by mechanical (vacuum-induced capillarity) or chemical (ion-exchange) processes, so the release of their content can be trigger by different stimulus e.g. mechanical damage, time or pH variations. At neutral pH the inner part of HNT is positively charged, which means that it is able to host negatively charged agents attracted by electrostatic interactions, however when increasing pH the charge of the lumen of the nanotube changes, which forces the release of the incorporated agent. This is especially interesting for corrosion protection of magnesium alloys, where corrosion inhibitors can be released to the media when detecting electrochemical activity arisen from pH variations, remaining encapsulated while the coating is intact.

The main challenge faced in this work is to achieve the non-reactive incorporation of the loaded nanotubes to PEO coatings since the high temperatures and pressure reached during the coating synthesis might compromise the 3D integrity of the nanotubes. The obtained materials are evaluated in terms of characterization and corrosion resistance.

A positive outcome would not only increase the life-time of PEO coated components used in high performance applications, but also would expand their applicability to other fields, potentially to biomaterials, with the development of drug-loaded coatings used in orthopaedic implants.

Topical Symposia
Room Sunrise - Session TS3

Coating of Synthetic Materials – Engineering for the Future

Moderators: Klaus Böbel, Bosch GmbH, Fred Fietzke, Fraunhofer FEP

8:00am **TS3-1 Development of PVD Coatings by R2R on Basis of TI/AG, TI/ZN and TI/AG/ZN on Textile Fabrics**, ***Martin Fenker,*** *H Kappl,* FEM Forschungsinstitut Edelmetalle & Metallchemie, Germany

Silver and zinc coatings are interesting materials in the biomedical field as they possess antimicrobial properties. Therefore, PVD coatings on the basis of Ti/Ag, Ti/Zn and Ti/Ag/Zn have been deposited by non-reactive DC magnetron sputtering on textile fabrics like polypropylene (PP), polyvinylidene fluoride (PVDF) et cetera. These polymers are used for example as implant material or for wound bandage. A roll-to-roll (R2R) unit was constructed and installed in our semi-industrial PVD machine and tests have been performed with elemental targets as well as with compound targets. Coating thickness was measured on coated glass samples. Ageing test were performed by ultrasonic agitation of the coated fabrics. Light optical microscopy and scanning electron microscopy were used for visual inspection of the as-deposited as well as the sonicated samples. Delamination of the coating occurred for some samples and will be discussed.

8:20am **TS3-2 Coating of Plastic Components by Electron-beam Evaporation**, ***Fred Fietzke,*** *H Klostermann, J Heinß,* Fraunhofer FEP, Germany

Vacuum coating of plastic components as an alternative to electroplating already has a long tradition in industrial practice. The applications range from metallization of headlamp reflectors over decorative controls and instruments up to EMC shielding of electronic devices. Predominantly used methods are magnetron sputtering and thermal evaporation.

A particular challenge is the low thermal stability of many engineering plastics in conjunction with the high energy input of PVD processes and the limited possibilities of substrate cooling in vacuum. Furthermore, for most plastics a sufficient adhesion of PVD coatings directly on the substrate material still cannot be achieved, so that primers or lacquers have to be used as sublayers.

A new approach for PVD direct metallization is taken by Fraunhofer FEP. Here, a short-cycle system for the coating of components by high-rate electron beam evaporation is used to coat components made of polycarbonate (PC) and PC/ABS (acrylonitrile butadiene styrene copolymer) blend. After a short treatment in oxygen plasma the parts are coated with

an aluminum layer of some microns thickness in less than one minute, without showing thermal deformations or film delamination.

The key to meet these challenges lies in a high evaporation rate already at low power input in combination with a substrate movement adapted to the component geometry. Possibilities and limitations of the method are explained, properties of coated parts are analyzed in comparison with the current state of the art, and further possible applications are discussed.

8:40am **TS3-3 Aspects of Coatings on Plastic products for Decorative and automotive parts.**, ***Roel Tietema,*** IHI Hauzer Techno Coating BV, Netherlands*; D Doerwald, C Trivedi, I Kolev, J Landsbergen,* IHI Hauzer Techno Coating B.V., Netherlands **INVITED**

Plastic products are playing an ever bigger role in our daily life and they draw more and more attention of the market. Reasons for this trend are low cost, ease of producibility, large freedom of design and low weight.

Coatings on plastic products have mainly been produced by electroplating and lacquers.

Since the 1980's PVD coatings have been used for decorative applications in the watch industry. Nowadays decorative coatings are applied on watches, faucets, door handles, spectacles (both frames and glasses) and mobile phones.

In recent years a new market has emerged for PVD-coatings on plastics driven by the requirement to reduce weight. This occurs because on one side the expectations of a growing market share for electrical cars exists as well as on the other side CO_2 emissions and fuel consumption can be reduced by weight reduction. The consequence is that the use of plastics in the automotive industry as light weight base material for both interior and exterior parts will have an increasing share. Until now electroplating is the major applied technology, but PVD will get an increasing share in this market due to the requirement for replacement of electroplated chromium. Electroplating is a technology requiring the use of carcinogenic hexavalent chromium (in form of trichromate) during several steps of the plating process. This material is on the list of SVHC's (Substances of Very High Concern) and imposes severe health dangers on personnel working with the plating lines. Besides this plating technology requires intensive efforts to dispose waste materials.

As replacement for electroplating in-line processes where plastic parts are coated with UV-cured lacquer and a subsequent chromium PVD layer have been developed and are available on the market. Mass production for automotive plastic products is already applied.

In this presentation the developments will be discussed beginning from initial applications on watches and faucets by sputter and arc technology in the 1990's. In the early 2000's coatings have been introduced on mobile phones, whereas finally in the last decade the application of coatings on plastic parts by hybrid lacquer/PVD-PECVD processes have been developed.

Different aspects of the requirements for coated products and the related processes will be discussed from the point of view of technologies, productivity, performance and sustainability.

9:20am **TS3-5 Combined Impact and Sliding Testing for Evaluation of Surfaces on Different Materials**, ***Claus Rebholz,*** University of Cyprus, Cyprus **INVITED**

Light-weight materials such as polymers and magnesium alloys exhibit tremendous challenges for surface engineering, not only in terms of selecting appropriate coating architectures and processes, and therefore reducing or avoiding issues that can result in premature coating failure at relatively low stress levels compared to more rigid substrates, but also for the development of sophisticated testing methods for quality evaluation and inspection.

Several well established testing methods (e.g. impact, pin-on-disk, scratch) have been widely used to evaluate the properties of coatings on various substrates. However, many of these existing techniques have limitations, since they mainly focus on a single mode of loading and wear (e.g. only impact or sliding). Here, a combined impact and sliding test for the tribo-mechanical evaluation of surfaces under complex loading conditions is presented, where materials are simultaneously subjected to sliding and impact loading. Such modes exist in many critical applications, from biomedical (e.g. hip/knee implants) to automotive applications (e.g. diesel injectors, engine valves, cam shafts), in cutting tools, general machine parts and systems, etc. The proposed testing set-up offers a feasible way for fast, economical and reliable evaluation of complex coating/tribo systems. Benefits include the time and cost effective evaluation of various surfaces (testing time usually less than a minute) and the better understanding of their properties such multi-mode loading conditions. Some of the unique characteristics of this new instrument (e.g. combined impact and sliding, wear area in a single small "point", etc.) are discussed and examples of evaluated metallic bulk materials/coatings are presented.

10:00am **TS3-7 Interfacial Stability of the Aluminium-Polyimide Interface Against Thermal Treatments**, ***Barbara Putz,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; G Milassin, Y Butenko,* European Space Research and Technology Centre, Netherlands*; B Völker, C Gammer,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; C Semprimoschnig,* European Space Research and Technology Centre, Netherlands*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Monanuniversität Leoben, Austria

Metal-polymer systems are usable for innovative high-tech applications, including flexible and rigid microelectronics or spacecraft and satellite insulation. The metal-polymer interfaces, which have to bridge the distinct physical and chemical properties of the adjacent materials, are critical elements determining the overall reliability of the composite. A thorough understanding of the thermal stability of these interfaces is essential for reliable devices, considering the inevitable thermal treatments such as annealing or cycling which typically occur during manufacturing or operation. Considering the low homologous temperature of polymers combined with the difference in thermal expansion coefficients (factor 2-3) between the two components thermal treatments are likely to cause interfacial degradation and need to be critically investigated. In this study the interfacial stability of Aluminum-Polyimide (Al-PI), used as multilayer insulation blankets on satellites, is investigated as a function of thermal cycling (±150°C) and thermal annealing treatments (150-300°C). Mechanical adhesion measurements are combined with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) in order to relate the interface strength to the interface chemistry and structure. The interfacial adhesion energy was measured using tensile induced delamination. In order to assess the chemistry of the interface, a 180° peel test was used to provide access to the metal side and the polymer side of the interface without additional etching or sputtering steps that would alter the interface chemistry. XPS survey and high resolution core level scans were recorded on both sides of the peeled interfaces to identify and understand relevant interfacial bonding and distinguish between adhesive failure of the interface and cohesive failure in the substrate during peeling. TEM cross-sections were used to examine the interface microstructure and morphology. It was determined that the Al-PI interface, which initially shows very good adhesion, is resistant to thermal cycling of +/-150°C up to 200 thermal cycles. After thermal annealing, however, small mutations in the interface chemistry and structure were detected and identified starting at 225°C. Mutations were invisible to mechanical adhesion measurements and include the thickness increase of an amorphous interlayer between Al and PI of about 2nm and a change in the failure mechanism during the peeling. Being able to trace and identify subcritical mutations with the presented experimental approach before they become fatal is essential to predict the reliability and improve the design of metal-polymer composites.

Exhibitors Keynote Lecture
Room Grand Hall - Session EX

Exhibition Keynote Lecture

11:00am **EX-1 Enabling Tomorrow's Transportation Mobility with Surface Technology*, Nazlim Bagcivan,*** Schaeffler AG, Germany **INVITED**

Among the focus areas of future transportation needs are the development of environmentally-friendly vehicle drive components including the engine, transmission, and axels. Environmentally-friendly vehicle drive systems are one of the major factors determining energy efficiency and the environmental compatibility of transportation. Therefore, development of energy-efficient drive systems is a high priority. In addition to other measures, improvement of tribological conditions along the entire drive systems of passenger cars and commercial vehicles will provide longer component lifetimes and decreased vehicle emissions.

With modern surface technology, the properties of vehicle drive system components can be adjusted in order to minimize friction losses and meet more stringent environmental requirements. Innovative vacuum coating technology has the ability to reduce vehicle CO_2 emissions by lightweight design, reduce friction losses in all drive system components, and therefore provide improved fuel efficiency.

A sustainable reduction of CO_2 emission can only be achieved if friction reduction is ensured during the entire lifetime of the coated product. Therefore, the goal can be summarized as “minimum friction at highest wear resistance.” For innovative products, it is extremely important to consider coatings as design elements and integrate them into the product development process at a very early stage. Development of tribological coatings has to be accomplished within a holistic and design-oriented context.

Close collaboration between research and production teams, industry, and academia is required to achieve such a challenging goal. In the future, the role of coatings as a vital design element will also increase in many other technical applications.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-2

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Qi Yang, National Research Council of Canada, Jyh-Ming Ting, National Cheng Kung University

2:10pm **B1-2-3 Impact Analysis of Power Source Operating Parameters on Hardness, Adhesion and Film Composition of TiN Functional Coatings**, *K Ruda, W Gajewski,* ***Jakub Świątnicki****, A Oniszczuk,* TRUMPF Huettinger Sp. z o.o., Poland

ncreasingly important in determining the optimal plasma processing parameters are the functionalities of the power supply. The flexibility in output current and voltage shaping, tunable pulsing frequency, advanced arc and power delivery management are the driving factors for successful usage of bipolar technology in a variety of industrial applications. The flexibility and modifiability of bipolar power supplies are the key factors making them an interesting alternative for the classical MF units with sinusoidal output. This contribution summarizes recent industrial experience with the application of bipolar technology for deposition of protective and decorative TiN coatings.

First, the dependence of the deposition rate on different output frequency will be discussed in details including the relationship with the process stability due to arcing in reactive processes. It will be shown how a combination of novel arc management algorithms together with applicability of different pulsing frequencies can be used for process stabilization by reduction of arcing probability. The discussion will be followed by the impact assessment of the output signal shape and frequency on TiN film hardness. Films prepared with different power delivery settings show comparable adhesion property with critical load in the range of 62 N, hardness H > 6500 Mpa and Young's modulus E ~ 300 Gpa. The distinct differences in the film properties obtained with different operating parameters will be discussed in details. The discussion will be summarized with cost and benefit analysis of industrial implementation of bipolar technology based on process results.

2:30pm **B1-2-4 Substitution of Commercially Coated Tungsten Carbide Tools in Dry Cylindrical Turning Process by HiPIMS Coated Niobium Carbide Cutting Inserts**, *E Uhlmann,* ***Daniel Hinzmann****, K Kropidlowski,* Institute for Machine Tools and Factory Management - Technical University Berlin, Germany*; P Meier,* Institute for Machine Tools and Factory Management - Technical University Berlin*; L Prasol,* Institute for Machine Tools and Factory Management - Technical University Berlin, Germany*; M Woydt,* BAM Berlin, Germany

Coated tungsten carbide (WC) tools are applied for machining of various workpiece materials in industrial applications. The recent development of alternative cutting materials shows the potential of niobium carbide (NbC) for turning of iron-based materials. Its use in cutting tool applications is based on advantages regarding hot hardness and low solubility of binderless NbC in solid chrome, nickel, cobalt or iron. With a reduced tendency for adhesive and diffusion wear in uncoated state, a higher material removal rate combined with a higher process reliability at increased cutting speed represents state of the art machining results. In order to draw a comparison between commercially available WC tools, NbC tools are tested in uncoated and coated condition during dry cylindrical turning of carbon steel C45E. Two different NbC substrate materials are included in machining trials, each differing in chemical composition and mechanical properties. A cobalt (Co) bonded niobium carbide defined as $NbC_{0.88}$-14Co and a nickel (Ni) bonded NbC with the specification $NbC_{1.0}$–12Ni4Mo4VC are selected and compared to submicron grain WC-6Co tool material. The coating was deposited via physical vapor deposition (PVD) in a HiPIMS process where a coating thickness of s_D = 3 µm was achieved on both WC and NbC cutting inserts. Tool performance is evaluated based on tool wear and lifetime. Coated $NbC_{1.0}$-12Ni4Mo4VC accomplished similar cutting times compared to coated WC tools without exceeding tool life criterion of VB_{max} = 0.2 mm.

2:50pm **B1-2-5 Controlled Deposition of Alpha, Beta, and FCC Tantalum Thin Films by Magnetron Sputtering**, ***Qiaoqin Yang****, S Shiri,* University of Saskatchewan, Canada **INVITED**

Due to its high chemical stability, excellent biocompatibility, and refractory nature, metallic Tantalum (Ta) has been used in many areas, including microelectronics (e.g. in capacitors), biomedical implants, surgical instruments, masks in X-ray lithography, and structural applications at high-temperatures. Metallic Ta can have three different crystal structures: body-centered cubic (alpha phase), tetragonal (beta phase), and face-centered cubic (FCC). Bulk Ta generally exists as alpha phase, which is relatively ductile and soft whereas Ta thin films obtained by vapor deposition are usually a mixture of alpha and beta phases. The beta phase, hard and brittle, is metastable and converts to the alpha phase upon heating to 750–775 °C. FCC Ta has only previously been reported as dispersed nano-grains embedded in alpha or βeta phased ultrathin films or highly deformed bulk Ta. In this presentation, we report on the controlled synthesis of Ta thin films of a few micrometers on both Co-Cr-Mo alloy and Si substrates with the three different crystal structures, including single-phased alpha Ta, single-phased beta Ta, a mixture of alpha and βeta Ta, single-phased FCC Ta, by magnetron sputtering. X-ray diffraction pattern of FCC Ta and the accurate determination of its lattice parameter are reported for the first time. Based on the results, a multilayered gradient Ta thin film, β-Ta/ β-Ta+α-Ta/ α-Ta, with high adhesion has been obtained on biomedical CoCrMo alloy sheets.

3:30pm **B1-2-7 High Power Impulse Plasma Magnetron Sputtering: Review of Critical Parameters Ensuring Successful Industrialization**, *W Gajewski, P Różański, P Lesiuk, P Ozimek,* ***AnnaWiktoria Oniszczuk****,* TRUMPF Huettinger Sp. z o.o., Poland

Since the first presentation of the High Power Impulse Magnetron Sputtering idea by *Kouznetsov and co-workers* in 1999 the basic architecture of a DC-charged capacitor bank dissipating periodically its energy into the plasma in pulses evolved to a sophisticated electronic device commercially available for industry from 2003. In order to meet rigorous requirements of industrial application, engineers have proposed different modifications of HiPIMS power delivery units to make the pulse shape and duration independent on the size of the capacitor bank and time-dependent plasma impedance.

Until now anti-wear and protective coatings prepared by HIPIMS won an established position and are used commercially. Newest market trends show the HIPIMS technology will soon became a standard production tool for oxide coatings, both conductive and non-conductive. In order to keep pace with market development HIPIMS power supplyies also requires further evolution to meet high productivity, stability and reproducibility demands of the industry. To fulfill these rigorous requirements HIPIMS power supplies must offer versatile arc management, unique control of voltage and current peak shape and the average power delivery control – sophisticated features previously unavailable in any other HIPIMS power supply units. Furthermore, those functionalities must be available both for small, laboratory size targets as well as for industrial scale where delivery of current density of 1 A/cm^2 requires a precise control of HIPIMS pulses with current of 1000 A and above.

(i) peak current regulation, *(ii)* pulse frequency, and *(iii)* pulse length.

3:50pm **B1-2-8 Investigation of the Formation of Ni-Ti Intermetallic Layers Produced by Cathodic Arc Electron-metal Ion Treatment**, ***Nagihan Sezgin****, E Kacar, K Kazmanli, M Urgen,* Istanbul Technical University, Turkey

A novel cathodic arc plasma treatment was used to obtain Ni-Ti intermetallic layers. The method was named cathodic arc electron metal ion treatment is a diffusion/coating process. During this process, AC bias was applied to the substrates and in-situ heating was achieved with electrons. AC bias potential has positive and negative cycles. At the positive cycle, electrons were directed to the substrate and the substrate was heated; at negative cycle, ions deposited on to the surface. In this study, the formation of Ni-Ti intermetallic phases were investigated for 2 different diffusion couples: Ni substrate – Ti cathode and Ti substrate – Ni cathode. Depending on the substrate-cathode diffusion couple, formed phases and sequence of the phase formation vary. To obtain desired phases should be possible by tuning the couples and process parameters. Time (5- 45 min) and temperature dependent (900 °C-1100 °C) diffusion reactions and formation sequence of phases were determined. The samples were analyzed by SEM, EDS, XRD.

4:10pm **B1-2-9 Exploring the High-temperature Stability of Nanocrystalline Cu-W Coatings**, ***Yao Du****,* Northwestern University, USA*; L Li,* Northwestern Polytechnical University, China*; J Pureza,* Universidade do Estado de Santa Catarina, Brazil*; Y Chung,* Northwestern University, USA*; K Pradeep, S Sen, J Schneider,* RWTH Aachen University, Germany

Nanocrystalline coatings are harder than their bulk or microcrystalline counterparts due to their grain size. Their hardness tends to degrade with increasing temperature due to grain growth. It has been suggested that introduction of proper alloying elements can provide thermal stabilization of the nanoscale grain structure, even at elevated temperatures. To this

end, Cu-W coatings was synthesized by magnetron sputtering to investigate the grain boundary stabilization by W segregation. The thickness of the coatings is around 800 nm. The room-temperature hardness of the as-deposited coatings based on nanoindentation is 3.7 ± 0.3 GPa. Annealed at 400°C, these coatings exhibit hardness decrease of 3 % after 20 minutes, probably due to stress relaxation. The hardness achieves a stable value of 3.6 GPa after two hours. The average grain size was barely changed after this extended annealing, with an average value of 36.5 nm after two hours. Atom probe tomographic analysis shows the segregation of W to the grain boundaries of Cu. These results validate the strategy for designing thermally stable nanocrystalline coatings.

4:30pm **B1-2-10 Governing the Wettability Properties of the Nanostructured Surfaces of Metallic Coatings Fabricated by Thermal Annealing***, **Feras Alzubi**, A Alkandary,* Kuwait Institute for Scientific Research, Kuwait

In this work, we report the measurement and controlling of contact angle of metallic coatings deposited by physical vapor deposition technique. We create nanoparticles on the surfaces of these coatings by thermal annealing the deposited coatings in inert environment. Thin films of Ag, Cu, Al, In, and other metals were deposited on Si substrates with 4 nm thickness. After being thermally annealed at 800 C, the ex perimental measurements of the contact angle of DIW droplets dispensed on the deposited thermally annealed metallic thin films were carried out by Optical Contact Angle system (OCA 100 Dataphysics). Our results agree with fact that the contact angle is affected by several parameters such as liquid's surface energy, roughness of the coatings' surface, type of material of the surface. Results show that the contact angle depends strongly on the type deposited material. Contact angle of all studied metals have shown a decrease towards making the surface more hydrophilic surfaces when coatings were thermally annealed. The creation of nanostructured on the surface of coatings, which was investigated by atomic force microscope, has shown to affect the hydrophobicity or hydrophilcity of the surfaces. 4 nm silver thin-film has shown a reduction from 107° contact angle to 49.7° making it a hydrophilic surface after thermal annealing. These findings contribute to understanding the role of metallic nanostructured on surface wettability.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B2-2

CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

1:50pm **B2-2-2 Highly Efficient Light trapping by Fractal, MOCVD Processed CoO-based Surfaces on Polymers***, E Amin-Chalhoub, O Debieu, D Samelor, **Thomas Duguet**, C Vahlas,* CIRIMAT, CNRS - University of Toulouse, France

Low reflective films containing CoO are processed by chemical vapor deposition from direct liquid injected solutions of $Co_2(CO)_8$ in heptane, in the presence of oxygen. The films are deposited on silicon and epoxy resin – carbon fiber composite coupons in a cold wall reactor operated at 5 Torr between 50 °C and 160 °C. Those processed at 50 °C, 125 °C and 160 °C present a cauliflower-type nodular morphology, with distinct nodules grown on a relatively smooth background, with similar microstructure but on a finer scale. XRD and FTIR analysis reveal that low temperature processed films are composed of CoO, while those processed at 125 °C and above also contain the spinel structure Co3O4. All films contain significant concentration of amorphous, aliphatic carbon. The optical reflectivity in the visible region stems from 1 to 14% depending on deposition temperature. The combination of specific microstructural features of the coatings, namely a fractal "cauliflower" morphology and a grainsize distribution more or less covering the near UV and IR wavelength ranges enhance light scattering and gives rise to a low reflectivity. In addition, the columnar morphology results in a density gradient in the vertical direction that we interpret as a refractive index gradient lowering reflectivity further down. The coating formed at 125◦C shows the lowest reflectivity (1 %) in the range 400 – 750 nm and presents an interesting deep black diffuse aspect. It can thus be applied as antireflective coating in startracking instruments used for spacecrafts navigation.

2:10pm **B2-2-3 Deposition Kinetics, Gas Phase Analysis and Film Characterization of Silicon Carbide by Low Pressure Chemical Vapor Deposition using Vinyltrichlorosilane and Hydrogen***, **Anthony Desenfant**,* LCTS-University of Bordeaux, France*; G Laduye,* AIR LIQUIDE, Paris-Saclay Research & Development, France*; C Descamps,* Safran Ceramics, France*; G Vignoles, G Chollon,* LCTS-University of Bordeaux, France

SiC/SiC composites are of great interest for high temperature structural applications such as jet engines. The SiC matrix is usually deposited by chemical vapor deposition (or infiltration: CVD/CVI) using a mixture of methyltrichlorosilane (MTS, CH_3SiCl_3) and hydrogen. If not handled carefully, this process can lead to silicon co-deposition and inhomogeneous infiltration of the fiber fabrics. In this context, we have studied vinyltrichlorosilane (VTS, $C_2H_3SiCl_3$) as an alternative precursor for SiC. The low-pressure CVD reactor was associated to a microbalance and an FTIR spectrometer to record the deposition rate and the gas concentrations as a function of the deposition temperature, pressure, $\alpha = (P_{VTS}/P_{H2})_{initial}$ and total flow rate. Model porous substrates were also submitted to CVD/CVI, to evaluate the homogeneity of infiltration in a few selected conditions. This approach allowed proposing a basic mechanism for the CVD using VTS/H_2 and, besides, identifying proper conditions for the growth of pure and crystalline SiC. The Arrhenius plots of the deposition rate show three distinct kinetic domains. Free carbon is co-deposited within the low-temperature kinetically-controlled regime CRR1, while VTS is only partially decomposed. Such a carbon excess results from the formation of highly reactive carbon-bearing species, e.g. $C_2H_3^{\bullet}$, in contrast with the silicon-bearing species. Changes in the heterogeneous reactions are responsible for a transient regime CRR2 characterized by a particularly high apparent activation energy and a hysteresis phenomenon. The higher temperature CRR3 domain, of lower activation energy, is more favorable to deposit pure SiC. In the gas phase, H_2 seems to play a role in the homogeneous decomposition of VTS. In the solid, the replacement of H_2 by Ar leads to carbon-rich coatings, as observed in the CRR1 domain. Low deposition temperatures are usually beneficial to the homogeneity of infiltration for the CVI process. The lowest thickness gradient between the surface and the core of porous substrates is indeed observed in the CRR1 domain. A carbon-rich coating is deposited at the entrance of the model channel pore but the composition sharply turns to pure SiC deeper in the channel. The influence of residence time τ_r and the depletion of the reactive carbon precursors in the gas phase is likely responsible for such a change in the nature of the deposit. By following the VTS concentration as a function of τ_r, the apparent activation energy of the homogeneous decomposition of the precursor could be evaluated at about 290 kJ/mol. A simple homogeneous and heterogeneous mechanism was constructed based on the previous investigations.

2:30pm **B2-2-4 Hydrothermal Corrosion Behaviors of CVD Silicon Carbides and Cr-based Alloy Coated CVI SiC_f/SiC Composites***, **Jung Ho Shin**, D Kim, H Lee, J Park, J Park, W Kim,* Korea Atomic Energy Research Institute, Republic of Korea

Replacing Zircaloy with ceramic materials having high accident resistance currently used as fuel cladding on pressurized water reactor have been actively studied after the Fukushima Daiichi nuclear accident. It is expected that the ceramic material with a low amount of hydrogen generated by reaction with a coolant during abnormal operation of the reactor and excellent in high temperature mechanical properties can be utilized as a next generation reactor cladding material. Among them, SiCf/SiC composites have attracted much attention due to its excellent corrosion resistance and high temperature strength as well as its high thermal conductivity and low neutron absorption cross section. Additionally, it does not suffer from fretting wear and hydrogen reactions. The SiC has a very good oxidation resistance due to the formation of a SiO2 protective coating in a high temperature gas environment, but mass reduction of the SiC is occurred by the dissolution of oxide layers of SiO2 / Si(OH)4 in a high temperature hydrochemical environment. Microstructural change and defects occurred during the SiCf/SiC synthesis process affect neutron irradiation deformation and corrosion behavior.

For improving these problems, corrosion resistant coating on cladding is one of the candidate technologies to improve the corrosion resistance of SiCf/SiC composites cladding in the PWR environment. By applying coating technology to SiCf/SiC composistes cladding, it is easy to obtain corrosion resistance without a change in the base materials. Among the surface coating methods, arc ion plating (AIP) is a coating technology to improve the adhesion owing to good throwing power, and a dense deposit. Owing to these advantages, AIP has been widely used to efficiently form protective coatings on cutting tools, dies, bearings, etc. Thus, considering

the advantages of AIP, we attempted to improve the corrosion resistance of SiCf/SiC using AIP. For this purpose, we coated Cr-Al alloy on SiCf/SiC composites claddings and their corrosion behavior in the simulated PWR primary water condition.

2:50pm **B2-2-5 Temperature Driven Microstructural Evolution of Nano–lamellar CVD fcc–$Ti_{1-x}Al_xN$**, ***Michael Tkadletz***, *C Hofer,* Montanuniversität Leoben, Austria*; C Wüstefeld,* Technische Universität Bergakademie Freiberg, Germany*; N Schalk,* Montanuniversität Leoben, Austria*; M Motylenko,* Technische Universität Bergakademie Freiberg, Germany*; D Rafaja,* Technische Universität Bergakademie Freiberg, Gustav-Zeuner-Straße 5, 09599 Freiberg, Germany*; C Giacobbe, C Dejoie,* ESRF, France*; H Holzschuh, W Bürgin,* SuCoTec AG, Switzerland*; B Sartory,* Materials Center Leoben Forschung GmbH (MCL), Austria*; C Mitterer,* Montanuniversität Leoben, Austria*; C Czettl,* CERATIZIT Austria GmbH, Austria

In recent years, nano-lamellar face centered cubic (fcc-) $Ti_{1-x}Al_xN$ coatings with x as high as ~0.8 to ~0.9 deposited by thermal chemical vapor deposition (CVD) have been investigated extensively. However, detailed information about microstructural evolution, decomposition and fcc-wurtzitic (w) transformation at elevated temperatures is still missing. Thus, within the present work, the temperature-induced microstructural changes were studied up to temperatures of 1300 °C for a nano-lamellar fcc-$Ti_{0.2}Al_{0.8}N$ coating that was deposited using thermal CVD at ~850 °C. *In situ* high-temperature X-ray powder diffraction and differential scanning calorimetry experiments were employed to follow the phase evolution at elevated temperatures. Scanning and transmission electron microscopy, carried out *ex situ* for six different microstructural states after isothermal annealing, revealed the distribution of individual phases, morphology of the phase regions and the orientation relationship of fcc-TiN clusters embedded in the w-AlN matrix. Complementary atom probe tomography investigations provided 3D information about the distribution of Ti and Al and about the formation of clusters after annealing. In the as-deposited state, the coating is characterized by columnar, relatively large fcc grains exhibiting a nano-lamellar microstructure. Initial decomposition of supersaturated fcc-$Ti_{1-x}Al_xN$ and transformation of Al-rich fcc-(Al,Ti)N to w-(Al,Ti)N were detected at temperatures of ~850-1000 °C. Up to ~1200 °C, intact nano-lamellar fcc areas were still observed, but they already co-existed with fully decomposed and transformed areas. The results indicate a wavefront-like decomposition/transformation within and across individual grains that constantly reduce the fcc fraction with increasing temperature.

3:10pm **B2-2-6 Dense, Uniform, Transparent SIO_2/TIO_2 Coatings Derived from a Single Precursor Source of Tetrabutyl Titanate Modified Perhydropolysilazane**, ***Zongbo Zhang***, Institute of Chemistry, Chinese Academy of Science, China*; D Wang,* University of Chinese Academy of Sciences, China*; Y Luo, C Xu,* Institute of Chemistry, Chinese Academy of Sciences, China

SiO_2/TiO_2 thin or multilayers of SiO_2 and TiO_2 coatings have being widely investigated and applied in the fields of optical waveguiding, antireflection coatings, thermal protection systems, self-cleaning coatings, and semiconductor devices, for their excellent optical, photocatalytic, superhydrophilic, electrical, and mechanical properties. Various methods have been adopted to prepare SiO_2/TiO_2 coatings, such as electron-beam evaporation, chemical vapor deposition (CVD), and sol-gel process. Among these methods, the sol-gel method is simple and inexpensive, especially suitable for preparation of coatings on components with complex surface or big dimensions. However, due to the faster hydrolysis rate of Ti precursor, co-hydrolysis of alkoxylsilane and tetra-alkyl orthotitanate usually achieve inhomogeneous dispersion of SiO_2 and TiO_2 sol, which results in aggregates, cavities, rough surface in the formed SiO_2-TiO_2 coating.

In this work, dense, uniform, transparent, robust SiO_2/TiO_2 composite coatings have been successfully prepared by hydrolysis and subsequent thermal treatment of tetrabutyl titanate-modified perhydropolysilazane. The composition analysis revealed that Ti element was uniformly distributed in the composite coatings. The anatase TiO2 formed initially in the coating when the heat-treatment temperature reached 700oC. The as-prepared coatings have their thickness in range of 100 to 142 nm, and transmittance over 90% in the visible region. The refractive index, surface hardness, and elastic modulus of coatings enhanced continuously with the increasing pyrolytic temperature. Besides, the obtained coating possesses excellent hydrophilicity with contact angle below 40o and low roughness with Sa below 3.5nm.

3:30pm **B2-2-7 Emerging Photoluminescence in Chemical Vapor Deposition Grown $MoSe_2$/*h*-BN Van der Waals Heterostructure**, ***Pramoda K. Nayak***, Indian Institute of Technology Madras, India*; S Ahn, C Hyun, K Ma, H Shin,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Atomically thin transition metal dichalcogenides (TMDCs) with chemical formula MX_2 (M = W, Mo and so on, and X = S, Se, or Te) have attracted considerable interest today owing to their sizable band gap in a technologically interesting range1–3 eV [1], which paves the way to consider these materials for new generation field–effect transistors, sensors and optoelectronic devices. In parallel, hexagonal boron nitride (*h*-BN) have also gained a great deal of attention in the last few years with the emergence of two-dimensional atomic crystals and its unique electronic properties including wide band gap, low dielectric constant, high thermal conductivity and chemical inertness [2]. Van der Waals heterostructures made up of TMDs and *h*-BN are supposed to exhibit improved materials properties which are different from that of individual counterparts [3]. Mechanical transfer process is the most preferred way to prepare TMDCs/*h*-BN HS, which includes a deposition of polymers and a solution-based washing process [4], that degrades the quality of sample. Therefore, it is very necessary to develop a simple, fast, and scalable direct growth process to avoid any material deterioration that arises during wet-chemical assisted transfer processes.

In this work, we report direct growth of $MoSe_2$ onto high-quality multilayer *h*-BN using chemical vapor deposition. Interestingly, we observed emerging photoluminescence in $MoSe_2$/*h*-BN HS, *i.e.* the PL intensity of monolayer $MoSe_2$ increases by one order of magnitude with reduced FWHM of 45 meV, implying high crystallinity of $MoSe_2$ while prepared on *h*-BN substrate. This is attributed due to the good interlayer coupling, cleaner and sharper interfaces, smaller lattice strain, and lower doping of the underlying *h*-BN substrate [5]. Our work allows fabrication of a variety of TMDCs/*h*-BN heterostructures and paves new direction to consider these materials for next-generation optoelectronics devices including solar cells, LEDs, Laser diodes and so on.

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[3] L. Fu, Y. Sun, N. Wu, R. G. Mendes, L. Chen, Z. Xu, T. Zhang, M. H. Rümmeli, B. Rellinghaus, D. Pohl, L. Zhuang, L. Fu, *ACS Nano* 10, 2063−2070 (2016).

[4] G. H. Lee, Y. J. Yu, X. Cui, N. Petrone, C. H. Lee, M. S. Choi, D. Y. Lee, C. Lee, W. J. Yoo, K. Watanabe, *et al. ACS Nano* 7, 7931–7936 (2013).

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3:50pm **B2-2-8 Innovative Concepts for Advanced CVD Carbide Coatings Grown by Direct Liquid Injection of Metalorganic Precursors**, ***Francis Maury***, CIRIMAT, CNRS - University of Toulouse, France*; A Michau,* CEA Saclay, France*; G Boisselier,* CIRIMAT, France*; F Schuster,* CEA Saclay, France

DLI-MOCVD is an emerging CVD process that combines the use of metalorganic precursors (MO) and direct liquid injection (DLI) of the reactive sources. The main advantages are a significant reduction of the deposition temperatures and the feeding of the reactor by high vapor flow rates. Even if the process can operate at atmospheric pressure, *e.g.* for continuous scrolling treatment, it is under moderately reduced pressures (0.1-5 kPa) that application prospects are greatest due to the diversity of coatings that can be deposited for surface engineering.

Initially DLI technology has been developed and has grown rapidly for the deposition of functional oxide thin films for optical and electronic devices. In that case, oxygen-containing precursors can be selected due to their good volatility, stability and solubility in organic solvents. A solution of precursor is injected and O_2 flow rate is frequently added to prevent the film contamination by carbon originating both from the solvent and the precursor since it can be consumed by combustion in the reactor. Oxidation of the film is not a problem since it is an oxide that is deposited.

The challenge of depositing non-oxide coatings as carbides is more complicated because oxygen must be excluded from the process, including from the solvent and the precursor. Then the control of C incorporation in the coating is tricky to deposit the desired phase. The knowledge of the chemistry implemented is a key factor.

Recently, we have developed DLI-MOCVD processes for depositing non-oxide coatings. For instance bis(arene)M precursors, where M is a transition metal in the oxidation state zero (Cr, Mo, W, V…) are an important family of CVD precursors for deposition of carbides, nitrides and

even the metal. Other new DLI-MOCVD processes were developed for SiC and HfC coatings.

Based on the deposits of CrC_x, SiC and HfC, we will highlight and discuss innovative concepts specific to these DLI-MOCVD processes. This includes *(i)* related surfactant effect induced by the solvent to produce smooth surfaces (SiC), *(ii)* positive effects of nanostructuration for hard metallurgical coatings as CrC/CrN multilayers and refractory nanostructured SiC/HfC coatings for high temperature environments, *(iii)* uniform and high conformal coverage coatings (CrC) on 3D pieces for corrosion protection, *(iv)* infiltration efficiency of SiC/HfC multilayer coatings for advanced ceramics, *(v)* self-healing of SiC cracks during the growth of SiC/HfC and *(vi)* deposition of mixed carbides (CrSiC).

4:10pm **B2-2-9 Computational Fluid Dynamics (CFD) Simulation of CVD Process for $(Ti,Si)_x(C,N)_y$ Coating**, ***Lianchang Qiu,*** Central South University, China*; S Wang,* Shijiazhuang Tiedao University, China*; Y Du, Z Zhong,* Central South University, China*; H Shi,* Ganzhou Achteck Tool Technology Co., Ltd., China*; L Albir,* Layyous Consulting Ltd., Israel

In the present work, the CVD process for $(Ti,Si)_x(C,N)_y$ coating in the vertical hot-wall reactor was studied through the Computational Fluid Dynamics (CFD) simulation method. By means of ANSYS Fluent software, the reactor model was established and meshed. The CVD process of $(Ti,Si)_x(C,N)_y$ coating from $TiCl_4$-$SiCl_4$-CH_3CN-NH_3-H_2 gas mixture was investigated under different deposition conditions. The thermal and hydrodynamic characteristics inside the reactor were simulated. The influence of concentration of gas species on the growth rate of $(Ti,Si)_x(C,N)_y$ coating deposited on specimens, which were located at different position of the reactor, was predicted. The computational predictions of the growth rate were in reasonable agreement with the experimental measurements. The CFD method is of great importance to optimize the process parameters and provide theoretical guidance for improving the coating uniformity in thermal CVD process.

4:30pm **B2-2-10 Tribological Evaluation and Behavior of DLC Coatings on Steel in PE-CVD System with TiO_2 Over Layer using ALD Technique**, ***Marco A. Ramirez R.,*** Univap, Brazil*; E Saito,* Federal University of São Paulo, Brazil*; N Fukumasu,* University of São Paulo, Brazil

Diamond-Like Carbon (DLC) coatings have attracted significant attention due to low friction, high hardness and high wear resistance. These films meet conditions that can be used in some mechanical applications in aerospace, medical and automotive industries. The major disadvantage of these coatings is a low adhesion on metallic substrates, caused by elevated compression residual stresses after deposition. Some plasma conventional methods require a high consumption of energy that are used to grow DLC films, resulting in a high level of temperature and pressure during the deposition, which affects the adhesion of the film to the substrate. DLC coatings were deposited employing an asymmetrical bipolar pulsed-DC PECVD system, in a very low temperature and pressure (about 87° C and 0.1 Pa) which allowed lower level of collisions and a higher plasma density. Methane gas was used as a precursor. In order to overcome low adhesion of DLC films on steel substrate, a thin amorphous silicon inter-layer was deposited at the interface, and to the last process was to deposit a thin TiO2 film over DLC using ALD Technique. Resulting coatings were observed with SEM and Raman spectroscopy to analyze atomic arrangement. The total residual stress was evaluated by the curvature method. The tribological behavior (friction and wear) was analyzed by lubricated reciprocating wear tests at room temperature. The elevated coating hardness (higher than 25 GPa) promoted good wear resistance. These results suggest that the PECVD-DC Pulsed with additional cathode and methane as a precursor gas to grow DLC films on metallic substrates may represent a new alternative to improve the mechanical behavior in some applications.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Sunrise - Session C1

Optical Metrology in Design, Optimization, and Production of Multifunctional Materials

Moderators: Nikolas Podraza, University of Toledo, Juan Antonio Zapien, City University of Hong Kong

1:50pm **C1-2 Design Principles for Binary and Multicomponent Conductive Nitrides for Applications in Electronics Plasmonics and Photonics**, ***Panos Patsalas,*** Aristotle University of Thessaloniki, Greece*; N Kalfagiannis,* Nottingham Trent University, UK*; S Kassavetis,* Aristotle University of Thessaloniki, Greece*; G Abadias,* Université de Poitiers, France

Although conductive nitrides, such as TiN, ZrN, and $Ti_xAl_{1-x}N$, were intensively studied for mechanical applications since 1980s and as diffusion barriers since 1990s, their combination of thermal and mechanical stability, with the compatibility of their growth to CMOS fabrication, and with their refractive character and electronic conductivity, paved the way for their emergence as important plasmonic and photonic materials [Naik, G.V. *et al*, Adv. Mater. 25 (2013) 3264-3294; Kassavetis, S. *et al*, Surf. Coat. Technol. 295 (2015) 125-129; Kassavetis *et al*, Appl. Phys. Lett. 108 (2016) art. No. 263110; Metaxa *et al*, ACS Appl. Mater. Inter. 9 (2017) 10825-10834]. In this work, we review the optical properties, in terms of ellipsometry, FTIR spectroscopy, and XPS valence band spectra, of a wide range of binary (TiN, ZrN, HfN, VN, NbN, TaN, MoN, WN) and multicomponent ($Ti_xMg_{1-x}N$, $Ti_xSc_{1-x}N$, $Ti_xAl_{1-x}N$, $Ti_xZr_{1-x}N$, $Ti_xHf_{1-x}N$, $Ti_xNb_{1-x}N$, $Ti_xTa_{1-x}N$, $Ti_xMo_{1-x}N$, $Ta_xZr_{1-x}N$) films and we establish correlations between their optical behavior, electron conductivity and work function with the intrinsic (*e.g.* the valence electron configuration of the constituent metal) and extrinsic (*e.g.* point defects and microstructure) factors. We also correlate the plasmonic performance of nitride nanostructures and nitride/dielectric interfaces with the electron density of states of their valence band. We demonstrate that, indeed TiN and ZrN along with HfN are the most well-performing plasmonic materials in the visible range, while VN and NbN may be viable alternatives for plasmonic devices in the blue, violet and near UV ranges, albeit in expense of increased electronic loss. WN is disregarded as candidates for plasmonics, opposing recent theoretical works, due to the excessive concentration of point defects, even in epitaxial form. Finally, TaN has a substantial plasmonic activity in the metastable, cubic rocksalt structure, however, in most cases tends to form mixed cubic-hexagonal samples that are also excessively lossy. Furthermore, we consider the alloyed ternary conductive nitrdes and by critical evaluation and comparison, we identify the emerging optimal tunable plasmonic conductors among the immense number of alloying combinations. As a result, we provide design principles of nitride conductors for plasmonic, photonic, and optoelectronic devices, such a nanoantennas, SERS-based biosensors, selective absorbers of solar or other radiation, stable Bragg-mirrors, epsilon-near-zero (ENZ) metamaterials, and ohmic contacts for light emitting diodes based on III-V semiconductors.

2:10pm **C1-3 Tip Enhanced Optical Microscopy and Spectroscopy Based on Near Field Force Detection – a Review**, ***H. Kumar Wickramasinghe,*** University of California, Irvine, USA **INVITED**

Near field scanning optical microscopy (NSOM) has evolved into a rich field of study with many different variants over the past 25 years. Many different modes of NSOM based on apertureless/scattering NSOM techniques have evolved such as near-field fluorescence and Tip Enhanced Raman Spectrosocopy (TERS) etc. All these techniques are based on measuring a local tip enhanced near-field interaction in the far field. In this talk we present a review of a new modality where optical microscopy/spectroscopy is performed by measuring the dipole-dipole interaction force between an optically driven sample and a dipole created in the tip – here, a near field optical interaction is measured *in the near-field*. Photo induced force microscopy (PIFM) is capable of measuring both the linear and non-linear optical response of a sample on the nanoscale. We will present recent experimental and theoretical data both in the visible and in the mid infra-red.

2:50pm **C1-5 Crystallite Grain Orientation Manipulation through Deposition Flux Angle and Composition in $CdSe_{1-x}Te_x$**, ***Dipendra Adhikari,*** *M Junda, C Grice, P Koirala, Y Yan, R Collins, N Podraza,* University of Toledo, USA

Cadmium telluride (CdTe) based semiconductors are of interest as absorber layers for thin film photovoltaics. In particular, alloying with selenium ($CdSe_{1-x}Te_x$) has helped to significantly improve device efficiency by

reducing parasitic absorption losses in the vicinity of the n-type heterojunction partner. Here microstructural properties of two series of films are studied using grazing incidence x-ray diffraction measurements (GIXRD), scanning electron microscopy, and spectroscopic ellipsometry. A CdTe series consists of films deposited by sputtering onto soda lime glass substrates mounted at 0°, 45°, 55°, 65°, 75°, and 85° source flux angles relative to the substrate normal (i.e. glancing angle deposition). A $CdSe_{1-x}Te_x$ series is fabricated by co-sputtering CdSe and CdTe with varying combinations of individual cathode powers resulting in a film series that spans the full range of compositions from x = 0 to 1. Influence of deposition angle and film composition on resultant crystalline grain size and orientation are tracked for these films. All CdTe films studied are found to have cubic crystal structure and (111) preferential grain orientation. Films deposited at 0° and 45° are almost entirely (111) oriented, whereas films deposited at intermediate angles exhibit a wider variety of competing grain orientations, suggesting that deposition angle can be used as an effective parameter towards controlling grain orientation. With increasing numbers of grain orientations, grain size is found to decrease. $CdSe_{1-x}Te_x$ alloys exhibit diffraction peaks corresponding to both cubic and hexagonal crystal systems. The films have a (111) preferred grain orientation that shifts from lower to higher values of 2ϑ with increasing Se content. These $CdSe_{1-x}Te_x$ films are measured in both as-deposited and $CdCl_2$ treated states with all $CdCl_2$-treated samples having increased grain size compared to corresponding as-deposited samples. Generally, the diffraction patterns transition from CdSe-like to CdTe-like with increasing x. However, interesting behavior is observed for intermediate compositions, such as the (103) diffraction peak corresponding to hexagonal crystal system becoming relatively strong for a few compositions with low x, but being weak for all others.

3:10pm **C1-6 Durable Electrochromic Coating Systems for Advanced Smart Windows and Security Devices**, *F Blanchard, B Baloukas, S Loquai, J Klemberg-Sapieha,* ***Ludvik Martinu,*** Polytechnique Montréal, Canada

The present work is our latest contribution to the development of large area smart windows based on electrochromic materials that have yet to properly breach the market due to the following main limitations: 1) the fabrication costs are still quite high, and 2) the durability of the system as a whole still requires significant improvements.

In response, this study offers a highly attractive and counterintuitive solution to both of these issues. Traditional WO_3 films, the main constituent of electrochromic windows, are traditionally deposited by magnetron sputtering at relatively high pressures (10-30 mTorr) to generate sufficient porosity and thus ensure a high ionic mobility. In this work, we explore a new and different approach to control the porosity involving intense ion bombardment during deposition at low pressures (< 5 mTorr). The resulting films' performance is tested through cyclic voltammetry using both H+ and Li+ ions and other complementary methods. We systematically categorize the coating properties based on their coloration efficiency, dynamic behavior and chemical durability. The present ion bombardment approach leads to a deposition rate increase of five times compared to the standard fabrication method, while the long term stability is significantly enhanced. The film characteristics are explained in terms of a microstructural model based on the formation of a unique nanocrystalline porous structure. In combination with an appropriate control of the surface reactions, this offers a possibility to tailor the transmission and reflection spectra of such coatings with enhanced durability for various applications such as advanced glazings for architectural glass, color shifting active security and authentication devices, and others.

3:30pm **C1-7 From "n" and "k" to Solar Cell Functionality: The Importance of Optical Property Characterization**, ***Nikolas Podraza,*** *M Junda, I Subedi, K Ghimire,* University of Toledo, USA

Predominate types of photovoltaic (PV) technologies studied at present were invented in the last century. Industrially manufactured devices based on wafer silicon (Si) and thin film cadmium telluride (CdTe) still have relevant problems with respect to their characterization. Methylammonium lead iodide perovskite (CH3NH3PbI3) materials have recently achieved very high efficiency when implemented as PV absorber layers. Here the optical properties of layers in each of these types of devices will be discussed. For "past-to-present" generation materials, Si wafer based PV with aluminum (Al) back surface fields (BSF) are modeled with particular attention paid to the characterization of Al+Si interfacial region optical properties as obtained by through-the-Si spectroscopic ellipsometry. When Al+Si optical properties are obtained and incorporated into the ray-tracing simulation of Si wafer solar cell modules, good convergence is obtained between those simulations and experimental results also with device performance parameters such as short circuit current density (Jsc) from quantum efficiency simulations (QE) aligned with experimental results. Next, "present" generation thin film PV including CdTe device structures are characterized by through-the-glass spectroscopic ellipsometry and modeled with QE based on reference optical properties to illuminate sources of optical and electrical losses. When CdTe is alloyed with selenium (Se), the band gap is narrowed and device performance is altered both in simulation in experimental QE results. Similarly, "future" generation CH3NH3PbI3 perovskite based solar cells are characterized by through-the-glass ellipsometry with QE modeling matching experiment. Band gap narrowing of this class of perovskites is characterized with spectroscopic ellipsometry. The resulting optical constants are used in the simulation of perovskite based single junction and tandem junction solar cells.

3:50pm **C1-8 Bipolar Resistive Switching Performance of MoS_2 Based ReRAM Devices using WN as Bottom Electrode for Non-volatile Memory Application**, ***Ravi Prakash,*** *S Sharma, D Kaur,* Indian Institute of Technology Roorkee, India

The reproducible resistive switching characteristics of sputtered deposited MoS_2 thin film has been investigated in Cu/MoS_2/WN stack configuration for resistive random access memory (ReRAM) application. Excellent bipolar resistive switching (RS) properties have been observed at a low voltage of +2.1 V and -2.5 V respectively, which favors device to reduce the power consumption. The advantages of employing WN over Pt or Ti as bottom electrode material were demonstrated such as the low resistive state value and uniformity of other RS parameters like endurance and retention. Formation/disruption of the conducting filament is verified as the main cause of exhibiting the RS properties. Ohmic behavior and trap-controlled space charge limited current (SCLC) conduction mechanisms are confirmed as dominant conduction mechanism at low resistance state (LRS) and high resistance state (HRS). High resistance ratio (10^2) corresponding to HRS and LRS, good write/erase endurance (10^3) and non-volatile long retention (10^3 sec) are also observed. This study demonstrated that the MoS_2 thin films with WN bottom electrode have a great potential for future non-volatile ReRAM application.

Coatings for Biomedical and Healthcare Applications
Room Royal Palm 1-3 - Session D4

Biointerfaces: Improving the Cell Adhesion and Avoiding Bacteria Adhesion. What Kinds of Coatings Should be Used?

Moderators: Marcela Bilek, The University of Sydney, Margaret Stack, University of Strathclyde, Vincent Fridrici, Ecole Centrale de Lyon - LTDS

2:10pm **D4-3 Titanium Oxide Coatings to Improve Cell Adhesion and Differentiation**, *V Garcia-Perez, A Almaguer-Flores,* Universidad Nacional Autónoma de México, Mexico*; R Olivares-Navarrete,* Virginia Commonwealth University, USA*; A Fonseca-Garcia,* ***Sandra Rodil,*** Universidad Nacional Autónoma de México, Mexico **INVITED**

Amorphous titanium oxide ($aTiO_2$) coatings were produced by magnetron sputtering using a Ti target and a reactive Ar/O_2 atmosphere. The coatings were deposited on commercially pure titanium ($aTiO_2$/cpTi) and stainless steel ($aTiO_2$/SS) substrates with a thickness of about 60-70 nm. For the SS substrates, a Ti buffer layer was used to improve the film-substrate adhesion. The results from different cell-surface interactions clearly show that a thin but dense and stoichiometric TiO_2 oxide film present a better biological response than the cpTi, even when deposited on the SS substrate. A significantly larger initial attachment (2 hours) of human osteoblasts cells was observed on the TiO2 films in comparison to cpTi even at protein-depleted conditions, i. e, using serum-free culture media. The attachment was comparable to that obtained on collagen-coated plastic dishes (100%), while on cpTi only a 40% of attachment was obtained. The cell adhesion at longer period of times (24h and 7 days) was also demonstrated for human mesenchymal stem cells (MSCs). Similarly, a larger differentiation into osteoblasts of the MSCs was observed on the $aTiO_2$/cpTi coatings in comparison to the native oxide layers (cpTi) for two different surface roughnesses: smooth (0.3 µm) and micro-rough (2.6 µm). As a final test, the cell adhesion, differentiation and inflammatory response of MSCs on $aTiO_2$/SS surfaces was compared to the cpTi and the SS metallic surfaces. The results clearly show that the amorphous TiO2 surfaces presented the highest expression of integrins and production of osteogenic

proteins in comparison to the uncoated SS surfaces, reaching a very similar response to that presented by the typically used titanium surfaces. Moreover, the pro-inflammatory factors were inhibited while anti-inflammatory factors were up-regulated, demonstrating the advantage of using thin TiO_2 films for the development of orthopedic and dental implants with improve bone regeneration and osseointegration.

Acknowlegments: PAPIIT IN100116 and CONACYT 251279

2:50pm **D4-5 Antibacterial Thin Films with Controlled Antibiotics Release Based on Plasma Polymer**, ***Vitezslav Stranak***, *J Kratochvil, D Kahoun, J Sterba, H Langansova, J Lieskovska,* University of South Bohemia, Czech Republic; *J Hanus, J Kousal, A Kuzminova, O Kylian,* Charles University in Prague, Czech Republic

Bacterial infections developed after implant surgery can cause serious medical complications for the patients. Current approach for infection suppression is to use systemic treatment of the patient by antibiotics. An alternative and very promising approach, that gains increasing attention, is to cover the surface of the implant with bioactive thin film, which prevents creation of the biofilm. Main benefit of this method are local treatment and possible supporting effect to the conventional systemic treatment.

Two different methods, which are able to gradually release antibacterial agents, will be presented. First method is based on immobilization of Ampicillin (i.e. common antibiotic) into magnetron sputtered Nylon 6,6 thin films. It was proven that Ampicillin is immobilized equally in the volume of Nylon 6,6 film, so it is possible to easily tune the amount of antibiotics in the coatings simply by changing their thickness. Controlled release kinetics can be achieved by deposition of diffusion barrier. Nanocomposite consisting of Cu nanoparticles, embedded into plasma polymerized PTFE represent the second method. Advantage of nanoparticles is their huge area against their volume, which reduces side effects of antibacterial metals in human body to minimum. Both methods are applicable to any substrate including smooth metals or polymers.

Acknowledgement: This work is supported by GACR 16-14024S.

3:10pm **D4-6 Development of a Microfluidic Based Multianalyte Biosensor Device for Medical Diagnostics**, ***Emma MacHugh***, Dublin Institute of Technology, Centre for Research in Engineering Surface Technology (CREST), Ireland; *B Duffy, M Oubaha,* Centre for Research in Engineering Surface Technology (CREST), Ireland

Over the past decade, the biosensor research community has intensively investigated the development of innovative point-of-care (POC) devices often targeting the improvement of the platforms sensitivities for single analyte detection. However, in certain situations the detection of several in parallel is desired for economical and practical reasons, making the development of multianalyte platforms one of the most promising methodologies in the medical diagnostic industry.

Most biosensors also require an integrated microfluidic system for the flow of analyte liquids (blood, saliva and urine) onto the sensor areas of the POC. In order to enable a rapid and efficient delivery of these analytes, of the most important parameters, the surface properties of the microchannels have to exhibit as high a surface energy as possible. Unfortunately, to date, most materials employed in the fabrication of microfluidics are based on hydrophobic materials, the most popular of those being PDMS, and utilises low resolution fabrication processes, such as injection moulding and often require external pumps to activate the circulation of the liquids.

In this study, we propose a new fabrication concept of optical multianalyte biosensor platforms based on the integration of multiple sensor spots onto a microfluidic platform. The originality of the study resides in the development of high surface energy hybrid sol-gel materials that can be simultaneously photoreactive for microstructuration of high resolution microchannels by standard photolithography processes and irreversible immobilization of biological species. The preparation and characterisation of these innovative materials as well as the development of multianalyte biosensors will be presented. Correlation between the structure and surface properties of these materials along with the correlation of these properties against the fluidic performances of the biosensors platforms will be discussed. Finally, demonstration of concept of the multianalyte capability of the biosensor platform via optical fluorescence and a sandwich ELISA will be presented.

3:30pm **D4-7 Bactericidal Activity and Cytotoxicity of a Zinc Doped PEO Titanium Coating**, ***Luciane Santos***, Pontificia Universidade Católica do Paraná, Brazil; *K Popat,* Colorado State University, USA; *P Soares,* Pontificia Universidade Católica do Paraná, Brazil

Metallic implants are susceptible to bacterial colonization even years after the implantation impairing the osseointegration process. The treatment of a colonized implant is highly demanding, and in most cases implant replacement is the only effective solution. To avoid the bacterial attachment and proliferation, bactericidal coatings are proposed as a long-term prevention tool. Those coatings must assure a bactericidal activity for a long period and cannot induce cytotoxic responses in eukaryotic cells. Among all the bactericidal agents Zinc is one of the most investigated due to its broad bactericidal activity spectrum and its stimulatory effect on bone formation. The aim of this study is to obtain a titanium oxide coating containing Zinc and evaluate its bactericidal activity, cytotoxicity and ion release profile. The coating was obtained by Plasma Electrolytic Oxidation (PEO) on commercially pure titanium grade 4 at 350 V for 60 s. Samples were divided in two groups, the reference group was obtained in a base electrolyte containing calcium acetate and calcium glycerophosphate (called CaP group). The experimental group has added Zinc acetate as a Zinc source to the base electrolyte (called Zn-CaP group). The surface was characterized by Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS), while the ion dissolution was evaluated by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). The bactericidal activity was determined against *Staphylococcus aureus* by fluorescence microscopy using a live/dead viability kit. The cytotoxicity against eukaryotic cells was evaluated using adipose derived stem cells (ADSC) using the lactate dehydrogenase (LDH) assay. Zinc, Calcium and Phosphorous were incorporated to the titanium oxide coating and no changes on the coating structure and morphology were observed by the addition of Zn to the electrolyte. ICP-AES results show the coatings released Ca, P and Z ions after 28 days of immersion in DI water. The ICP-AES profile suggests the ion release reach an equilibrium state after 7 days of immersion. The Zn-CaP coating presented bactericidal activity against *S. aureus*, showing a higher number of dead bacteria after 6 h of incubation and a lower number of living bacteria after 24 h compared to CaP group. No cytotoxic effect was observed against ADSC by the presence of Zn on the coating, indicating the Zn-CaP coating has a potential to prevent bacterial colonization in metallic implants.

3:50pm **D4-8 Antibacterial Effects of Titanium Embedded with Silver Nanoparticles Based on Electron-Transfer-Induced Reactive Oxygen Species**, ***Guomin Wang***, *W Jin, A Qasim, A Gao, X Peng, W Li, H Feng, P Chu,* City University of Hong Kong, Hong Kong

Although titanium embedded with silver nanoparticles (Ag-NPs@Ti) are suitable for biomedical implants because of the good cytocompatibility and antibacterial characteristics, the exact antibacterial mechanism is not well understood. In the present work, the antibacterial mechanisms of Ag-NPs@Ti prepared by plasma immersion ion implantation (PIII) are explored in details. The antibacterial effects of the Ag-NPs depend on the conductivity of the substrate revealing the importance of electron transfer in the antibacterial process. In addition, electron transfer between the Ag-NPs and titanium substrate produces bursts of reactive oxygen species (ROS) in both the bacteria cells and culture medium. ROS leads to bacteria death by inducing intracellular oxidation, membrane potential variation, and cellular contents release and the antibacterial ability of Ag-NPs@Ti is inhibited appreciably after adding ROS scavengers. The whole process can be found in Fig. 1. Even though ROS signals are detected from osteoblasts cultured on Ag-NPs@Ti, the cell compatibility is not impaired. This electron-transfer-based antibacterial process which produces ROS provides insights into the design of biomaterials with both antibacterial properties and cytocompatibility.

4:10pm **D4-9 Tribocorrosion and Cytotoxicity of FeB-Fe_2B Layers on AISI 316 L Steel**, *I Campos-Silva,* Instituto Politecnico Nacional, Surface Engineering Group, Mexico; *M Palomar-Pardavé,* Universidad Autonoma Metropolitana-A, Mexico; *R Perez Pasten-Borja,* Instituto Politecnico Nacional, ENCB Zacatenco, Mexico; *O Kahvecioglu,* Argonne National Laboratory, USA; *D Bravo-Bárcenas,* Universidad Autonoma Metropolitana-A, Mexico; *C López-García,* ***RodolfoYael Reyes-Helguera***, Instituto Politecnico Nacional, Surface Engineering Group, Mexico

All metallic biomaterials are required to satisfy various criteria, such as adequate strength, high resistance to corrosion, biocompatibility, and high wear resistance. However, the various biomaterials that have been developed thus far do not satisfy all of the above requirements. Wear and

corrosion have been reported to be the primary reasons for the failure of implant elements.

One alternative to reduce corrosion and wear is the boriding process. Boride layers have excellent resistance to crevice and pitting corrosion, high temperature performance as well as outstanding mechanical properties in corrosive environments. Based on that, new results about the tribocorrosion resistance and cytotoxicity of borided AISI 316 L steel are presented in this work. The powder-pack boriding process was conducted at 1273 K with 4 h of exposure, whereas a FeB-Fe_2B layer, with 50 microns of thickness, was obtained at the material surface. The tribocorrosion tests were performed in Hank's solution, using a ball-on-flat tribometer, which was connected with a three electro-chemical cell. The system comprised Al_2O_3 ball as the counterpart, the borided AISI 316 L steel as the working electrode, platinum rod as the counter electrode, and Ag/AgCl as the reference electrode. All sliding test, in the presence or absence of corrosion, was performed under 20 N normal force, considering a total sliding distance of 100 m.

The *in vitro* cytocompatibility of borided AISI 316 L steel was evaluated and compared with a conventional AISI 316 L steel. The immortalized human fibroblast CHON-002 and Vero established cell line from ATCC collection were used. Cells were exposed to conditioned leachates produced by immersion of the materials in culture medium (DMEM). Polyurethane film containing 0.1% zinc diethyldithiocarbamate (ZDEC) and polyurethane film containing 0.25% zinc dibuthyldithiocarbamate (ZDBC), as well as high density polyethylene films were used as reference materials. Cells cultured in fresh medium was used as negative control. Cell viability was established with the cellular metabolic activity assay by means of MTT (3-(4,5-dimethylthiazol-2-yl)-2, 5diphenyl- tetrazolium bromide). The data were analyzed statistically by ANOVA, considering a significance of 5%.

The results showed that the presence of FeB-Fe_2B layer increases the tribocorrosion performance in comparison with the AISI 316 L steel. In addition, the AISI 316 L steel samples modified by boron denoted satisfactory properties in terms of effects on survival and proliferative activity of human fibroblasts; results that reveal that the boride layers are excellent candidates for the use as biomedical layers.

4:30pm **D4-10 Optical Spectroscopic study for Atmospheric Pressure Plasma by Radio Frequency Power**, ***Chuan Li,*** National Yang Ming University, Taiwan*; J Hsieh,* Ming Chi University of Technology, Taiwan*; C Yu,* National Yang Ming University, Taiwan

Atmospheric plasma techniques developed rapidly in the past decade. High-performance atmospheric plasma harnesses the power of plasma for surface treatment such as cleaning and coating. Due to the nature of atmospheric environment, the atmospheric plasma functions more like an ion carrier rather than reaction producer. This particular indicates that much less destructive processes such as ionization and excitation occur in the plasma zone. The less destruction implies more intact molecules or atoms survive their journeys through the plasma zone, which is crucial if one would like to maintain certain levels of the integrity of molecules delivered by the plasma to the surface of a substrate. Such a condition is particularly necessary for depositing macromolecules such as proteins, DNA/RNA in biomedical applications. It is also found useful in the task of surfaces activation and modification where the atmospheric plasma can be straightforwardly utilized for large scale productions without complicate vacuum facilities. The roll-to-roll process for coating and etching metallic or polymeric surfaces is a typical example in aviation, marine, automotive and civil applications. In this study, we investigate the effects of radio frequency of power and gas flow rates on the chemical compositions and morphology of atmospheric He plasma. A customized plasma system was setup and equipped with a radio frequency power supply, an optical emission/absorption spectrometer, deuterium halogen light source, x-y-z automated table, intensified charged coupled device camera, various flow controller and pressure gauges. The study focuses on the analysis of optical emission and absorption of spectra, temperature and power of He plasma by varying the radio frequency and flow rates. The chemical compositions of plasma are further analyzed using the optical spectra to identified possible ions and radicals. Along with the assistance of digital camera, additional information on the density of plasma is acquired for visualization. As a final touch, films of lactic acid are deposited on glass substrates via the He atmospheric plasma to demonstrate its capability as a carrier and reaction center.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Royal Palm 4-6 - Session E1-2

Friction, Wear, Lubrication Effects, and Modeling

Moderators: Albano Cavaleiro, University of Coimbra, Carsten Gachot, Vienna University of Technology, Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

2:10pm **E1-2-3 Physical Mechanisms for Nanoscale Friction of a-C:H/D Thin Films**, *F Echeverrigaray, S de Mello,* UCS, Brazil*; F Alvarez,* UNICAMP, Brazil*; A Michels,* ***Carlos Figueroa,*** UCS, Brazil

The friction forces are originated in energy dissipation events owing to the lost work of non-conservative forces. The surface structure of hydrogenated/deuterated amorphous carbon thin films in air, which plays an important role in nanoscale friction, is constituted by hydrogen and/or deuterium terminated bonds and physisorbed oxygen, nitrogen, and water molecules. In spite of friction models were well established to explain the tribological behaviour of carbon-based thin films in different atmospheres, the fundamental physical understandings of these phenomena remain open. In this work, we report the friction behaviour of a diamond spherical dome sliding on different amorphous carbon thin films containing different amounts of hydrogen and/or deuterium inspecting at the nanoscale indentation. Three different experimental setups are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film bulk, the friction coefficient decreases with the increasing of deuterium content. Secondly, for samples where hydrogen content is increased at the surface, the friction coefficient decreases with the increasing of the ratio H/C at the surface. Thirdly, for samples where the ratio H/C was fixed, the friction coefficient increases with the increasing of the relative humidity, effect that can be tuned by an external electrical field. Finally, we discuss three different physical mechanisms describing these experimental results: dissipation effects associated with phonon coupling, van der Waals forces, and orientation of water dipoles determining the friction behaviour of a-C:H/D for the above described experimental setups.

2:30pm **E1-2-4 Relocation Profilometry of Micro-tribology Experiments of Uncoated and DLC Coated Steel**, *M Gee, J Nunn, L Crocker,* National Physical Laboratory, UK*; K Holmberg,* VTT Technical Research Centre of Finland Ltd, Finland*; L Li,* City University of Hong Kong, Hong Kong*; G Stachowiak,* Curtin University, Australia*; C Gachot,* Vienna University of Technology, Austria*;* ***Tony Fry,*** National Physical Laboratory, UK

Relocation profilometry was used to evaluate the damage that occurred in micro-tribology experiments on a range of DLC coated and uncoated steel samples. Three roughness conditions were tested ranging from a ground surface to a smooth surface for both the coated and uncoated materials. The effect of varying orientation of the micro-tribology experiments with the directionality of the finished surfaces. The micro-tribology experiments were carried out using single pass scratch tests using a diamond indenters. The same areas were examined with an Olympus Lext confocal microscope which gave image and height maps from each area examined. The same areas were examined before and after scratching, and the resulting pairs of height maps registered and subtracted using Image J. The true volume of damage was thereby calculated for all experiments. Friction measurements were also made. This enabled the energy dissipated in the damage formation to be calculated.

Little effect of orientation on the damage was observed. What was quite surprising was that there was also no effect of roughness on the damage that was observed.

2:50pm **E1-2-5 Microstructural Design of Self-lubricating Laser Claddings for use in High Temperature Sliding Applications**, ***Carsten Gachot,*** TU Wien, Austria*; M Rodríguez Ripoll, H Torres,* AC²T Research GmbH, Austria*; B Prakash,* Lulea University of Technology, Sweden

Nickel-based self-lubricating claddings with the addition of Ag and MoS_2 were prepared by means of laser cladding on stainless steel substrates, aiming at their implementation in metal forming applications involving demanding tribological conditions at high temperature. The novelty of our approach relies in the addition of MoS_2 with the aim achieve a uniform silver distribution within the resulting cladding by means of an encapsulation mechanism, preventing it from floating to the surface during the deposition process and being subsequently lost during surface preparation. The role of Ag and MoS_2 concentration on the encapsulation process is discussed in terms of phase composition and resulting microstructures. The tribological behaviour of the resulting laser claddings

was evaluated at high temperature under unidirectional sliding. The encapsulation of Ag led to outstanding tribological properties while keeping the amount of Ag used at lower concentrations, thus increasing the economic feasibility of the claddings. The improvement in terms of both friction and wear was observed for the self-lubricating claddings compared to the reference alloy, making them good candidates for use in high temperature applications such as metal forming.

3:10pm **E1-2-6 Fretting Wear Behavior of Duplex PEO-Chameleon Coating on an Al Alloy**, ***Andrey A. Voevodin,*** University of North Texas, USA*; Y Liu,* University of Leeds, UK*; A Yerokhin,* University of Manchester, UK*; A Korenyi-Both,* Tribologix, Inc., USA*; M Lin,* University of Manchester, UK*; J Zabinski,* Army Research Laboratory, USA*; A Matthews,* University of Manchester, UK*; T Liskiewicz,* University of Leeds, UK

Plasma electrolytic oxidation (PEO) is an attractive technology for improving wear resistance and environmental protection of aluminum alloys. PEO results in the hard alumina based ceramic coatings of up to 100-150 micrometer thickness which are well adhered to the surface with morphology graded from a dense region near the coating-substrate interface to a porous outer region [1]. Such properties may provide PEO as an ideal underlying layer for the application of solid lubricants which can be entrapped in outside porous and provide reservoirs for the tribological contact lubrication, however the relevant work is scarce. This study investigates the fretting wear behavior and adaptive mechanisms for the PEO produced Al_2O_3 surface of about 11-12 GPa hardness with a top layer of an MoS_2-Sb_2O_3-C chameleon solid lubricating coating, which is named such for its ability to self-adapt tribological contact surface and provide friction and wear reduction in variable humidity [2]. Coupons of AA 6082 alloy were coated by the PEO process and then were over-coated by a burnishing process with a MoS_2-Sb_2O_3-C chameleon coating to prepare such duplex coating combination. The coated surfaces were then subjected to over 10,000 cycles of fretting wear against steel and alumina balls with variable amplitude (0 to 100 micrometers) and loads (10-100 N) in both humid air and in dry nitrogen, including cycled (air/nitrogen) environment conditions. The tests demonstrated low friction coefficients, considerable reduction in critical amplitude for the stick-slip transition, and self-adaptive tribological behavior in the cycled environment tests. Friction coefficients of the order of 0.10 to 0.15 in humid air and 0.06 to 0.09 in dry nitrogen were recorded and linked with the surface self-adjustment from graphite to MoS_2 lubrication, respectively. Raman, SEM and cross-sectional FIB/SEM/EDX analysis of the wear tracks were used to investigate the mechanisms of the adaptation and fretting wear performance. The study demonstrate the effectiveness of the adaptive PEO-Chameleon coating system performance for the fretting wear mitigation in changing environment.

[1] A.L. Yerokhin et al., Surface and Coatings Technology, 122 (1999) 73.

[2] J.S. Zabinski et al., Tribology Letters, 23 (2006) 155.

3:30pm **E1-2-7 Lubricant/Coating Interactions and Their Effect on Tribological Performance: In-situ XAS Analysis of a Dynamic Lubricated Interface**, ***Ardian Morina,*** University of Leeds, UK **INVITED**

The ability to model and predict friction and wear performance in boundary-lubricated conditions is limited by the lack of qualitative and quantitative information on transient tribochemical reactions between the lubricant additives and surfaces. It is these reactions that define tribofilms ' physical and chemical properties, essential for friction and wear performance of industrial boundary lubricated systems, such as valve train, piston ring/liner and pumps. In addition to tribofilm formation, recent work has shown that some of the lubricant additives, such as Molybdenum dialkyl dithiocarbamate (MoDTC), can have a detrimental impact on hydrogenated Diamond-Like-Carbon (DLC) coating durability.

In the current paper, a bespoke tribometer has been designed to be coupled with the Raman spectroscopy and synchrotron X-ray Absorption Spectroscopy for in-situ study of the tribochemical reactions between the lubricant additives and the surface. The focus will be on two typical lubricant additives: Zinc dialkyl dithiophosphate (ZDDP) used as an anti-wear, and MoDTC used as a friction modifier additive. The growth of tribofilms on heat-treated and DLC coated surfaces, in relation to friction and wear performance, will be discussed in detail.

4:10pm **E1-2-9 Friction and Wear Mechanism of MoS_2/C Composite Coatings under Atmospheric Environment**, ***Peiling Ke,*** *S Cai, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Tribological properties of MoS_2/C coatings with different carbon contents (44.7~84.3 at.%) deposited by magnetron sputtering were systematically investigated under atmospheric environment. During tribological tests, the coating with the least MoS_2 content exhibited the lowest friction coefficient and wear rate, while coating with the most MoS_2 showed the worst performance. To understand friction and wear mechanism, multiple analytical tools such as SEM, EDS, Raman, XPS and TEM were applied to investigate the composition and structure. TEM and SEM characteristics proved that the tribofilm with multilayered structure was formed on the tribo-pair. The C rich layer adhered to the tribo-pair and the top layer was well-ordered MoS_2 tribofilm, and the dominated amorphous MoS_2 was found between the two layers. It suggested that the shear plane was mainly made of well-ordered MoS_2 transfer film, while carbon improved the mechanical properties of the coatings, served as a lubricant and also inhibited the oxidation of MoS_2.

4:30pm **E1-2-10 Adhesion and Mechanical Properties of Ti Films Deposited by DC Magnetron Sputtering**, ***RobertoCarlos Vega-Morón,*** *G Rodríguez-Castro,* Instituto Politecnico Nacional, Surface Engineering Group, Mexico*; D Melo-Máximo,* Tecnológico de Monterrey-Campus Estado de México, Mexico*; J Méndez-Méndez,* Instituto Politécnico Nacional, Mexico*; L Melo-Máximo,* Instituto Tecnológico y de Estudios Superiores de Monterrey, Mexico*; J Oseguera,* Tecnológico de Monterrey-Campus Estado de México, Mexico

Titanium (Ti) films were deposited by DC Magnetron Sputtering by changing deposition times and substrate temperature on AISI 316L steel to evaluate different thicknesses and its properties. Cristal orientation was determined by grazing angle X-ray diffraction (XRD). Scanning electronic microscope (SEM) was used to determine the surface composition and deposition characteristics through elemental analysis, and also to measure film thickness. Ellipsometry measurements were performed to compare film thicknesses estimated with SEM. Surface topography was obtained by atomic force microscope (AFM). Using nanoindentation test with a spherical indenter, mechanical properties were estimated. Furthermore, failure mechanisms and critical loads were determined by progressive load scratch tests. Wear behavior was studied through pin-on-disk tests with a 6 mm-diameter WC ball. SEM and optical profilometry were used to examine wear tracks; wear rates and coefficient of friction were analyzed.

4:50pm **E1-2-11 Tribology of New Surface Modifications for Cold Rolling Mill Rolls**, ***Henara Costa,*** Universidade Federal do Rio Grande, Brazil*; J Gonçalves Jr., J de Mello,* Universidade Federal de Uberlandia, Brazil **INVITED**

The present work analyzed the tribological behavior of coatings/surface modifications traditionally used in cold rolling mill rolls and new coatings/surface modificationswith potential to replace the carcinogenic hard chrome. The study started with identification of wear mechanisms occurring in real coldrollingmill rolls. Due the high cost and dimensions of the rolls, thereplication technique was used. Replicas were obtained from 4 different rolling millBrazilian companies before and after a normal rolling campaign. Initial sliding tests were conducted using spherical and cylindrical counter bodies in order to verifywhichtribological conditions allowed to reproduce the wear mechanisms found in the replicas. These tests indicated the use of reciprocating sliding tests with cylindrical counter bodies (line contact), normal load of 100 N, and test times of and 1 h and 5 h. Different surface modifications were carried out on samples produced from a fragment of a rolling mill roll. The specimens were heat treated and ground on both sides. After, some specimens were surface textured by electrical discharge texturing (EDT). For both groups (ground and EDT), subsequent treatments of chromium plating, electroless NiP coating and plasma nitriding were carried out. The results of the reciprocating tests showed that specimens with electroless NiP coating presented the lowest friction coefficients, while plasma nitrided specimens showed the highest. In general, previous surface texturing before the coating/surface modification increased the wear of the counter bodies. Oneexception was for EDT with subsequent electroless NiP coating, which presented the lowest counter bodies wear rate. The samples withelectroless NiP coating promoted a tribolayer consisting of Nickel, Phosphorus and Oxygen on both the specimens and thecounter bodies, which was apparently responsible for the reduction of friction coefficient and wear rate. The increase of the test time reduced the wear rate of the samples, apparently due the stability of the tribolayers formed, except for the nitrided samples. For the

textured specimens, NiP coating showed the best performance in maintaining the surface topography of the specimens after the sliding tests

New Horizons in Coatings and Thin Films
Room San Diego - Session F1

Nanomaterials and Nanofabrication

Moderators: Ulf Helmersson, Linköping University, Vitezslav Stranak, University of South Bohemia

1:50pm **F1-2 Kinetic Engineering of Crystal Phases in Core-shell Nanowires: Heteroepitaxial Radial Growth of Wurtzite and Zincblende Structured AlSb Shells on InAs Nanowires**, ***Hanna Kindlund***, *R Zamani, A Persson, S Lehmann, R Wallenberg, K Dick,* Lund University, Sweden

AlSb and InAs are III-V semiconductors belonging to the so-called 6.1 Å family, with room-temperature band-gaps of 1.61 and 0.36 eV, respectively. Their combination, especially to form low-dimensional heterostructures, is important to develop devices with potentially new applications based on the band-lineups that these heterostructures form. While zincblende (ZB) is the stable structure of conventional bulk III-V semiconductors, it has been shown that low dimensional structures such as nanowires can be grown in the wurtzite (WZ) crystal phase. Previous studies have also demonstrated the growth of nanowires composed of segments with both ZB and WZ crystal structures.[1-4]

Here, we use Au-seeded InAs nanowire core templates with engineered lengths of axial WZ and ZB segments and demonstrate selective, heteroepitaxial radial growth of AlSb on either ZB- or WZ-InAs nanowire segments. We grow InAs/AlSb/InAs core-double-shell nanowires on InAs(111)B substrates by metal-organic vapor phase epitaxy (MOVPE). The precursors used are trimethylindium (TMIn) and arsine (AsH_3) for the growth of InAs core templates, and tritertiarybutylaluminum (TTBAl) and trimethylantimony (TMSb) for AlSb. Using scanning electron microscopy, transmission electron microscopy, electron tomography, and energy-dispersive x-ray spectroscopy, we determine the AlSb shell thickness, crystal-phase, and nanostructure as a function of the shell growth temperature ($390 < T_s < 490$ °C).

We find that ZB and WZ structured AlSb shells grow epitaxially around the ZB and WZ segments of the InAs core, respectively. Interestingly, the WZ structured AlSb shells are thicker than the zincblende AlSb shells at $390 < T_s < 450$ °C with thickness increasing with decreasing growth temperature. In contrast, the ZB-AlSb shell thicknesses increase little with increasing T_s. In addition, detailed electron tomography studies show that the thicker WZ-AlSb shells form on the {11-20} facets rather than on the more commonly grown {1-100} sidewall facets. These results indicate that the growth of WZ-AlSb is preferred over the thermodynamically stable ZB-AlSb at lower growth temperatures. We attribute this behavior to kinetic limitations of MOVPE of AlSb on ZB and WZ phases of InAs.

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2:10pm **F1-3 Understanding the Friction of Sub-nanometer Thick Ionic Liquids (Ils)**, *A Lertola,* ***Lei Li,*** University of Pittsburgh, USA

Ionic liquids show promise as lubricants for nano- and micro-electromechanical systems (NEMS/MEMS). When deposited on solid substrates as thin films, these liquids can exhibit solid-like layering structure, which makes them ideal as nano-lubricants. Moreover, Ionic liquids are "designer" materials with many possible molecular structures and tunable properties. In this work, we have investigated the friction of various nanometer-thick ionic liquids. While many previous studies showed the impact of cation, we found a dramatic difference in the friction coefficients for 1-Ethyl-3-methylimidazolium bis(trifluorome thylsulfonyl)imide (EMIIm) and 1-Ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluoro phosphate (EMIM FAP), suggesting that anion structure also bears a significant effect on the friction. The effect of water at the interface has also been investigated and the friction profiles of the ionic liquids proved resistant to moisture manipulations. Film thickness, uniformity and adhesion to the substrate were also studied to relate molecular structure and surface morphology to tribology performance. The significance of these results in terms of Ils as potential MEMS lubricants will be discussed.

2:30pm **F1-4 Facile Synthesis of $MoSe_2$ Nanoplates on Black Phosphorus Nanosheets for Enhanced Hydrogen Evolution Reaction Performance**, ***Wan Li,*** City University of Hong Kong, Hong Kong; *D Liu, J Wang,* Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, China; *M Huang,* City University of Hong Kong, Hong Kong; *N Yang,* Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, China; *L Liu,* Peking University Shenzhen Graduate School, China; *X Peng, G Wang,* City University of Hong Kong, Hong Kong; *X Yu,* Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, China; *P Chu,* City University of Hong Kong, Hong Kong

Today, seeking for cost-effective and efficient electrocatalyst is desired because hydrogen evolution reaction (HER) has been highly recognized as a promising approach to produce clean and renewable energy. $MoSe_2$ is an attractive candidate due to its fascinating properties. Unfortunately, aggregation as well as low conductivity restricts its developments. Here we report a smart strategy that $MoSe_2$ nanoflakes adhered on the surface of BP nanosheets through van der Waals interactions, aiming to increase conductivity and expose much more active sites simultaneously. It is found that the prepared $MoSe_2$-BP exhibits an enhanced electrocatalytic performance with a lower onset potential (200 mV), a smaller Tafel slope (109 mV dec^{-1}) and excellent stability. Such this performance can be attributed to the support provided by BP, which benefit efficient electrons transfer and prevent $MoSe_2$ from aggregating.

2:50pm **F1-5 Synthesis and Magnetic Properties of $Mn_xZn_yFe_{3-x-y}O_4$ Nanoparticles Prepared using a Co-precipitation Method**, ***Kuan-Wei Chen,*** *J Ting,* National Cheng Kung University, Taiwan

(Mn, Zn) ions were doped into Fe_3O_4 to form $Mn_xZn_yFe_{3-x-y}O_4$ nanoparticles for enhancing the magnetic property of. The $Mn_xZn_yFe_{3-x-y}O_4$ nanoparticles were synthesized through an easy, one-step, and quick aqueous co-precipitation method. Iron(III) chloride [$FeCl_3 \cdot 6H_2O$], manganese(II) chloride [$MnCl_2 \cdot 4H_2O$], and zinc chloride [$ZnCl_2$] were dissolved into hydrochloric acid to form the precursor solution. NH_4OH was then added into the precursor solution as reagent to the pH value. After vigorous agitation of the pH-adjusted precursor solution, precipitates were then collected. To investigate the microstructure, chemical composition, and magnetic properties, the obtained nanopowders were characterized using field emission scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffractometry, electron Spectroscopy , and a superconducting quantum interference measurement device. The effects of Mn and Zn ion additions on the chemical composition and magnetic properties are presented and discussed. The and mechanism of $Mn_xZn_yFe_{3-x-y}O_4$ nanoparticle formation is also discussed.

3:10pm **F1-6 Effects of Nano Particles on the Thermal Stability and Scratch Resistances of Epoxy Coatings**, ***Mourad Boumaza,*** *K Rawaiz,* King Saud University, Saudi Arabia

Coatings are susceptible to damage caused by scratch and/or abrasion and thermal instability. Clearly, the consumer prefers to retain the aesthetic appearance of coated materials and for this reason clear coats used on automobiles must have good scratch and abrasion resistance. An added problem is that scratches may also cause damage to the underlying substrate. Scratch resistance can be obtained by incorporating a greater number of cross links in the coating's binder but unfortunately highly cross linked (hard) films have poor impact resistance due to less flexibility. A less cross linked (softer) film will show better performance with regard to other properties such as anti-finger print and impact resistance but will have less scratch and abrasion resistance

On the other hand thermal performance of materials is crucial in many industries, ranging from pharmacy, battery and aerospace and electronics tod construction industries. For optimum thermal stability, heat dissipation, bonding and homogeneity are key parameters of thermal characterization and thermal conductivity, Many researchers recently worked on thermal stability of epoxy/nanoparticles coatings by using different types of nanoparticles

The purpose of this work is to investigate the effect of inorganic nanoparticles on scratch resistance and thermal properties of epoxy/Polyamid coating system. The nano composite coatings are formulated by incorporation of various types of nanoparticles (ZrO_2, ZnO, SiO_2, and Fe_2O_3) with 2 wt. % loading for each type of nanostructure.

The results showed that all the composite coatings with 2% loadings of Nanoparticles increased and passed the impact test of 120 lbs/in as compared to the unreinforced coating which cracks at 112 lbs/in. However the impact value for EPZN remains the highest and showed 57% increase in the impact resistance. Similarly the Scratch resistance for all the samples increased in all compositions, while EPSI was found to have highest Scratch load. The increasing trend in the scratch hardness values can be attributed to the improvement in the adhesion between composite coating and metal substrate.

Thermal analysis of these nano composites revealed that the addition of SiO_2 and ZrO_2 enhanced the thermal stability of the nano composite coating, while Fe_2O_3 and ZnO reduce the thermal stability due to catalytic effect of these nanoparticles, which facilitate the thermal degradation process.

3:30pm **F1-7 Corrosion Study of Silane-functionalized Graphene Oxide Coatings on Copper**, ***Mohsin Ali Raza,*** *Z Rehman, F Ghauri,* University of the Punjab, Lahore, Pakistan

This research work aims to produce corrosion resistant silane-functionalized graphene oxide (GO) coatings on copper (Cu) metal. Two types of precursor graphite (flakes and powder) were utilized to synthesize GO following improved Hummers' method, and resulting GO was labelled as FGO and PGO, respectively. GO was deposited on copper metal, which was made anode and platinum was made cathode, from GO/water suspension by electrophoretic deposition (EPD). Silane functionalization was performed by immersing GO-coated samples in 3-aminopropyltriethoxy silane (APTES) solution. The role of precursor graphite, deposition time, surface roughness of substrate, and post-treatment of GO coating with silane on corrosion protection ability of GO coatings was studied. Characterization of GO and silane-functionalized GO coatings was performed by X-Ray diffraction, atomic force microscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. Optimum EPD parameters for the development of uniform coatings were found to be 5 V and 30 sec with GO/water concentration of 1:10. Corrosion behavior of GO and silane-functioanlized GO samples was studied by Tafel analysis, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in 3.5 % NaCl solution. The results showed that precursor graphite effects quality of GO, and consequently the corrosion behavior of the GO coatings. PGO-coated Cu deposited at optimized parameters showed better corrosion protection compared to FGO-coated Cu. Tafel analysis showed that PGO coating and silane-functionalized PGO coating developed at optimized parameters enhanced corrosion resistance of Cu by ca. 6× and 25×, respectively, compared to bare Cu. Tafel results were well validated by EIS and CV.

3:50pm **F1-8 Growth of MnO_2 on Carbon Materials for Electrochemical Capacitor**, ***Chia-Jung Tu,*** *M Wu,* National Changhua University of Education, Taiwan*; W Wu,* Da-Yeh University, Taiwan

Manganese oxide (MnO_2) has attracted intensive attention and been widely used as catalysis, ion exchange, molecular adsorption, biosensor, and electrodes for lithium ion batteries and supercapacitors due to its low cost, abundance and environmental-friendliness. For supercapacitors, MnO_2 is the most investigated oxide for pseudocapacitors on the basis of its high theoretical specific capacitance of 1370 Fg^{-1}. However, the theoretical specific capacitance of MnO_2 has rarely been achieved due to its poor electrical conductivity. Therefore, a hybrid electrode architecture which incorporates nanostructured MnO_2 on high-surface-area conductive carbon materials was used to improve the electrical conductivity and the specific capacitances. In this study, activated carbon fiber cloth (CFC) and vapor grown carbon nanofiber (VGCNF) was used as the carbon support material. The pretreatment condition of the vapor grown carbon nanofiber were first discussed. Then, nanostructured MnO_2 was grown on activated carbon fiber cloth and vapor grown carbon nanofiber using three different wet chemical methods and conditions. It was observed that different concentration of the precursor $KMnO_4$ play a crucial role in the crystal growth of MnO_2, which result in different morphology.

4:10pm **F1-9 Fabrication of a CMOS Compatible Ferroelectric Tunnel Junction Memory**, ***Fabian Ambriz-Vargas,*** Énergie, Matériaux et Télécommunications, Canada*; G Kolhatkar,* Institut National De La Recherche Scientifique, Canada*; R Nouar, A Sarkissian,* PLASMIONIQUE Inc, Canada*; M Gauthier, A Ruediger,* Institut National De La Recherche Scientifique, Canada

Semiconductor memories are the key component of any electronic device. Among the different types of semiconductor memories, Dynamic Random Access Memory (DRAM) is the most used memory in the semiconductor market. However, the continue miniaturization of the electronic devices leaded to reach the DRAM physical limits. Then, new types of semiconductor memories based on different physical approaches are now attracting attention. One candidate to replace DRAM technology is the Ferroelectric Tunnel Junction memory (FTJ), which offers advantages such as a low operating energy, high operation speed (read/write access; ~10ns/10ns), high endurance (10^6 cycles) and non-volatility.

Recently, it was reported the successful fabrication of the first FTJ devices. They were based on perovskite tunnel barriers such as barium titanate ($BaTiO_3$), bismuth ferrite ($BiFeO_3$), lead titanate ($PbTiO_3$) etcetera. However, FTJs based on perovskite tunnel barriers require of specific substrates (strontium titanate, $SrTiO_3$) and high processing temperatures (~700°C) which makes them incompatible with the complementary metal oxide semiconductor process (CMOS). In comparation to perovskites, Hafnium-Zirconium oxide ($Hf_{0.5}Zr_{0.5}O_2$) films offer advantages such as CMOS compatibility as well as ferroelectric properties in ultrathin form.

Thus, in the present work, we report on the fabrication of the first FTJ memory device based on a CMOS compatible tunnel barrier $Hf_{0.5}Zr_{0.5}O_2$ (6 unit cells thick, ~3nm thick film) on an equally CMOS compatible TiN electrode. Such a device will give rise to a new generation of semiconductor memory devices.

4:30pm **F1-10 Polyacrylonitrile Nanofibers Prepared via Electrospinning for High-efficiency PM2.5 Capture Application**, ***Kuan-Nien (G.N.) Chen,*** Unaffiliated*; J Ting,* National Cheng Kung University, Taiwan

TiO_2 surface-residing electrospun PAN nanofibers with controllable density of TiO_2 on the fiber surface were prepared by means of an electrospinning technique and microwave hygrothermal method. The nanofiber diameter was controlled by the voltage, precursor viscosity, and flow rate during the electrospinning process. The surface morphology was controlled by adding TiO_2 with different concentrations. The surface chemistry was optimized to enhance PM adsorption. SEM, TEM and XRD pattern analyses demonstrated that TiO_2 was formed and resided on the nanofiber surface, and surface chemical composition was analyzed by XPS. Selected samples were evaluated for filtering efficiency by examining the particle counter (CEM) and the removal efficiency was calculated by comparing the PM particle number concentration before and after filtration.

Surface Engineering - Applied Research and Industrial Applications

Room Sunset - Session G6

Application-driven Cooperation Between industry and Research Institutions

Moderators: Tobias Brögelmann, Surface Engineering Institute - RWTH Aachen University, Joern Kohlscheen, Kennametal GmbH, S.P. Kumar Yalamanchili, Oerlikon Balzers, Oerlikon Surface Solutions AG

1:50pm **G6-2 Performance Evaluation of Precious Metal Coatings in Precision Glass Molding**, ***Marcel Friedrichs,*** *A Saksena, M Hans,* RWTH Aachen University, Germany*; O Dambon,* Fraunhofer Institute for Production Technology IPT, Germany*; J Schneider, F Klocke,* RWTH Aachen University, Germany

Precision Glass Molding (PGM) is a replicative technology for producing complex optical components with high surface quality and form accuracy. The efficiency of PGM process depends primarily on the lifetime of the high-precision molding tools made of cemented tungsten carbide. During each molding cycle, the molding tools have to withstand severe thermo-chemical and thermo-mechanical loads. Using protective coatings, the lifetime of the molding tools can be increased. The most versatile coatings for molding various glass types are based on precious metals due to reduced chemical interaction in contact with heated glass.

In this study, platinum-iridium (Pt-Ir) protective coatings were deposited on cemented tungsten carbide molding tools by physical vapor deposition (PVD) process. The investigated Pt-Ir coatings differed in their chemical composition. Based on predictions of the enthalpy of mixing, additional ternary Pt-Ir-X (X = Cu, Au) coatings were evaluated. To investigate the operational capability of the protective coatings, molding tests were carried out at an in-house built lifetime testing bench and at an industrial glass molding machine. Subsequent analyses of coated specimens were performed by white light interferometry and scanning electron microscopy (SEM). Depending on the chemical composition of the coating, different

degradation phenomena as glass adhesion, interdiffusion and coating delamination were observed and discussed.

2:10pm **G6-3 Plasma-dependent Phase Formation of TiAlN Coatings**, ***Anders Eriksson***, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *M Hans, S Mráz, J Schneider,* RWTH Aachen University, Germany; *M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

The industrial success of TiAlN as wear-resistant and protective coatings is enabled by the well-known favourable age-hardening characteristics. However, the ability to control microstructure, mechanical and thermal properties of the coatings is also essential for application-specific coating design. In this contribution we study the deposition process of coatings deposited from $Al_{67}Ti_{33}$ (at%) targets. By varying the arc source settings, the resulting coating properties have been optimized in industry for different cutting tool applications: either a single phase cubic solid solution or a mixture of cubic and hexagonal phase was obtained. Gaining in-depth understanding of the deposition processes leading to the different phase formation scenarios is a topic in our cooperation for application-inspired fundamental research within an industrial-scale deposition system. For the two arc source settings, we have characterized the plasma composition and ion energies in an Oerlikon Balzers INGENIA P3e™ deposition system by energy-resolved mass spectrometry. The phase formation was observed to depend significantly on the arc source configuration and hence plasma properties. Our findings illustrate that a collaboration between industry and academia enables knowledge-based design of protective coatings for specific applications.

2:30pm **G6-4 Reactive HiPIMS Deposition of Ti-Al-N: How to Adjust the Cubic to Wurtzite Transition**, ***Helmut Riedl***, *L Zauner, P Ertelthaler,* CDL-AOS at TU Wien, Austria; *T Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria; *H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S Kolozsvári,* Plansee Composite Materials GmbH, Germany; *P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

High power impulse magnetron sputtering (HiPIMS) is often seen as one key-technology in the deposition of future hard and multifunctional coating materials. Through the introduction of high amplitude impulses at relatively low duty cycles, the amount of ionized species, either target near gas atoms or sputtered target atoms, can be increased drastically. These highly dense plasmas have various consequences on the film growth and hence coating properties, as well as on the sputter behavior of the target material itself. Applying reactive gas mixtures such as N_2/Ar atmospheres, e.g. for the deposition of TiN coatings, lead to further complex effects within the plasmas (self-sputtering, gas recycling, or poisoning). However, several studies clearly highlighted the outstanding coating properties as well as metastable phases accessible, using HiPIMS compared to conventional DC magnetron sputtering, whereas a majority of these investigations concentrate on the plasma physics itself.

Therefore, we focused in this study on the reactive HiPIMS deposition of Ti-Al-N coatings using $Ti_{1-x}Al_x$ compound targets (x = 0.50, 0.60, 0.66, 0.80) in mixed Ar/N_2 atmospheres. The influence of the HiPIMS parameters such as frequency, pulse length, and power density, but also of the deposition parameters like partial pressure, deposition temperature, or total pressure was investigated methodically. The so obtained coating structures were analyzed with respect to phase stability, thermomechanical properties, and morphology applying nanoindentation, X-ray diffraction combined with electron imaging techniques (SEM and HR-TEM). In addition, to gain an in-depth understanding of the HiPIMS parameters on the used compound target materials a special in-situ target-temperature measurement system was utilized during all depositions (min. distance to sputtered target surface about 1 mm).

2:50pm **G6-5 AlTiN Coatings deposited by HIPIMS: A Study of Mechanical Properties, Tribological and Wear Performance during Machining of Superduplex Stainless Steel**, *J Paiva,* ***Edinei Locks***, *Y Seid Ahmed, P Stolf, J Dosbaeva,* McMaster University, Canada; *C Bork,* IFSul - Federal Institute Sul-rio-grandense, Brazil; *G Fox-Rabinovich, S Veldhuis,* McMaster University, Canada

AlTiN PVD coatings represent a generation of coatings designed to work at high temperature applications. The aluminum in the film converts to aluminum oxide as the coating heats up, resulting in increased oxidation resistance. The use of this coating is related to the cutting tool applications where a lot of heat is generated. In this work, an advanced High Power Impulse Magnetron Sputtering (HIPIMS) technique was utilized to deposit dense AlTiN coatings on cemented carbide cutting inserts. The influence of HIPIMS process deposition was compared with AlTiN PVD Coating deposited by Arc method and evaluated in terms of microstructure, mechanical and tribological properties, by means of SEM /EDS, XRD structural characterization, nanoindentation testing, and Pin-on disc high temperature tribotesting. To relate the coatings properties with the wear performance, cutting tests were performed during turning of superduplex stainless steels at finishing operations. FEM modeling of the turning process was employed to determine the cutting temperatures, cutting forces and stresses at the cutting tool edge. The results obtained demonstrate that the tribological and wear performance of the AlTiN PVD coatings deposited by HIPIMS showed significantly improved wear behavior as compared to arc deposited AlTiN coating. This is because HIPIMS process allows to deposit very dense, defect free coatings, with low residual stresses and excellent surface finish that improves wear performance of the coated tool.

3:10pm **G6-6 FunMat-II – an Industry-Academia Competence Center for Research on Coating Materials for Advanced Applications**, ***Lina Rogström***, *M Odén, I Abrikosov, G Greczynski, P Eklund, E Björk,* Linköping University, IFM, Sweden

FunMat-II (Functional Nanoscale Materials) is a second-generation competence center in material science, continuing the successful VINN Excellence Center FunMat inaugurated in 2007 (ended 2016). The center starts late 2017 and will continue for five years. FunMat-II is financed by the Swedish Agency for Innovation Systems (VINNOVA), Linköping University and our 12 industry/institute partners.

FunMat-II is focusing its efforts to three application areas for functional surfaces: cutting tools, fuel cells, and batteries. We obtain basic knowledge about materials behavior and the physics and chemistry of the synthesis processes, and design new materials with unique properties. We study all aspects using combinations of theory, modeling, experiments, and field tests. The information obtained is generic and can be applied to a wide range of applications, which makes FunMat-II a true competence center in functional surfaces optimized at the nanoscale.

This presentation gives an overview of the partnership and the way of working within the competence center, including application-inspired fundamental research, industry-oriented PhD education, continuing education, and intellectual property handling. Scientific highlights from recent studies of materials for advanced application are given as examples, including high-temperature contacts [1], *in situ* characterization of hard coatings in turning operations, and experimental and theoretical studies of coatings with improved thermal stability for high-speed cutting [2-4].

[1] H. Fashandi et al., Nat. Mater. 16(8) (2017) 814.

[2] L. Rogström et al., J. Appl. Phys. 118 (2015) 035309.

[3] I. Schramm et al., Acta Mater. 119 (2016) 218

[4] F. Wang et al., Acta Mater. 127 (2017) 124.

3:30pm **G6-7 Oxygen Diffusion Pathways in High Temperature Oxidation Resistant Ti-Al-N/Mo-Si-B Multilayer Coatings**, ***Elias Aschauer***, CDL-AOS at TU Wien, Austria; *P Felfer,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany; *M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Polcik,* Plansee Composite Materials GmbH, Germany; *H Riedl,* CDL-AOS at TU Wien, Austria; *P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

In high temperature oxygen containing atmospheres, the oxidation resistance of a protective coating is mainly based on the ability of the participating metals to form adherent and continuous oxide scales separating the reactants from the oxidizing atmosphere. Corundum type Al_2O_3 or Cr_2O_3 represents such highly stable oxide structures, whereby the formation of Al-rich scales was crucial in the success story of $Ti_{1-x}Al_xN$. Nevertheless, oxide scales only constitutes semipermeable barriers slowing down scale growth, where the kinetic of the growing scale is determined by the fastest species - e.g. metal or oxygen ion outward and inward diffusion, respectively. With respect to the temperature ($T < 0.6\ T_m$), the dominant transport mechanism in growing scales is along fast-diffusion pathways such as dislocations, voids, or especially column boundaries rather through the bulk crystal lattice. To further enhance the oxidation resistance of e.g. $Ti_{1-x}Al_xN$, a fundamental understanding of the oxidation process and a distinct knowledge on the phase evolution and present diffusion pathways in the atomic scale range is highly desired.

Therefore, we used atom probe tomography (APT) to analyse the diffusion pathways in our high-temperature oxidation resistant Ti-Al-N/Mo-Si-B multilayer coatings. The repeated incorporation of very thin sputtered Mo-Si-B layers ($\lambda \approx 25$ nm) in arc-evaporated Ti-Al-N ($\lambda_l \approx 100$ nm) leads to an

interrupted growth of the V-shaped Ti-Al-N columns, and hence to highly distinct areas in 3D chemical mapping. To overcome the difficulty of mass/charge peak overlap during APT investigations, the samples were annealed in O^{18} for 60 min at 900 °C. For optimized volume analysis, three tips parallel to the layered structure, next to the growing scale, were prepared by a standard FIB lift out technique – uniformly distributed from top to bottom in the unaffected coating region. These results were correlated with a detailed analysis on the phase evolution applying nano-beam X-ray diffraction as well as morphology by using high-resolution transmission electron microscopy in the as deposited and thermal treated state.

3:50pm **G6-8 Novel ta-C Coatings with Outstanding Tunable Properties Deposited by Industrially Scaled PLD***, **Martin Hess**,* Fritz Stepper GmbH & Co. KG, Germany*; S Weißmantel, R Bertram,* Hochschule Mittweida, Germany

ta-C deposited by PVD is successfully introduced for quite some time for wear protection applications of engine components (piston rings, injection parts, etc.). Due to their geometrically relatively simple functional areas, batching as well as a posttreatment of coated surfaces is common compared to more complex shaped parts. Due to its prominent mechanical properties ta-C is actually increasingly introduced to commercial PVD-systems. However, limitations are high intrinsic stresses, roughness and also tribochemistry. As a consequence ta-C is still rarely found on industrial tools for stamping and chip removing processes.

Acting in the spirit of our company founder (“If you want to improve something, you have two options: Optimizing existing procedures or rethinking the whole process”) we decided in early 2016 not to add another PVD-system to our equipment park (CARC, PECVD, HIPIMS). We thought rather about a surface enhancement technology which would be dedicated and designed towards our internal requirements to maximize quality of small, one-digit ccm volume, parts in batches of only some 10 to a few 100 pieces per day.

Our primary motivation was that in one of our high performance modular stamping tools up to 5000 moving components are facing stroke rates exceeding 2000 strokes per minute. In this context our boosting ambition is the creation of maintenance free tools up to production lots of 100 million electrical contact parts and more. However even latest PVD-coatings on carbide substrates of highest quality are actually limited to some million strokes before showing critical wear leading to expensive tool downtime. As abrasion was isolated as the dominant life-time limitation our obvious conclusion was to seek for significantly higher abrasion resistance than our latest 35-40 GPa nanolamellar or nanocomposite PVD coatings. At the end ta-C was assessed as the most promising evolution.

Preceding benchmark tests regarding the ta-C coating process options isolated the so far for wear protection applications relatively unknown or rather unusual PLD as a promising process, due to some unique inherent features: smooth surfaces, homogeneous erosion of the target and last but not least: precise control of mechanical coating properties such as Y and H as well as tunable intrinsic stresses by laser energy. As a result smooth and well adherent coatings of up to 6 µm thickness were deposited on steel and carbide substrates. The purpose of the present contribution is to give an introduction to this novel technology and its first successful applications.

4:10pm **G6-9 Application-driven Cooperation Between Industry and Research Institutions: Success Factors, Obstacles and Success Stories***, **Oliver Lemmer**, W Koelker,* CemeCon AG, Germany **INVITED**

Development of new products and new technologies should be triggered by market needs. Depending on the respective subjects and the economic constraints, the market expects those needs to be met either in short term or in mid/long term. Subsequently two major challenges have to be mastered:

- The different time line expectations have to be addressed by different styles of cooperation and by selectively chosen partners, in order to succeed in creating new products and technologies.
- The "chicken and egg" problem: new products often need new technologies to produce them.

Recently, two new technologies have gained prominent importance for advanced coatings for demanding applications, e.g. in aerospace industry: HiPIMS technology and CVD diamond technology. In this context, the different roles of partners in R&D-networks will be described, and the different objectives and tasks with respect to the different time horizons will be presented. An outlook will be given on the potential of new products created by the combination of these two high-end technologies.

Coatings for Use at High Temperatures
Room Royal Palm 1-3 - Session A2

Thermal and Environmental Barrier Coatings

Moderators: Kang Lee, NASA Glenn Research Center, USA, Lars-Gunnar Johansson, Chalmers University of Technology, Sweden, Pantcho Stoyanov, Pratt & Whitney, USA

8:00am **A2-1 Corrosion Degradation of High Temperature Coatings: Similarities and Differences for Marine and Aero-Turbine Applications***, **Daniel Mumm**,* University of California, Irvine, USA **INVITED**

Gas turbine engines are utilized throughout the world, as aircraft and ship propulsion systems and as stationary power generation systems. The materials utilized in the hot-section of marine gas turbines are subject to a wide range of high temperature oxidation/corrosion degradation processes, dependent upon the fuels used and the site-specific environments. Operation in marine environments leads to salt-laden intake air, whereas additional constituents in the intake air (pollutants, atmospheric particulate matter, etc.) have unique influences on the oxidation/corrosion degradation mechanisms of thermal and environmental barrier coating utilized with hot-section components. Ongoing research has also illustrated that the performance and lifetime of such materials is also highly dependent upon the exposure temperatures and the specific thermal cycling history associated with operational service demands. This talk will discuss ongoing efforts to explore high temperature oxidation and corrosion processes, and the resulting materials degradation, under more complex exposure conditions – with a focus on the synergistic role of mixed-mode (Type II, Type I and oxidation condition) exposures and complex corrosive deposit chemistries including sulfate mixtures and oxides. The research findings are discussed in relation to the performance of marine propulsion, aero-propulsion and power-generation turbines operating in marine environments. Implications for understanding of the observed degradation mechanisms is essential for enabling the design of materials capable of being utilized in increasingly hostile gas turbine operational scenarios.

8:40am **A2-3 Evolution of Microstructures and Interfaces in Doped, Layered, and Composite Coatings Exposed to Sand Laden Flows in a Gas Turbine Engine***, **Andy Nieto**, M Walock, A Ghoshal, M Murugan,* US Army Research Laboratory, USA*; D Zhu,* NASA Glenn Research Center, USA*; W Gamble, J Swab, B Barnett, M Pepi,* US Army Research Laboratory, USA*; R Pegg, C Rowe,* US Navy Naval Air Systems Command, USA

Calcia-magnesia-alumina-silicate (CMAS) attack on thermal barrier coatings (TBCs) have led to a need for new TBC coating designs that incorporate mechanisms for mitigating CMAS deposition and infiltration, while maintaining or enhancing the critical properties of TBCs, namely durability and strain tolerance under high temperature and velocity in cycling engine operating conditions. Several approaches have been investigated here, including the use of dopant elements and phases, multi-layered coatings, and blended composite coatings. These included doped ZrO_2 based coatings, layered Y_2O_3 stabilized ZrO_2 (YSZ), HfO_2, and Gd_2O_3 coatings, as well as composite YSZ/Gd_2O_3 coatings. The coatings were deposited on turbine nozzle vanes and tested inside of a full scale engine with air flow temperatures at ~1400 °C and several sand ingestion cycles. SEM, EDS, and TEM were utilized to compare the microstructures before and after exposure to the sand laden combustion flows within the gas turbine engine. Emphasis was placed on the interfaces formed between the coatings and the formed CMAS deposits. Interfaces within the coatings, such as those in between phases or between layers, were also evaluated in order to understand which microstructural designs were most effective at mitigating CMAS infiltration/attack and particulate adhesion, whilst maintaining structural stability and integrity.

9:00am **A2-4 The Effect of HVOF Bond Coating with APS Flash Coating on TBC Performance***, **Michael Lance**, J Haynes, B Pint,* Oak Ridge National Laboratory, USA

Previous work reported the benefit of a ~50 µm thick air plasma sprayed (APS) "flash" coating to improve the performance of high-velocity oxygen fuel (HVOF) bond coatings. In this study, NiCoCrAlYHfSi HVOF bond coatings were deposited on directionally-solidified (DS) 247 disk substrates with APS yttria-stabilized zirconia (YSZ) top coatings. The HVOF-only bond coatings were compared to APS flash coatings of NiCoCrAlYHfSi and NiCoCrAlY using 1-h cycles at 1100 °C in air with 10% H_2O. Photo-stimulated luminescence spectroscopy was used to map residual stresses in the thermally-grown Al_2O_3 scale as a function of exposure time. Five specimens of each coating type were cycled to determine an average coating lifetime under these conditions and, after failure, oxide thickness and morphology were compared on various bond coatings to better understand the influence of the flash coating presence and composition.

Research sponsored by the U. S. Department of Energy, Office of Fossil Energy's Turbine Program.

9:20am **A2-5 Influence of Process Conditions and Ceramic Doping on the Performances of Advanced TBCs Based on Al Slurry***, **Germain Boissonnet**, B Grégoire, J Balamain, G Bonnet, F Pedraza,* University of La Rochelle, France

Current processes of fabrication of thermal barrier coatings (TBCs) for the hottest sections of aeronautical engines are very complex and quite expensive. Therefore, they cannot be applied to other sections that require thermal insulation due to the increase of the turbine inlet temperatures. Among the alternative coating techniques, slurries from Al microspheres that result in the formation of hollow alumina top foam appear particularly attractive [1-3]. Their insulation properties are indeed equivalent to those of conventional APS YSZ coatings [4]. However, the current process of fabrication leads to poor mechanical resistance of this light foam [5].

Therefore, the effects of the annealing atmosphere and of the introduction of Al_2O_3 and YSZ ceramic particles on the strengthening and on the thermal insulation potential of the ceramic foam will be presented. Alumina was chosen due to its good chemical compatibility with the Al slurry to harden the top coat while binding with the hollow oxide spheres. Concurrently, YSZ is expected to lower the overall thermal conductivity of the top coat while simultaneously increasing its stress compliance *because of the high thermal expansion coefficient of this material*. Low water vapor pressures will also be shown to thicken the shells of the hollow particles compared to Ar and oxygen [5]. Also, the reaction mechanisms of YSZ particles with molten Al to result in the formation of Al_3Zr/α-Al_2O_3 composites [6] that leads to remarkable changes in thermal and mechanical properties of the top coat will be described in light of the results from DSC, XRD, Raman micro-spectrometry and thermal diffusivity.

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9:40am **A2-6 Synthesis and Characterization of Combined Oxides and Ni Superalloy Coatings by Cathodic Arc Evaporation for Bond Coat Application***, X Maeder, J Ast,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Döbeli,* ETH Zurich, Switzerland*; K von Allmen, A Neels, A Dommann,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, Switzerland*; B Widrig, **Jürgen Ramm**,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Typical coating systems in gas turbines are made of several layers, generally consisting of (1) a bond coat, which guarantee the mechanical stability over a wide range of temperature, (2) a thermally grown oxide, acting as an oxygen diffusion barrier and (3) a top porous ceramic, acting as a temperature barrier. Such a stack presents many interfaces where internal stresses and failure can occur. We will show here the capability of creating a complete layer stack for a bond coat by cathodic arc evaporation in an in-situ process sequence, i.e. without interruption of vacuum. Superalloy targets were produced from Ni-(Al-C-Co-Cr-Mo-Ta-Ti-W) and Ni-(Al-B-C-Co-Cr-Hf-Mo-Ta-Ti-W-Zr) powders by spark plasma sintering and processed in subsequent non-reactive and reactive modes. The phases, microstructure and composition of the powder, target and synthesized coatings are characterized by TEM, transmission EBSD, X-ray diffraction and RBS analyses and discussed. An epitaxial growth of the pure metallic coating can be observed on both multi and single crystalline superalloy substrates, which guaranty an enhanced mechanical stability of the first coating interface. The thin transition layer between the reactive and non-reactive depositions is composed of nano-crystalline partially oxidized Ni superalloy. Fully oxidized Ni superalloy and Al-Cr-O layers can be deposited on top. The thermal stability of the stack has been tested by in-situ high temperature XRD analyses as well as post mortem TEM, transmission EBSD and RBS analyses.

10:00am **A2-7 Steam Oxidation Behavior of $Yb_2Si_2O_7$-Based Environmental Barrier Coatings**, ***Kang Lee***, NASA Glenn Research Center, USA

Increased fuel efficiency is a game changer for gas turbines as fuel is the single most important cost, accounting for up to about 40% of the overall operation cost of commercial aircrafts. Increased fuel efficiency is obtained through increasing the thermal efficiency of the engine by increasing the overall pressure ratio (OPR). Increased OPR requires increased turbine inlet temperature, which is paced by advances in turbine hot section materials temperature capability. High turbine inlet temperature also contributes to environmentally friendly engines by reducing NOx. SiC/SiC Ceramic Matrix Composites (CMCs) are the most promising materials to revolutionize the temperature capability of turbine hot section materials because of their high temperature mechanical properties and light weight. Environmental barrier coatings (EBCs) is an enabling technology for CMCs by protecting CMCs from environmental degradation, especially from water vapor. One of the most likely EBC failure modes is oxidation by water vapor generated by combustion reactions (steam oxidation). The current state-of-the-art EBC is based on $Yb_2Si_2O_7$ and Si bond coat. In gas turbines water vapor migrates through $Yb_2Si_2O_7$ and oxidizes Si bond coat, forming a layer of silica (SiO_2), known as TGO, at the Si/$Yb_2Si_2O_7$ interface. As TGO grows in thickness with time the strain energy increases, ultimately leading to an EBC failure. This paper will discuss steam oxidation behavior of $Yb_2Si_2O_7$-based EBCs.

10:20am **A2-8 The Fatigue Behavior of TiCrAlTaSiN Coated and Uncoated Titanium Alloys**, *B Lerch,* ***Dongming Zhu***, *S Kalluri,* NASA Glenn Research Center, USA

Advanced multi-component TiCrAlTaSiN-based multilayered coatings were processed onto Ti-6Al-4V (Ti-6-4) and GammaMet PX (GMPX or TiAl) alloys by magnetron-enhanced physical vapor deposition technique. The coatings have been in developments aiming for improving advanced Ti alloy turbine engine component durability and oxidation-erosion resistance. In this work, the performance of the multi-component titanium nitride based coating systems (including the outer layer nitride based coating and inner TiCrAlSi barrier bond coat) was studied, and the coating influence on the fatigue behavior of the titanium-based alloys were compared. Although the multi-component coating was initially optimized to improve the coating high temperature oxidation and erosion resistance, the lower ductility nitride based coatings need further microstructure or composition optimizations to improve the mechanical stress resistance and stain tolerances for the highly loaded and high cycle fatigue turbine blade operating conditions, in particular for GMPX and other gamma TiAl alloys because the intermetallic Titanium alloys have limited ductility and are sensitive to defects. The preliminary results showed that the inner layer TiCrAlSi coatings had better adhesion and ductility, may help improve the oxidation resistance for the Ti alloys.

10:40am **A2-9 Crack Propagation Behavior of Thermal Barrier Coatings with Cyclic Thermal Fatigue Tests**, ***Dowon Song***, *T Song,* Hanyang University, Republic of Korea; *H Park, Y Jung,* Changwon National University, Republic of Korea; *J Zhang,* Indiana University Purdue University Indianapolis, USA

Crack formation and propagation behavior in thermal barrier coatings (TBCs) was observed through cyclic thermal fatigue (CTF) test for further understanding of TBC failure mechanisms. An analytical model was employed to predict residual stress distribution in the TBC samples to explain the experimentally observed crack-growth behavior. Initial cracks were formed on the surface and cross-section of TBCs prepared by air–plasma spray using Vickers indentation, and then CTF tests were performed for both cracked TBCs. Surface-cracked top coats were partially delaminated depending on their initial crack lengths that were formed with each loading level, suggesting a threshold surface crack length and showing a parabolic growth behavior. In the cross-sectional cracked TBC, cracks were strongly dependent on the direction, showing longer crack lengths in the direction parallel/horizontal to the interface between the top and bond coats than the direction perpendicular/vertical to the interface. The horizontal cracks grew in the similar manner as those on the surface, but the cracks in the vertical direction did not grow too much with CTF tests. All fatigue crack-growth rates show a negative dependence on stress intensity range in the Paris law due to the competing interaction of the residual stresses from indentation and thermal cycling. This study and analysis can be helpful for the further understanding of TBC failure in the design of reliable TBC systems.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-3
PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Qi Yang, National Research Council of Canada, Jyh-Ming Ting, National Cheng Kung University

8:20am **B1-3-2 High Quality Oxide Films Deposited at Room Temperature by Ion Beam Sputtering**, ***Gerard Henein***, National Institute of Standards and Technology, USA; *J Topolancik,* Roche Sequencing Solutions, USA

The highest quality oxides such as SiO_2, Al_2O_3 and Indium Tin Oxide (ITO) require high temperature processing either during the growth of the film or annealing post-growth. Thermal SiO_2 is grown at ≈1000 °C , ALD Al_2O_3 is deposited at ≈300 °C , and magnetron-sputtered ITO must be annealed above 350 °C in order to turn the film conductive . These elevated temperature requirements are not compatible with polymer substrates used for flexible electronics .

We have deposited dense and pinhole-free thin films of SiO_2, Al_2O_3 and ITO at room temperature via ion beam sputtering. The deposition system consists of a 3-grid 14 cm RF ion gun directed at 200 mm targets of SiO_2, Al and ITO. All three processes require a small flow of O_2 to achieve stoichiometry. Typical conditions were: argon flow rate $3.3x10^{-7}$ m^3/s, beam voltage 600 V, beam current 220 mA and acceleration voltage 150 V. The substrate wafers were kept at 20 °C. The base vacuum prior to deposition was $2.6x10^{-6}$ Pa.

The SiO_2 films were 100 nm thick and measured by the mercury probe technique to obtain the C-V and I-V characteristics. The films were found to be of similar quality as thermal oxide with a resistivity of 10^{14} Ω·m, breakdown field in excess of $7x10^8$ V/m, and pinhole-free with an etch rate in 6:1 Buffered Oxide Etch (BOE) of 1.6 nm/s.

The Al_2O_3 films were part of a Pt- Al_2O_3-Pt vertical tunnel junction and were kept extremely thin, from 3 nm to 4 nm. The current-voltage characteristics of these junctions indicated a breakdown field roughly twice that achieved by ALD films for the same structure. This breakdown voltage was found to be independent of junction area, strongly suggesting the absence of pinholes in the film.

The ITO films were 50 nm to 100 nm thick. As deposited, they are fully transparent with an electrical resistivity of $5x10^{-6}$ Ω·m.

In conclusion, the ion beam deposition technique has proven to be a powerful tool for the room temperature production of very high quality oxides, as thin as 3 nm. In addition, this process allows for a sub-nanometer control over the film thickness.

8:40am **B1-3-3 van der Waals Oxide Heteroepitaxy**, ***Ying-Hao Chu***, National Chiao Tung University, Taiwan **INVITED**

The research field of oxide heteroepitaxy suffers from the characteristics of misfit strain and substrate clamping, hampering the optimization of performance and the gain of fundamental understanding of oxide systems. Recently, there are demonstrations on functional oxides epitaxially fabricated on layered muscovite substrate. In these heterostructures, due to the weak interaction between substrate and film, they show the lattice of films close to bulk with excellent strictive properties, suggesting that these critical problems can be potentially solved by van der Waals oxide heteroepitaxy. In addition, by exploiting the transparent and flexible features of muscovite, such a heteroepitaxy can deliver new material solutions to transparent soft technology. In this paper, the history, development, and current status of van der Waals oxide heteroepitaxy are addressed and discussed. In the end, new research directions in terms of fundamental study and practical application are proposed to highlight the importance of this research field.

9:20am **B1-3-5 Color Controllable TiO_xN_y Coatings Deposited by Magnetron Sputtering**, ***Tun-Yi Chang***, *J Ting,* National Cheng Kung University, Taiwan

TiO_xN_y-based decorative coatings were deposited using a reactive DC magnetron sputter deposition method. The substrates included Al, stainless steel, and Ti. Optical properties of single-layered and double-layered TiO_xN_y coatings were both investigated. The color of the coating was controlled by manipulating the sputter deposition conditions, including gas pressure and composition, DC power, electrode distance, and substrate type. Selected coatings were also deposited with an anti-reflective layer. The resulting coatings were characterized using SEM, XRD, XPS, TEM, UV-vis spectroscopy, a-step, ellipsometry, and colorimetry. We show that at

least 6 different colors were obtained on each type of the substrate, either single- or double-layered.

9:40am **B1-3-6 $SiO_2/Sc_{0.31}Al_{0.69}N/LiNbO_3$ Multilayer Structure for SAW Device Applications**, ***Chun-Ting Shen***, National Cheng Kung University, Taiwan; *S Wu,* Tung-Fang Design University, Taiwan; *J Huang,* National Cheng Kung University, Taiwan

We report a temperature compensated surface acoustic wave (SAW) device on a SiO_2/ $Sc_{0.31}Al_{0.69}N$ /$LiNbO_3$ structure. The $Sc_xAl_{1-x}N$ films (x=0.23, 0.24, 0.26, 0.29, 0.31, 0.34, 0.39) are deposited on lithium niobate substrate by reactive magnetron co-sputtering using Al and Sc as targets. The films have (002) texture and different degree of lattice strain caused by Sc atoms replacing specific Al sites. The highest piezoelectric coefficient (d_{33}) value 22.2 pm/V is achieved at x=0.31, which corresponds to the largest lattice distortion presented in 2D-XRD data. The electromechanical coupling coefficient (K^2) and temperature coefficient of frequency (TCF) of SAW devices with different SiO_2 thickness on $Sc_{0.31}Al_{0.69}N$ /$LiNbO_3$ are compared. The SiO_2/ $Sc_{0.31}Al_{0.69}N$ /$LiNbO_3$ structure have a great potential in high bandwidth, high temperature stability SAW device application.

10:00am **B1-3-7 Self-lubricant CrO-Ag Coatings for Machining Tools**, ***Filipe Fernandes***, University of Minho, Portugal; *A Cavaleiro,* University of Coimbra, Portugal

High performance dry machining is one of the major trends in modern manufacturing. This is a very hot topic inside the tribology community; PVD tool-coaters and cutting tools costumers are seeking innovative coating solutions which could improve the performance and lifetime of tools, as well as, increase the material volume removal rates through increasing cutting speeds; this could be achieved by eliminating the use of harmful liquid lubrication. Dry machining cutting conditions generate severe shear stresses and high temperature harsh conditions on the cutting zone which, consequently, lead to a premature degradation of the tool. Thus, coating solutions should exhibit, simultaneously, high toughness, low friction coefficient, low wear rate and thermal stability at high temperature. Self-lubricant coating systems, with control release of the lubricious species, have enormous potential to be used in the protection of these tools. However, solutions developed up to now do not allow the control of the lubricious phase release leading to the easy degradation of the coating after a short period of time. In this investigation, we propose the development of self-lubricant coating system based on a matrix of Cr-O, well known by their good high temperature performance and antidiffusion properties, alloyed with Ag, which has lubricious properties. The goal is to observe if Cr-O coating can work as an efficient barrier to Ag ions diffusion. The deposition rate of Cr-O coating is 1.6 times higher than a single Cr coating, taken as reference, deposited with identical conditions. Incorporation of Ag in the Cr-O coating increases the deposition rate. Transition from a dominant columnar to a very compact morphology, as well as from crystalline to amorphous structure, was observed with the O addition. However, no morphological changes were observed with Ag additions. Annealing at temperature≥500 °C promotes the crystallization of Cr-O and Cr-O-Ag coatings, i.e. the formation of a crystalline composite structure, formed by: Cr, Cr2O3 and Ag phases, the later in the case of Cr-OAg coatings. Thermogravimetric analysis showed that O and Ag additions to Cr have no influence on the onset point of oxidation. The oxidation kinetics of the Cr-based coatings is controlled by the outward diffusion of Cr ions through a top Cr2O3 layer. A dual oxide layer was formed for Cr-O and Cr-O-Ag coatings, when exposed to a continuous increase of the temperature up to 1200 °C. Cr2O3 layer controls the Ag ions diffusion to the surface.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B6

Coating Design and Architectures

Moderators: Nina Schalk, Montanuniversität Leoben, Shou-Yi Chang, National Tsing Hua University

8:00am **B6-1 Ab Initio Inspired Design of Ternary Boride Thin Films**, ***Vincent Moraes***, *D Holec,* CDL-AOS at TU Wien, Austria; *H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Polcik,* Plansee Composite Materials GmbH, Germany; *H Riedl, P Mayrhofer,* CDL-AOS at TU Wien, Austria

The demand for discovering new materials is, scientifically as well as industrially, a continuously present topic covering all fields of application. The recent scientific work on thin film materials (especially nitride based protective coatings) has shown, that computationally-driven understanding and modelling serves as a reliable trend-giver and can be used for target-oriented experiments.

Boride-, or diboride thin films in particular, show promising results when considering their use as hard protective coatings. Their drawback in ductility for binary systems calls for improvement via further alloying elements. Instead of trial and error, when designing novel ternary coating systems, we use a semi-automated High Throughput Search (HTS) calculating the basic properties (e.g., lattice parameters, bulk moduli, elastic constants, etc.) of all different TMB_2s´ in two stable/metastable hexagonal structures (space group 191 with prototype AlB_2 vs space group 194 with prototype W_2B_{5-x}) via density functional theory (DFT).

After analyzing the data on behalf of different criteria such as matching lattice constants, high bulk moduli, brittle/ductile transition and experimental feasibility, promising ternary boride thin films were synthesized via physical vapor deposition (DC magnetron sputtering). Analyzing their structure and mechanical properties reveal the potential of this material combination, by reaching superhardness-level and allowing for phase transformation induced toughening effects.

8:20am **B6-2 Enthalpy/Entropy-driven Segregation of Solute Elements of Cu Alloy Films to Self-form < 2 nm Unitary V to Quinary V-Nb-Mo-Ta-W Diffusion Barrier Layers**, ***Yu-Ting Hsiao***, *S Chang,* National Tsing Hua University, Taiwan

For next-generation integrated circuits, an ultrathin (< 2 nm) robust diffusion barrier layer between Cu wires and dielectric layers is demanded to inhibit the rapid diffusion of Cu atoms into Si devices. Due to the limitation of current thin-film deposition techniques, a “self-forming” or “barrierless” technique has alternatively been developed to generate an ultrathin barrier layer at Cu/dielectric interfaces, by annealing Cu alloy films at relatively low temperatures (~ 400°C) and segregating the solute elements of the Cu alloy films to the Cu/Si interfaces. In addition, multicomponent high-entropy alloys with severe lattice distortions and high resistance to Cu/Si interdiffusion have been suggested to be very promising diffusion barrier materials. Therefore in this study, Cu(V) to Cu(V,Nb,Mo,Ta,W) alloy films were prepared, and the self-forming technique was applied to fabricate ultrathin (< 2 nm) unitary V to Quinary V-Nb-Mo-Ta-W barrier layers. The segregation behaviors of the solute elements (V to V-Nb-Mo-Ta-W), thermodynamically driven by enthalpy and entropy-dominated free energy, were also investigated. High-resolution TEM observations and elemental mappings indicated that, owing to positive mixing enthalpies, the solute elements were separated from Cu during annealing (250-400°C). For the Cu(V) alloy film, the solute atoms segregated to the Cu/Si interface and formed a < 2 nm V layer. For the Cu(V,Nb), Cu(V,Nb,Mo) and Cu(V,Nb,Mo,Ta) alloy films, the solutes segregated to the grain boundaries of the Cu alloy films and formed intermetallic compound precipitates. For the Cu(V,Nb,Mo,Ta,W) alloy film, attributable to the high mixing entropy of the five solute elements, the solute atoms segregated to the interface and formed a < 2 nm V-Nb-Mo-Ta-W solid-solution alloy layer.

8:40am **B6-3 Mechanical Properties of $V_{0.5}Mo_{0.5}N_{1-x}O_x$ Thin Films**, ***Daniel Edström***, *D Sangiovanni, L Landälv, L Hultman,* Linköpings Universitet, Sweden; *I Petrov, J Greene,* University of Illinois, USA; *P Eklund, V Chirita,* Linköpings Universitet, Sweden

Improved toughness is one of the central goals in the development of wear-resistant coatings. Extensive theoretical and experimental work has revealed that single-crystal NaCl-structure VMoN ceramics possess inherently enhanced ductility, as well as high hardness (≈20 GPa) [Kindlund et al. APL Mat 2013]. These surprising findings demonstrate that VMoN-based materials are very promising candidates for replacing other ceramics in hard, refractory protective-coating applications. However, during applications, hard coatings inevitably oxidize which can compromise material properties. Herein, we use density functional theory to evaluate the mechanical properties, as well as the thermodynamical stability, of $V_{0.5}Mo_{0.5}N_{1-x}O_x$, with x approximately equal to 0.05, 0.1, and 0.5. We study cubic $V_{0.5}Mo_{0.5}N_{1-x}O_x$ solid solutions characterized by both high and low short-range cation/anion ordering. $V_{0.5}Mo_{0.5}N_{1-x}O_x$ is predicted to be thermodynamically stable for x < 0.1, although higher oxygen ratios can possibly be achieved with non-equilibrium growth techniques such as physical vapor deposition. Our results show that oxygen concentrations x = 5% and 10% have little effect on the mechanical properties of random $V_{0.5}Mo_{0.5}N_{1-x}O_x$ alloys, which retain both hardness and ductility. At x = 50%, bulk, elastic, and shear moduli, as well as Cauchy pressure, are reduced by ~25%, but the material is still predicted to remain ductile. For ordered

$V_{0.5}Mo_{0.5}N_{1-x}O_x$, x = 6% already results in a drastic change in mechanical properties, likely due to disruption of the cubic symmetry. A further increase in the oxygen content yields significant reductions in Cauchy pressures, indicating reduced ductility. However, the Cauchy pressure remains positive for all oxygen concentrations, suggesting that none of the investigated alloys are brittle according to the Pugh and Pettifor criteria.

9:00am **B6-4 Hard Transparent Coatings in the Al-Si-O-N System**, ***Maria Fischer**, M Trant, K Thorwarth,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Patscheider,* Ruebsteinstrasse 25, 8706 Meilen, Switzerland*; D Scopece, C Pignedoli, D Passerone, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The Al-Si-O-N material system allows for the creation of various hard, transparent thin films by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS). Combinations of the possible binary materials AlN, Al_2O_3, Si_3N_4 and SiO_2 lead on to ternary materials such as Al-O-N and Al-Si-N, and combining the latter two yields quaternary Al-Si-O-N. As long as the films are fully nitrided and / or oxidized, they are transparent and thus interesting for optical applications.

In the work reported here, polycrystalline AlN was chosen as starting point. By gradually adding O and / or Si, the material system first transformed into a solid solution with the dopant dispersed in the crystallites. Upon transgressing a distinct solubility limit at 6-8 at% for the foreign atoms, a nanocomposite evolved with an amorphous matrix surrounding shrinked crystallites. Yet higher O and / or Si amounts lead to an entirely amorphous network.

Along with these microstructural changes, physical parameters such as hardness, elastic modulus and refractive index vary. This renders it possible to tune thin films to desired properties by simply choosing according deposition conditions. Applying R-UCFDCMS as a deposition technique far off thermodynamic equilibrium for this purpose allows for the generation of metastable, yet highly inert phases.

9:20am **B6-5 Exploitation of Surface Modification and Architecture Control for Multi-Functional Coatings via Nano-Composite, Multilayer, Hybrid Organic/Inorganic and Bio-Inspired Approach**, *J Lee, H Chen, J Lee, P Chen, **Jenq-Gong Duh**,* National Tsing Hua University, Taiwan **INVITED**

The exploitation of surface modification technique in materials related fields opens the pathway of continuous development to render the coating to exhibit added-values on satisfactory mechanical strength, thermal stability and corrosion resistance. The design concepts of coating can be regarded as integration of architecture, composition, morphology and process control, leading to significant enhancement in properties and functionalities. The primary tasks focus on a series of nitride coating via nanocomposite and multilayer architecture to improve the hardness, corrosion and oxidation resistance. Incorporation of hybrid approach of organic/inorganic and bio-inspired conceptual framework is then conducted, paving ways for a new frontier in protective coatings. Recently anti-wear CrAlSiN nanocomposite coating under extreme environment is derived. Self-lubricating CrAlN/VN multilayer coating is fabricated via microstructure control for improved mechanical property and high-temperature tribological characteristics. A parallel study is conducted in CrMoSiN nanocomposite to enhance the mechanical reliability, especially the elevated temperature tribological property. In addition, a newly-designed Zr-Cu based thin film metallic glass with various nitrogen contents are developed for application in multiple functionalities, including mechanical property, thermal stability, corrosion resistance, antimicrobial and diffusion barrier characteristics.

10:00am **B6-7 The Effect of Hybrid PVD Process on the Mechanical and Antistatic Properties of TiO_2 Based Nanocomposite Thin Film**, ***Ding-Shiang Wang**, M Leu, T Chen, H Lai, J Chang, J Shih,* Industrial Technology Research Institute, Taiwan

In this paper, mechanical and antistatic properties of magnetron sputtered, filtered arc ion plating (FAIP) and a hybrid PVD process (magnetron sputtered+FAIP) prepared TiO_2 based nanocomposite thin film were investigated. Both of the antistatic properties of different thin films were analysis by measuring resistance values and decay times. The results showed that for magnetron sputtered and hybrid process prepared TiO_2 based nanocomposite thin film showed resistance around 10^6~10^8 W/sq and a short decay time. But for the FAIP process, the resistance uniformity is at about 80 %. In terms of mechanical properties, the FAIP and hybrid process nanocomposite thin film showed adhesion and hardness at around 15 N , 14 N and 15 GPa, 12GPa. For the nanocomposite thin film prepared by magnetron sputtered the adhesion and hardness are only about 9 N and 10 GPa. Thus for a high quality of antistatic tin film the hybrid PVD process was recommend due to the excellent mechanical and antistatic properties.

10:20am **B6-8 Optical, Electrical and Structural Characteristics of Mg-doped $CuCrO_2$ Transparent Conductive Thin Films**, ***Ruei-Sung Yu**, C Chu,* Asia University, Taiwan

$CuCrO_2$ is a transparent conductive oxide with a wide bandgap greater than 3.0 eV. The oxide is a p-type semiconductor that the main carrier is hole. $CuCrO_2$ can be used in various transparent optoelectronic p-n diodes. This study is focused on the features of magnesium (Mg) doping on the improvements of optical and electrical properties for the $CuCrO_2$ films. It is anticipated that the p-type $CuCrO_2$ with high conductivity, which is conducive to the developments of transparent p-n devices. We prepared $CuCrO_2$ films by using sol-gel method and the annealing under controlled argon atmosphere, with the attempt to identify the chemical composition, crystal structure, cross-section microstructure, surface morphology, and optoelectronic properties. The modulation of sol-gel process, the precursor solutions used were copper acetate, chromium acetate, magnesium acetate, triethanolamine, and anhydrous ethanol. The annealing temperature was 600°C for 120 minutes. XPS, XRD, FESEM, AFM, UV-Vis, and Hall effect measurements were employed to analyze the material properties. This study has established to decrease resistivity of p-type $CuCrO_2$ film by doping magnesium. The $CuCrO_2$ films with Mg were increased gradually from 0.20 at.% to 2.17 at.%. These compositions deviated from the stoichiometric proportion of 25, 25, and 50 at.% of Cu, Cr, and O, respectively. In the films, Cu and Cr were insufficient quantity. The oxygen was higher than the set proportion. The Mg were introduced in the delafossite $CuCrO_2$ films without any impurity phase. With the increase of the Mg doping, the surface root mean square roughness values of the $CuCrO_2$ decreased from 23.4 nm to 16.6 nm, and the direct bandgaps of the thin films increased from 3.09 eV to 3.13 eV. The proper contents of Mg doping in the $CuCrO_2$ can improve transmittance, and the films possess a higher absorption ability for ultraviolet light. The magnesium (Mg^{2+}) replaced chromium (Cr^{3+}) in the lattice sites of $CuCrO_2$, which can form carrier and increase the concentration. The resistivities of the undoped and optimal Mg-doped $CuCrO_2$ films were respectively 41.09 Ωcm and 0.64 Ωcm.

10:40am **B6-9 Brittle Film-induced Cracking of Ductile Substrates**, ***Xiaolu Pang**,* University of Sceience and Technology Beijing, China

Film and substrate mechanical integrity is essential for the whole system's performance. In the present study, cracking of brass ductile substrate induced by brittle TiN film fracture was observed. Counter-intuitively, instead of protecting the ductile substrate, a brittle film can cause its premature fracture, as demonstrated here experimentally. Brittle film fracture could induce cracking of ductile substrate at considerably low strain level. Analytical calculation based on energy conservation during crack propagation is presented to explain this phenomenon of film-induced cracking. It is shown that crack depth penetrated into the substrate is a function of both crack velocity and the number of dislocations emitted from the crack tip. Relatively thick brittle films and fast propagating cracks favor fracture of the ductile substrates. The critical crack velocity, which can induce the cracking of brass substrate, is 61 m/s. The presence of brittle film could not only prevent dislocations escaping from the surface of the crystal and inhibit dislocations emitting from surface dislocation sources, but also initiate a channel crack with high velocity due to brittle fracture. Both of them contribute to crack propagation in soft brass substrate. This study provides an alternative view to the notion that a brittle film can protect the ductile substrate from damage.

11:00am **B6-10 Ultra-high Vacuum dc Magnetron Sputter-deposition and Microstructural Characterization of Zr and ZrC_x Thin Films**, ***Hicham Zaid**, K Tanaka, J Fankhauser, A Aleman,* UCLA, USA*; M Mato,* Nagoya University, Japan*; D Yu, A Ebnonnasir, C Li,* UCLA, USA*; M Kobashi,* Nagoya University, Japan*; M Goorsky, S Kodambaka,* UCLA, USA

B1-structured, Group IVB and VB transition-metal carbides are some of the hardest (>20 GPa), high moduli (>270 GPa), and highest melting point solids with high-temperature mechanical strength, and good wear-, ablation-, and corrosion- resistance. In this talk, we present results from our recent efforts focused on the ultra-high vacuum dc magnetron sputter-deposition of thin epitaxial films of ZrC_x of desired composition and crystallinity.

Zr and ZrC_x thin films are deposited on single-crystalline Al_2O_3(0001) and MgO(001) substrates at temperatures T_s between 723 K and 1323 K using pure Ar and Ar/C_2H_4 gas mixtures, respectively. The as-deposited film surface structure and composition are characterized *in situ* using low-

energy electron diffraction and Auger electron spectroscopy. The bulk crystallinity, microstructure, and composition of the films are determined using a combination of x-ray diffraction, transmission electron microscopy, energy dispersive x-ray spectroscopy and x-ray photoelectron spectroscopy measurements. Using pure Ar discharges, we obtain single-crystalline hexagonal close-packed (hcp) Zr(0001)/Al_2O_3(0001) layers at 873 K ≤ T_s ≤ 973 K and {0001}-textured Zr layers at higher T_s. We attribute these results to the formation of Zr-Al intermetallic compounds at the Zr-Al_2O_3(0001) interfaces at higher T_s. With the introduction of C_2H_4, at low partial pressures of 2×10^{-7} Torr (with Ar pressure ~ 10 mTorr), we obtain smooth, hcp-Zr(0001):C layers. With increasing fraction of C_2H_4, we obtain increasingly C-rich ZrC_x layers whose crystallinity and composition vary sensitively with T_s. We expect that our results provide previously unknown information concerning the growth-related aspects of reactively sputter-deposited ZrC_x thin films.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Sunrise - Session C3

Thin Films for Energy-related Applications

Moderator: Per Eklund, Linköpings Universitet

8:00am **C3-1 Synthesis and Optical Characterization of Cds Thin Film Obtained by Colloidal Technique**, ***Laura Reyes***, *C Villa, R Villa, B Valdez, D Mateos, M Curiel, S Romero,* Instituto de Ingeniería, Universidad Autónoma de Baja California, Mexico

On the way to find a simple and economic technique that satisfy the requirements for further photonics applications; it was found out that the polymer-semiconductor nanocompound is a new generation of hybrid organic-inorganic materials. In this case, the inorganic semiconductors are synthesized in a polymeric matrix (organic). This kind of compounds has a huge interest due to its optical, electric, mechanical, thermal and magnetic properties comparing with other materials.

Semiconductors from groups II-VI such as CdSe, CdS, ZnS, PbS, among others, can be synthesized with polymers. In order to produce nano-polymer compounds, easily to remove if it is necessary, have great applications in optoelectronics devices. CdS meets these characteristics and can be used in photovoltaic (PV) cells, electronic and optoelectronic devices, e.g., due to the band gap of 2.42 eV.

In the present work CdS colloidal spheres were synthesized by using the solvothermal route technique, with the reaction given between a polymeric matrix (PVP), a Cd/Te salt and thiourea TU in a buffer alkaline solution technique. This allows the control of particle size and distribution to obtain: (i) thin, (ii) homogenous, (iii) strong adhesion and (iv) transparent films. The CdS colloidal spheres physical and optical properties were characterized by using FTIR spectroscopy, SEM-EDS and UV-VIS to compare the theorical - practical capacity of absorbing photons in a different emission.

FTIR measurements show two characteristic peaks at 600 cm^{-1} which correspond to the Cd-S stretching vibrational modes and 1100 cm^{-1} which correspond to presence of S. UV–VIS absorption spectrum measured correspond to CdS . EDS analysis reveals the presence of S and Cdin the deposited thin films.

A colloidal solution was prepare and multi-deposited on soda lime glass covered with ITO substrate by spin-coating technique and annealed at 120°C. Ellipsometry determined the transparency and film thicknesses.

The results shown that nanostructures can be deposited as thin films by colloidal technique at low-cost. This is attractive for optoelectronic applications as photonic absorbers as PV cells.

8:20am **C3-2 Electrochemical Characteristics of Ni_xN Thin Films Deposited by DC and HiPIMS Reactive Magnetron Sputtering**, *J Keraudy, L Athouel, J Hamon,* IMN - Nantes, France*; B Girault, D Gloaguen,* GeM - Saint-Nazaire, France*; M Richard-Plouet,* IMN - Nantes, France*;* ***Pierre-Yves Jouan***, Université de Nantes, CNRS, France

Ni_xN thin films can crystallized in many phases : Ni_4N crystallizes in cubic phase, Ni_3N in hexagonal phase and Ni_2N in tetragonal phase. Most studies, related to NiN by reactive sputtering, report a mixture of nitrided phases and the change from Ni_4N to Ni_3N can be highlighted by the change in the magnetic behavior from ferromagnetic to paramagnetic. This material have great interest as negative electrode for Li battery and super-capacitors.

This study deals with optimization of DC and HiPIMS reactive magnetron deposition process using a pure nickel target (99.995%) in an Ar-N_2 gas mixture with varied nitrogen gas flow and bias voltage (floating or -100V).

The characterization of the NiN films has been carried out by X-ray diffraction (XRD), X-ray photoelectrons spectroscopy (XPS), Energy dispersive X-ray Spectroscopy (EDXS), SEM and AFM.

XRD measurements have highlighted the deformation of the Ni cubic cell as a function of nitrogen content and a mixture of nitrided phases (Ni_4N, Ni_3N and Ni_2N) appears for 20% N_2 in the discharge.

XPS and EDX are well correlated and permit us to determine three zones : metallic between 0 and 20% N_2, Ni_4N between 20% and 42% N_2 and finally Ni_3N for higher than 42% N_2. These three zones are in good agreement not only with deposition rate and optical emission spectroscopy measurements but also with roughness, electrical resistivity and hardness.

Electrochemical characterizations, as cyclic voltametry, galvanostatic charge-discharge measurements and electrochemical impedance spectroscopy, have been performed in a conventional three-electrode cell using different aqueous electrolytes. The electrochemical behavior showing reversible faradaic peaks leads to the conclusion that the NixN film presents a charge storage mechanism of a so considered battery-type electrode, which is dependent of the amount of nickel implies in nickel-nitrogen bonds.

8:40am **C3-3 Photovoltaic Properties of Cu_2O-based Heterojunction Solar Cells using n-type Oxide Thin Films Prepared by Magnetron Sputtering System with Loading Chamber**, *K Watanabe, H Tokunaga,* ***Toshihiro Miyata***, *T Minami,* Kanazawa Institute of Technology, Japan

We recently reported that successfully obtained an excellent photovoltaic properties in p-n heterojunction solar cells fabricated by depositing appropriate n-type oxide semiconductor thin films using a pulsed laser deposition (PLD) method on p-type Cu_2O sheets. However, the PLD method is not suitable for practical use because the deposition rate is low and it is difficult to prepare a n-type oxide semiconductor thin film with a large area. Although the magnetron sputtering method is suitable for practical use, excessive oxidation of Cu_2O sheet surface due to oxygen plasma occurs. In this paper, we describe the photovoltaic properties for Cu_2O-based heterojunction solar cells using the various n-type oxide semiconductor thin films prepared by the newly developed magnetron sputtering system with loading chamber. The magnetron sputtering apparatus have loading and deposition chambers, and used a d.c. and an r.f.(13.56 MHz) power supply that was applied either separately or together. One example, pre-sputtering procedure was carried out in a deposition chamber before introducing the p-Cu_2O sheet from the loading chamber. After pre-sputtering, a p-Cu_2O sheet was introduced into the deposition chamber, and then the n+-AZO thin films were prepared at RT at a pure Ar pressure of 0.6 Pa. Photovoltaic properties of n+-AZO thin film/p-Cu_2O heterojunction solar cells was measured under AM1.5G solar illumination. A drastic improvement of the J–V characteristic was obtained by the pre-sputtering time was increased up to about 10 min. The J-V characteristics of the n+-AZO thin film/p-Cu_2O heterojunction solar cells, prepared using the sputtering method with 10 min pre-sputtering, exhibited better properties than the PLD method. In addition, the solar cell's leakage current prepared by magnetron sputtering with 10 min pre-sputtering, measured under a reversed bias, was as low as the solar cell prepared by PLD. These results suggest that amount of oxygen supplied from the moisture adsorbed on the target surface was decreased by about 10min pre-sputtering process. As a result, the excessive oxidation of p-Cu_2O sheets surface was suppressed. In addition, we also prepared AZO/n-type ZnO/p-type Cu_2O solar cells. The photovoltaic characteristics of the solar cell with the AZO/n-type ZnO/p-type Cu_2O structure improved compared with that of the solar cell with the AZO/p-type Cu_2O structure. Therefore, the magnetron sputtering system with loading chamber is promising as a technology for preparing an n-type semiconductor thin film by suppressing excessive oxidation of the Cu_2O sheet surface.

9:00am **C3-4 Synthesis of Tungsten Bronze by a Solution-based Chemical Route and the Near-Infrared Shielding Properties of Tungsten Bronze Thin Films**, ***Pin-Jhen Wu,*** National Cheng Kung University, Taiwan*; H Lu,* National Chin-Yi University of Technology, Taiwan*; S Brahma, J Huang,* National Cheng Kung University, Taiwan

In this study, we report the synthesis of Cs_xWO_3 powders by a solution-based chemical route. The precursors are H_2WO_4 and $CsOH{\cdot}H_2O$, and the solution is deionized water with triethylamine. The experiment can be done within a relatively short time. The as-synthesized and after heat-treatment Cs_xWO_3 samples are characterized by X-ray diffraction, scanning

electron microscopy, differential thermal and thermogravimetric analysis and fourier transform infrared spectroscopy. Next, the Cs_xWO_3 powders are sintered at a fixed temperature for different time and Cs_xWO_3 thin films are deposited by electron beam evaporation from the optimal sintered target. Then, the Cs_xWO_3 films are annealed at different temperatures under Ar and H_2 atmosphere. The effects of annealing on the microstructure, morphology and NIR shielding properties of the Cs_xWO_3 films are discussed.

9:20am **C3-5 ZnO Nano-structures Growth and Investigation***, **Alexander Axelevitch**, I Lapsker,* Holon Institute of Technology (HIT), Israel

One of the main problems in the energy production field is limitation of usual fossil fuel sources. At the same time, traditional energy production technologies significantly influence on the global climate and the ecological state of our environment. This is the very important reason to find novel renewable and ecologically pure alternative energy sources. One of such sources is utilization of the piezoelectric effect for energy generation, harvesting and transfer.

Various piezoelectric materials are widely investigated in recent years. Zinc oxide (ZnO) is one of those materials. Thin films of ZnO have attracted great attention due to their unique piezoelectric and piezooptic properties, making them suitable for various microelectronics and optoelectronics applications, such as surface acoustic wave devices, optical fibers, solar cells etc.

In our work, we investigated possibility to grow ZnO nanostructures using thermal oxidation of a metal Zn coating prepared by vacuum evaporation on the rigid and flexible substrates. We used the glass, sitall and polyimide substrates. Follows figure illustrates obtained nanostructure thin film. The structure and electrical properties of grown systems were studied. Also, it was shown application of the grown structures as the acoustic signal sensors.

9:40am **C3-6 Nitrogen Doping of ZnO Films by Decomposition of NO Gas using Heated Ir Wire in Catalytic Reaction-assisted CVD***, Y Adachi, S Ono, A Kato,* Nagaoka University of Technology, Japan*; A Hashim,* MJIIT, Universiti Teknologi Malaysia, Malaysia*; **Kanji Yasui**,* Nagaoka University of Technology, Japan

The large bandgap (3.37 eV) and exciton binding energy (60 meV) of ZnO[1)] have recently stimulated intensive research into optoelectronic device applications, such as light-emitting diodes and laser diodes in the ultraviolet region. We previously developed a new chemical vapor deposition (CVD) method for ZnO film growth using a catalytic reaction over Pt-nanoparticles between dimethylzinc and high-temperature H_2O. ZnO films grown on a-plane (11-20) sapphire (a-Al_2O_3) substrates exhibited excellent optical and electronic properties.[2)] In the present study, we attempted nitrogen doping of ZnO films by decomposition of NO gas using a heated Ir wire during film growth. The CVD apparatus and basic growth procedure have been previously reported, but without the use of the Ir wire. Epitaxial ZnO films were grown directly on a-Al_2O_3 substrates at a substrate temperature of 773 K for 60 min without a buffer layer. The NO gas pressure was varied in the range $4.4´10^{-3}$ to $1.3´10^{-1}$ Pa. Although the residual carrier concentration was reduced by the addition of the NO gas, the ZnO films did not become p-type. In X-ray photoelectron spectra, multiple overlapping N-1s peaks were observed from 395 to 406 eV. By deconvolution of the spectra, components such as Zn-N, N-N, N-O, and NO_x were identified. The relative intensity of the Zn-N peak at 395.5-361.1 eV increased when the heated Ir wire was used to decompose the NO gas.

Acknowledgement

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 16H03869) from the Japan Society for the Promotion of Science.

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10:00am **C3-7 Morphology-Controlled Growth of ZnO Nanorods by Chemical Bath Deposition and Seed Layer Dependence on Their Structural and Optical Properties***, **Tomoaki Terasako**, S Obara, S Sakaya, M Tanaka, R Fukuoka,* Ehime University, Japan*; M Yagi,* National Institute of Technology, Kagawa College, Japan*; J Nomoto, T Yamamoto,* Kochi University of Technology, Japan

Zinc oxide (ZnO) with a direct band gap energy of ~3.37eV at RT and a large exciton binding energy of ~60 meV is one of the promising materials for the optoelectronic devices. Chemical bath deposition (CBD) is performed at low temperatures (<100 ºC), which allows us to use polymers as substrate materials. We have reported the successful growth of the ZnO nanorods (NRs) on the Au/SiO_2/Si(100) substrates by CBD using different Zn precursors, *i.e.* $ZnCl_2$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ (ZnNit) so far [1,2]. In this paper, the possibility of morphology-controlled CBD growth of ZnO NRs on the Au and ZnO:Ga (GZO) seed layers and effects of the difference in seed layer on their structural and optical properties will be discussed.

The substrate materials were (1) Au/SiO_2/Si(100) wafers, (2) commercial Au/Ti/Si(100) wafers and (3) ion-plated GZO (200 nm)/glass films [3]. Mixed aqueous solutions of ZnNit and $C_6H_{12}N_4$ (HMT) were used as the CBD solutions. Growth time (t_g) was varied in the range of 5-360 min.

SEM observations revealed that all the NRs on the GZO/glass substrate were aligned perpendicular to the substrate surface. Within t_g=60 min, the average diameter and length of the NRs on the GZO/glass substrate increased rapidly with t_g. Above t_g=60 min, the average width and length of the NRs on the GZO/glass substrate were saturated at ~220 nm and ~1,000 nm, respectively. The average width and length of the NRs on the Au/SiO_2/Si(100) substrates were found to be much larger than those on the GZO/glass substrates over the whole growth time. The relation between the growth time and the stress for the NRs on the GZO/glass substrates showed a complex behavior. At t_g=5 min, the compressive stress of 0.9 GPa arose. The compressive stress decreased rapidly with t_g. In the t_g range of 10-15 min, the stress changed from compressive to tensile. After that, the stress was returned to the compressive. Above t_g=30 min, the compressive stress was kept at ~0.6 GPa. Although the absolute values of the stresses were different, the growth time-stress curve for the NRs on the Au/SiO_2/Si(100) substrates behaved similar to that for the NRs on the GZO/glass substrates. Regardless of the difference in the seed layer, the PL intensity ratio of the near-band-edge emission (380 nm) to the orange band emission (630 nm) became larger with t_g, indicating the improvement of the crystalline quality.

This work was supported by JSPS KAKENHI Grant Number JP17K04989 and Yashima Environment Technology Foundation.

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10:20am **C3-8 Piezoelectric Coefficient and Morphology Investigation of the Wurtzite Ga-doped MgZnO Thin Films via RF Magnetron Sputtering***, **Ping-Han Lee**, C Liu, J Huang,* National Cheng Kung University, Taiwan

The piezoelectric nanogenerators, which could convert the mechanical energy into electrical energy via piezoelectric effect, were considered to be the promising and environmentally friendly devices. The piezoelectric coefficient of the MgZnO thin films have been analyzed. In order to achieve higher piezoelectric coefficient precisely, introducing the Ga ions into the MgZnO thin films with the purpose of improving the crystallinity of the Ga-doped MgZnO. The thin films were deposited by the RF magnetron co-sputtering under 250 to achieve the thickness around 500nm, the ambient was controlled at argon 10 sccm and oxygen 20 sccm to reach MgZnO film with highest piezoelectric coefficient previously. The Ga content was varied by changing applied power from 30W to 80W of Ga_2O_3 target, while maintaining a constant power of 100W of $Mg_{0.3}Zn_{0.7}O$ target. X-ray Diffraction Analysis (XRD) confirmed that the Ga-doped MgZnO thin films showed great crystallinity and obtained strong preferential orientation along [0002] growth direction. Furthermore, the morphology and element constituent were examined by the Scanning Electron Microscope (SEM) and Energy Dispersive X-ray spectrometer (EDX). The optical property of diverse Ga content MgZnO thin films were investigated by UV-Vis spectrometer. We could obtain the superior piezoelectric coefficient with corresponding to the Ga content. Moreover, the optimal piezoelectric coefficient of MgZnO thin films, which will be utilized in piezoelectric nanogenerators, were measured by Piezoresponse Force Microscopy (PFM).

10:40am **C3-9 Growth of $Al_{1-x}Sc_xN$ Thin Films for Pyroelectric and Piezoelectric Applications***, **Agnė Žukauskaitė**, Y Lu,* Fraunhofer Institute for Applied Solid State Physics IAF, Germany*; N Kurz,* IMTEK, University of Freiburg, Germany*; M Reusch, A Ding, L Kirste, V Lebedev, V Cimalla,* Fraunhofer Institute for Applied Solid State Physics IAF, Germany **INVITED**

Aluminum nitride (AlN) is a well-established piezoelectric material used in telecommunication as well as sensing applications and is known for its good mechanical properties, high acoustic velocity, and high temperature stability. However, rather low piezoelectric coefficient d_{33} = 5-6 pm/V, electromechanical coupling $k_t^2 \approx 6$ % along with the low pyroelectric coefficient p^{eff} = 4-8 µC/(m²K) limit the potential of AlN in energy-related applications such as energy harvesting from motion (piezoelectric effect) or

temperature fluctuations (pyroelectric effect). In 2009 reactive magnetron sputtering was used to enhance AlN by alloying it with scandium nitride (ScN) to produce aluminum scandium nitride ($Al_{1-x}Sc_xN$) thin films, thus increasing the piezoelectric response by up to 400 % [1] and electromechanical coupling by up to 150-250 % [2] making this new material very attractive for a variety of applications. The pyroelectric properties of AlScN are largely unknown. However, our initial studies show an increase in p^{eff} by ~100 % for $Al_{0.7}Sc_{0.3}N$ compared to AlN [3]. One of the main challenges for growth of high quality c-axis oriented AlScN is its metastability, as the parent binary nitrides AlN and ScN have wurtzite and cubic crystal structures, respectively, making the thin films prone to phase separation and elemental segregation if the growth conditions are not optimized. In this work reactive pulsed DC magnetron co-sputtering was used to deposit 1000 nm thick AlN(0001) and AlScN(0001) films on 100 mm diameter Si(001) substrates and then test structures for piezoelectric and pyroelectric characterization were fabricated. The analysis of AlScN thin films was performed by using x-ray diffraction (XRD), piezoresponse force microscopy (PFM), Berlincourt method, and low-frequency temperature wave dynamic method. One of the most critical growth parameters is temperature [4], but process pressure, reactive gas composition, and, for example, target-to-substrate distance has to be taken into consideration as well [5]. With the goal of incorporating relatively high Sc amounts ($x > 0.2$) into c-axis oriented wurtzite type $Al_{1-x}Sc_xN$ while preventing the degradation of crystalline quality the investigation of different growth parameters and their influence on application-significant material properties will be discussed.

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11:20am **C3-11 A Simple Non-toxic Simultaneous Selenization/Sulfurization Process for the Cu(In,Ga)(S,Se)$_2$ Thin Film Solar Cells**, *H Wei,* ***Yuan-Chun Liang,*** *Y Lin,* National Changhua University of Education, Taiwan

This paper proposes a simple non-toxic simultaneous selenization/sulfurization process to replace conventional toxic H_2Se/H_2S used and two-stage selenization/sulfurization process in $Cu(In,Ga)(S,Se)_2$ (CIGSSe) solar cells. The proposed scheme involves sputter deposition of the absorber layer using Cu-In-Ga ternary targets, followed by the simultaneous introduction of selenium and sulfur vapor to produce a chalcopyrite CIGSSe film. Experiment results show that the total sulfur content of the absorber layer increases with an increase in the S/(S+Se) ratio. When S/(S+Se) ratio ≧ 0.12, the sulfur content at the surface of the absorber layer was higher than inside, which contributed to an increase in the surface energy gap and Voc of the solar cell. However, a S/(S+Se) ratio that is too high was shown to undermine the quality of the CIGSSe crystallinity, cause phase segregation at the surface of the absorber layer, and lead to the formation of ordered vacancy compounds (OVCs) and secondary phases, which tend to decrease cell efficiency. The inclusion of a suitable proportion of sulfur in the absorber layer can inhibit excessive growth of the $MoSe_2$ layer, and thereby enhance cell efficiency. At various S/(S+Se) ratios, small $CuGaSe_2$ grains were observed at the bottom of the CIGSSe absorber layer. The highest cell efficiency obtained in this study was 12.1%, when S/(S+Se) ratio = 0.12. This degree of efficiency is close to that of our reference specimen, produced via two-stage selenization/sulfurization using toxic H_2Se/H_2S gases.

11:40am **C3-12 Thin Films for Transparent Thermoelectric Modules**, *F Correia, J Ribeiro, P Salvador,* University of Minho, Portugal*; A Mendes,* University of Porto, Portugal*;* ***Carlos Tavares,*** University of Minho, Portugal

A great amount of solar energy is wasted as heat in a photovoltaic (PV) cell, due to thermalisation of excited high energy electrons and absorption of low energy photons, which increases the temperature of the photovoltaic cell [1]. Given so, the cooling of PV cells has been target of considerable interest, using several cooling techniques [2-4], from which the thermoelectric (TE) devices merge. The use of TE devices as a generator to convert waste heat into electricity is much coveted and a viable alternative [5], and the approach to integrate these devices in PV cells has already been studied [6-7]. The main purpose of this work is to investigate ZnO-based thin films for thermoelectric generators (TEG), that are optically transparent throughout the whole device. These are intended to coat the top of solar cells. The strategy is to tune the ZnO thin films properties by cationic and anionic doping: with Ga/Al to improve the type n conductivity, with N to have an p type conductivity and Bi to decrease the thermal conductivity. For the latter, the hypothesis is that this will lend a bigger mass to the phonon vibration modes. Consequently a reduction in the thermal conductivity is expected.The production methodology of these films via magnetron sputtering will be presented, highlighting the most relevant process parameters.

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12:00pm **C3-13 Efficiency Enhancement in Dye Sensitized Solar Cells using Silver Ion Embedded TiO_2 Photoanodes**, ***Navdeep Kaur,*** *A Mahajan,* Guru Nanak Dev University, Amritsar, India*; F Singh,* Inter University Accelerator Center, India*; S Kumar, D Singh,* Guru Nanak Dev University, Amritsar, India

Effect of Surface Plasmon Resonance (SPR) phenomenon of silver nanoparticles (Ag nps) on photovoltaic parameters of Dye sensitized solar cells (DSSCs) have been studied. Silver nanoparticles are implanted onto TiO_2 photo anodes of 3.2 µm thickness by using 65 KeV Ag^{2+} ion beam at different fluences varying from 10^{12} to 10^{14} ions/cm^2. The penetration depth of Ag nps was calculated to be around 17 nm through Stopping and range of Ions in Matter (SRIM). Ag nps embedment have been confirmed through X-Ray Diffractometer (XRD), FESEM, UV-Vis and Raman Spectroscopy techniques. Photoanode containing Agnps embedded TiO_2 loaded with N719 dye results in absorption enhancement leading to fabrication of improved DSSCs. Efficiency of DSSC containing Ag nps irradiated TiO_2 photoanodes with fluence ions/cm^2 shows maximum increase as compared to the reference cell.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Royal Palm 4-6 - Session E1-3
Friction, Wear, Lubrication Effects, and Modeling

Moderators: Albano Cavaleiro, University of Coimbra, Carsten Gachot, Vienna University of Technology, Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

8:00am **E1-3-1 A Study on the Tribological Behavior of the AISI 316L Steel Exposed to Boriding to Reduce its Friction Coefficient and Enhance its Wear Resistance**, ***Enrique Hernández- Sánchez,*** Instituto politécnico Nacional-UPIBI, Mexico*; J Velazqez,* Instituto Politécnico Nacional-ESIQIE, Mexico*; A Chino-Ulloa,* Instituto politécnico Nacional-UPIBI, Mexico*; I Torres-Avila,* Instituto Politecnico Nacional-UPIBI, Mexico*; J Castrejón-Flores,* Instituto politécnico Nacional-UPIBI, Mexico*; H Herrera-Hernández,* Universidad Autónoma del Estado de Mexico, Mexico

The AISI 316L stainless steel is well known by its high resistance to corrosion and its low response to the human fluids. Those are the main reasons that make it considered as a steel alloy suitable to medical applications. This study is on the application of the boriding process to an AISI 316L steel to evaluate its effect on the tribological behavior of it. The boride layers were achieved by applying the powder pack boriding process. The treatment time was set in 2, 4 and 6 h at temperatures of 900, 950 and

1000 °C. The morphology of the layer was evidenced by Scanning Electron Microscopy and nature of the boride layers was analyzed by X Ray Diffraction. The mechanical properties were evaluated by both instrumented nanoindentation and Vickers micro hardness test. The tribological behavior of the layers was evaluated by means of a sand/rubber apparatus by following the limits of the ASTM G-65 standard. The friction coefficient of the borided layers was estimated by means of the tribological pin-on-disk tests. The results showed a clear influence of the experimental parameters on the thickness of the boride layers. Also the mechanical properties were affected by the parameters of treatment especially by the temperature. The wear resistance of the layers tended to increase as the layer thickness increased according to the treatment conditions. However, wear mechanisms such as adhesion and micro-fatigue were mainly observed in the samples exposed to 6 h and 1000 °C. Finally, the friction coefficient was diminished from values of 0.7 for the as-received material to 0.2 for the borided samples.

8:20am **E1-3-2 Immersion Time-affected Tribocorrosion Behavior of Cr/GLC Multilayer Coating in Artificial Seawater**, ***Lei Li***, *L Liu, P Ke, A Wang,* Chinese Academy of Sciences, China

A chromium/graphite-like carbon (Cr/GLC) multilayer coating was deposited onto 316L stainless steel by direct current (DC) magnetron sputtering technique to enhance the tribocorrosion resistance of the substrate in marine environment. Taking into account intermittent use of some friction components accompanying long-time immersion in seawater, the influence of immersion time varying from 4 h to 48 h on the tribocorrosion behavior of Cr/GLC multilayer coating was studied in artificial seawater by a reciprocating ball-on-plate tribometer and an electrochemical workstation. The results of tribocorrosion tests after different time of immersion showed that the friction coefficient of Cr/GLC multilayer coating continuously increased from 0.070 to 0.085 with prolonged immersion time, while wear rate firstly decreased and reached its minim value of 5.20×10^{-7} mm^3/Nm at 12 h then gradually increase as the immersion time was in the range of 12 h to 48 h. Eectrochemical impedance spectroscopy (EIS) analysis, before and after the tribocorrosion test, clearly demonstrated that the corrosion resistance of Cr/GLC multilayer coating varied with immersion time, which is associated with the competitive effects of corrosion products blocking the micropores and contact stress promoting microcrack initiation and propagation. Such varying corrosion resistance led to time-affected tribocorrosion behavior of Cr/GLC multilayer coating, thus, more attention should be paid to the performance variation of protective coatings for tribocorrosion applications after long-term exposure to corrosive environments.

8:40am **E1-3-3 A Comparison of the Galling Wear Behaviour of PVD Cr and Electroplated Hard Cr Thin Films**, ***Jaimie Daure***, *P Shipway, G McCartney,* The University of Nottingham, UK

PVD chromium coatings exhibit good mechanical properties and are a possible replacement to electroplated hard chromium (EPHC) in various applications. Electroplated Cr is widely used but there is need to find an alternative to EPHC due to environmental legislation. One possibility is to use PVD Cr thin films as a replacement. However, insufficient information exists on the behaviour of PVD Cr. Therefore, the aim of the study was to compare the behaviour of two PVD Cr films deposited by different processes and compare with EPHC. Galling testing was selected as it is a useful method for testing the wear resistance and adhesion of a coating under high stresses.

Two PVD chromium coatings of approximately 8 µm thickness were investigated and compared to electroplated chromium of ~9.8 µm. The two PVD coatings were deposited by magnetron sputtering and electron beam physical vapour deposition (EBPVD). Coatings were deposited on 316 stainless steel substrates. Samples were characterised by SEM, XRD, EDX and profilometry. Mechanical testing consisted of nanohardness (ISO 14577-4), scratch testing (ASTM C1624-05) and galling testing (ASTM G98-02).

The nanohardness and surface roughness of the two PVD coatings were similar (around 5 GPa and 300 nm Ra respectively), the values were roughly double for the EPHC. All coatings exhibited similar scratch behaviour. Galling tests revealed that the EBPVD provided no improvement in galling resistance compared to self-mated stainless steel (22 MPa). The magnetron sputtered PVD and 9.8 µm EPHC failed at almost six times the stress of the EBPVD (125 Mpa).

Top surface SEM revealed the two chromium PVD coatings to have distinctly different microstructures. XRD revealed the EBPVD chromium coating had a strong preferred orientation in the {2 0 0} planes, whereas the magnetron sputtered chromium coating had preferred orientations in the {1 1 0} and {2 1 1} planes. The electroplated chromium revealed low intensities of crystalline peaks suggesting a lack of crystalline order or an orientation effect.

Overall, the hardness and surface roughness of the coatings appeared not to be a dominant factor in galling resistance. The crystal orientation of the PVD chromium coatings appears to play a large role in galling resistance. As BCC materials contain slip planes of type {1 1 0} in the <1 1 1> direction, the coating with a preferred orientation in the {1 1 0} planes is expected to provide better wear resistance due to the slip planes parallel to the surface. In the presentation, mechanisms for galling will be discussed and related to future development of thin Cr coatings for galling resistance.

9:00am **E1-3-4 Microstructural Evolution of Cold-sprayed Copper Coating during Reciprocating Sliding Wear**, ***Yinyin Zhang***, McGill University, Canada*; C Greiner,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; D Chern, R Chromik,* McGill University, Canada

Cold-sprayed Cu is characterized by various deformed microstructures including nano- and submicron-grains due to dynamic recrystallization, coarse grains containing dislocation forests, as well as deformation bands, deformation twins. When those microstructures were subjected to sliding wear loading, they turned into equiaxed micrometric recrystallized grains below the topmost tribofilm that consisted of nanocrystalline grains. The present work focuses on microstructural evolution mechanisms of the subsurface layer, i.e. grain boundary migration of the nano- and submicron-grains under tribological loading.

First, sliding wear tests were carried out on the as-sprayed and annealed Cu coatings and the subsurface microstructure before and after sliding were observed and analyzed by electron backscattered diffraction (EBSD) maps. This allows, firstly, to compare the difference between thermal-driven and stress-driven grain growth, and secondly, to explore the role of internal energy on microstructural evolution during sliding, given that annealing at different temperatures (i.e. 200 °C, 300 °C, 400 °C, and 500 °C) was to decrease the stored energy gradually. It was found that thickness of the sliding-induced grain growth layer deceased with annealing temperature and disappeared in the 400 °C-annealed specimen. Microstructural features (e.g. grain size, geometrically necessary dislocation density, texture, etc.) of this layer with increase in annealing temperature were discussed based on the EBSD maps. Nanoindentation was used to measure the hardness of the subsurface microstructures. The hardness profiles of the subsurface indicated lower hardness of the grain-growth layer compared to the initial microstructure and this layer became thinner with increase in annealing temperature and eventually disappeared at 400 °C. These results suggest a stored energy criterion probably existed, above which the grain boundary migration occurred under tribological loading.

9:20am **E1-3-5 Scratch Adhesion Resistance of Nickel Boride Layers on Inconel 718 Superalloy**, *I Campos-Silva,* ***Alan Contla-Pacheco***, *A Ruiz-Rios, J Martínez-Trinidad, G Rodríguez-Castro, A Meneses-Amador, W Wong-Angel,* Instituto Politecnico Nacional, Surface Engineering Group, Mexico

New results about the scratch adhesion resistance of nickel boride layer on Inconel 718 superalloy were estimated in the present study. The nickel boride layer was developed on the surface of Inconel 718 superalloy by means of the powder-pack boriding process conducted at 1173 K with 2, 4, and 6 h of exposure. The microstructure of the nickel boride layer was analyzed from optical microscopy, X-ray diffraction and energy dispersive spectroscopy (EDS) in order to verify the presence of Ni_4B_3, Ni_2B, Ni_3B and the distribution of alloying elements along the depth of the layer; the thicknesses of the nickel boride layer + diffusion zone were established between 23 to 40 micrometres for all the set of boriding conditions. Furthermore, and before the scratch tests, indentation properties of the nickel boride layers such as hardness, Young's modulus, plastic deformation resistance, and the distribution of residual stresses were estimated using Berkovich nanoidentation tests applying a constant load (50 mN) across the diffusion layers. The scratch tests were performed over the surface of the nickel boride layer-substrate systems using a Rockwell-C diamond indenter with a continuously increasing normal force from 1 to 80 N, whereas the behavior of the coefficient of friction and the residual depth as a function of the scratch length were monitored during the tests. For the determination of the critical loads, the combination of acoustic emission signal with microscopic observations of the worn tracks were used; the critical loads were estimated at which the layer cracks (cohesive failure) or is detached (adhesive failure) and they explained according to

the mechanical properties of the nickel boride layer-substrate system. For all the set of experimental conditions, the presence of different failure mechanisms over the worn tracks was detected, while the results showed that the critical loads increase with increasing nickel boride layer thickness.

9:40am **E1-3-6 Comparison of Surface Treatments for Adhesive Force Measurements Between Magnetron Sputtered TiW Thin Films and Alumina Substrates***, B Atabay,* ***Elif Apaydin,*** Aselsan Inc., Turkey

This work evaluates the adhesion characteristics of magnetron sputtered Titanium Tungsten (TiW) thin films to surface treated polycrystalline alumina (Al_2O_3) substrates. The experimental relationship has been established in the same region of substrates between four different sets of surface treatments of alumina (Al_2O_3) and TiW thin film adhesion. A progressive load scratch test for adhesion was performed between two surfaces by applying a gradually incremented vertical load and measuring the opposing horizontal force. The 132 N of adhesive force can be obtained by suitable surface pre-treatment of alumina. Results were evaluated by optical microscopy, SEM and surface scratch measurement techniques.

10:00am **E1-3-7 Influence Of Microstructure on Wear of Boroaluminized-Hot-Work Tool Steels***, **Undrakh Mishigdorzhiyn**, N Ulakhanov,* East Siberia State University of Technology and Management, Russian Federation*; Y Chen, H Liang,* Texas A&M University, USA

This research investigates a possibility in improving wear resistance in hot-worked toolsteels by means of high-temperature boroaluminizing in treatment pastes. Boroaluminizing was conducted in sodium fluoride (as an activator), boron carbide and aluminum (BC:Al=4:1) in a furnace. The treatment was administered for 4 hours at 1100°. The microstructure, microhardness, and phase compositions of the boroaluminized layers were evaluated and their effects on wear were studied. Results indicated that high-temperature boroaluminizing improves wear resistance of hot worked tool steels.

New Horizons in Coatings and Thin Films
Room San Diego - Session F4-1
Functional Oxide and Oxynitride Coatings

Moderators: Jörg Patscheider, Evatec AG, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, Marcus Hans, RWTH Aachen University

8:00am **F4-1-1 Self-healing Thermal Barrier Coating System for Prolonged Lifetime***, **Willem Sloof,*** Delft University of Technology, Netherlands**INVITED**

Thermal barrier coatings (TBCs) are applied on aircraft and industrial gas turbine engines protecting the operating components from demanding high temperature environments. However, the thermal mismatch leads to generation of stresses in the TBCs resulting in micro-cracks that grow and coalesce, leading to ultimate failure of the coating. A new, unique self-healing thermal barrier coating for turbines and other thermally loaded structures has been developed in orderto realize a significant extension of the lifetime of critical high-temperature components..

The concept is based on novel Al_2O_3 coated $MoSi_2$ particles embedded in the TBC layer, typically consisting of yttria partially stabilized zirconia (YPSZ) [1]. Upon high-temperature exposure in an oxidising environment the embedded $MoSi_2$ particles react to form a viscous silica (SiO_2), which fills the cracks and re-establishes adherence in the TBC. Subsequently the SiO_2 reacts with the matrix forming zircon ($ZrSiO_4$), which is a load bearing and solid crystalline ceramic phase. This new concept involves the creation of an inert, oxygen impenetrable, shell of alumina (Al_2O_3) around the actual healing agent, which prevents premature triggering of the healing reaction. With this approach, the healing mechanism will become active only when a crack penetrates the alumina shell.

The $MoSi_2$ particles are alloyed with boron to promote the kinetics of the healing reaction and filling of crack gap with amorphous silica [2]. For manufacturing the self-healing TBC by atmospheric plasma spraying, encapsulation by selective oxidation of aluminium, added to the healing particles, proved to be successful. The core of the encapsulated and embedded healing particles remained intact when exposed to high temperatures in air for long times.

In furnace cycle tests, mimicking TBCs in applications, the crack damage evolution due to mismatch in thermal expansion is determined. The lifetime of the self-healing TBC in the furnace cycle tests compared to a similar TBC but without healing particles, was prolonged and the scatter in the lifetime data reduced making the self-healing TBC more reliable.

[1] W.G. Sloof, S.R. Turteltaub, A.L. Carabat, Z. Derelioglu, S.A. Ponnusami and G.M. Song. *Crack healing in yttria stabilized zirconia thermal barrier coatings*. In: Self-healing materials - pioneering research in the Netherlands, S. van der Zwaag & E. Brinkman Eds., IOS Press, Amsterdam, 2015, pp. 217-225.

[2] Z. Derelioglu, A.L. Carabat, G.M. Song, S.V.D. Zwaag, W.G. Sloof. On the use of B-alloyed MoSi2 particles as crack healing agents in yttria stabilized zirconia thermal barrier coatings, J Eur Ceram Soc 35 (2015) 4507-4511.

8:40am **F4-1-3 TiO_2 Thin Films Deposited onto PET by High Power Impulse Magnetron Sputtering for Photocatalytic Degradation of Carbendazim***, R Marcelino,* Universidade Federal de Minas Gerais, UFMG, Brazil*; M Ratova, B Delfour-Peyrethon,* Manchester Metropolitan University, UK*; C Amorim,* Universidade Federal de Minas Gerais, UFMG, Brazil*;* ***Peter Kelly,*** Manchester Metropolitan University, UK

Photocatalysis has been widely studied for the removal of contaminants of emerging concern from water. The use of the catalyst in a powdered form results in high surface area, but hinders the catalyst recovery. An alternative approach is to deposit the photocatalyst onto a flexible substrate material that can conform to the shape of a reactor vessel. Titania (TiO_2) in the anatase phase is the most widely used photocatalyst, but when deposited by conventional magnetron sputtering, the coating usually requires elevated temperatures or post-deposition annealing in order to form the desired crystalline structure. This precludes the use of thermally sensitive substrates. However, deposition in HiPIMS (high power impulse magnetron sputtering) mode allows the deposition of anatase titania in a single stage process directly onto polymeric substrates. This paper, therefore, presents data on the performance of photocatalytic thin films of titania deposited onto polyethylene terephthalate (PET) supports via HiPIMS. Photocatalytic activity of the coated film was assessed by the degradation of the photostable fungicide carbendazim (CBZ) in aqueous solution, in the presence of a photosensitizing agent, reaching 35% of CBZ removal under UV-A and visible radiation. The reusability of the coatings was implied by negligible drop in activity after 5 cycles. The titania coatings have been characterized by SEM, XRD and UV-vis spectroscopy.

9:00am **F4-1-4 Thermal Stability of Structure and Enhanced Properties of Zr-Ta-O Films with Low and High Ta Content***, **Petr Zeman**, S Zuzjakova, J Vlček, J Rezek, R Čerstvý, J Houska, S Haviar,* University of West Bohemia, Czech Republic

Development of novel multicomponent ceramic oxide systems is the promising way how to extend application potential of binary oxides. Zirconia is one of the most studied oxide ceramic materials because of its excellent chemical inertness and good mechanical, electrical, optical and thermal properties. Tantalum pentoxide used as thin-film material exhibits interesting electrical and optical properties. The limit for an application of these oxides is the stability of their structure and properties at elevated temperatures.

The present study focuses on investigation of the thermal stability of the structure and optical and mechanical properties of Zr-Ta-O films with a low and high Ta content. Two ternary Zr-Ta-O films ($Zr_{25}Ta_5O_{70}$ and $Zr_5Ta_{25}O_{70}$) and two binary films (ZrO_2 and Ta_2O_5) were prepared by reactive high-power impulse magnetron sputtering of a single Zr-Ta target (with a varying Ta fraction in the target erosion area) in argon-oxygen gas mixtures using a pulsed reactive gas flow control. The films were deposited either without any external substrate heating or at 400°C onto Si substrates at a floating potential. In the as-deposited state, the structure, microstructure, mechanical and optical properties of the films were analyzed and their thermal stability in air in a temperature range of 700°C – 1300°C investigated.

We found that highly optically transparent Zr-Ta-O films exhibit a higher hardness, a higher refractive index and an enhanced thermal stability of the as-deposited structure and optical and mechanical properties than the corresponding binary oxides. The $Zr_{25}Ta_5O_{70}$ film is a single-phase material with a nanocrystalline structure corresponding to the ternary $TaZr_{2.75}O_8$ phase. This as-deposited phase is stable up to a maximum temperature investigated (1300°C) and the film retains its hardness of 19 GPa and refractive index of 2.25 (measured at 550 nm) even after annealing to 1000°C in air. The $Zr_5Ta_{25}O_{70}$ film exhibits an amorphous structure in the as-deposited state with its thermal stability up to 800°C, which is by about 100°C more than in the case of the Ta_2O_5 film. At higher temperatures a crystallization of a coarse-grained β-Ta_2O_5 phase occurs. The thermal stability of mechanical and optical properties will be discussed and presented in more detail.

9:20am **F4-1-5 Electrophysical Properties of Nanoparticle-Added PEO Coatings on Aluminium**, ***Noratiqah Yaakop***, *B Mingo, L Qiang, Z Wang, A Yerokhin, A Matthews,* University of Manchester, UK

Oxide ceramic coatings produced by Plasma Electrolytic Oxidation (PEO) in electrolytes with nanoparticle additions have been gaining increasing attention. Many electrical and electronic applications such as capacitors, resistors and integrated circuits would benefit from dielectric surface layers produced by green and facile PEO technology. The PEO coatings produced with incorporation of nanoparticles directly from electrolyte are known to be denser, however the influence of nanoparticle additions on electrophysical properties of such coatings requires further investigation.

The PEO coatings have been produced on AA6082 alloy samples using a pulsed bipolar current mode with 1-3 kHz frequency. The composition of the dilute alkaline electrolyte and the concentration of alpha alumina nanoparticles additions were varied from 10 to 30 g/l. Since incorporation of nanoparticles allowed coating porosity to be reduced, thin yet dense PEO coatings with thickness ranging from 10 to 30 micron have been produced in relatively short treatment times, varied from 5 to 15 min.

A Mott-Schottky analysis was performed on the coatings to determine the concentration charge carriers and the flat band potential. For that, electrochemical impedance spectroscopy (EIS) was conducted at increasing potentials from 0 to 1.3 V vs. OCP with step size of 100 mV. The capacitance of the coatings was calculated by fitting the experimental data to an equivalent circuit and a linear relationship between the inversed squared capacitance and applied voltage was found. The dielectric strength of the studied materials was evaluated in the metal-oxide metal configuration by applying an increasing DC voltage until the coating breakdown is achieved. Morphology of the coatings was studied by scanning electron microscopy (SEM) and phase composition of the coatings was analysed by X-ray diffraction. Correlations were sought between characteristics of surface morphology, phase composition and electrophysical properties of the studied coatings.

The results indicate that the electrophysical properties of PEO coatings are comparable and in some cases even better compared to epoxy-based materials used, up to now, for insulated metal substrates. Additionally, these coatings present higher thermal stability and lifetime which makes them potential candidates for electronic applications.

9:40am **F4-1-6 Titania Films Deposited by Constant Current High Power Impulse Magnetron Sputtering**, ***Arutiun P. Ehiasarian***, *D Loch,* Sheffield Hallam University, UK*; A Heisig, J Neidhardt,* Von Ardenne Anlagen Technik, Germany

TiOx films were produced by reactive High Power Impulse Magnetron Sputtering (HIPIMS) of a pair of metallic targets in an Ar-Oxygen atmosphere. During the HIPIMS process a fast rise and a constant current was maintained during the pulse by regulating the voltage. This resulted in the elimination of stability issues associated with runaway currents and target poisoning for oxygen flows ranging from 10 to 50% of the total gas flow. Time-resolved optical emission spectroscopy revealed that the plasma discharge developed through stages of gas ionisation, gas rarefaction and metal sputtering, the latter associated with cooling of the electron temperature. Evidence is presented of metal ionisation and atomic oxygen sputtering from the target at low pressure and produced in the gas phase at high partial pressure. Films were deposited without intentional heating or substrate biasing and had good transparency. The thickness uniformity was < 2% across a 100x100 mm area. The refractive index increased continuously as the oxygen flow reduced from 45 to 13% reaching a maximum value of 2.55 at a wavelength of 550 nm compared to 2.47 for bipolar pulsed sputtered films. The extinction coefficient in the HIPIMS coatings was of the order of 0.003, similar to bipolar pulsed sputtered films. The films were metallic (non-transparent) at 10% Oxygen flow. The films comprised a mixture of rutile and anatase phase with HIPIMS deposition producing higher fractions of rutile compared to bipolar pulsed DC operation. The hardness of the films and its relation to process conditions are discussed.

10:00am **F4-1-7 Study on Silicon Carbide Based Metal Oxide Semiconductor Capacitor with Magnetron Sputtered ZrO_2 High-k Gate Dielectric**, *S Mourya, J Jaiswal, G Malik, B Kumar,* ***Ramesh Chandra***, Indian Institute Of Technology Roorkee, India

A silicon carbide (SiC) based two terminal metal oxide semiconductor (MOS) capacitor with magnetron sputtered zirconium oxide (ZrO_2) as a high-k dielectric material using titanium (Ti) gate has been synthesized at room temperature. The structural, morphological and compositional analysis of the dielectric layer has been carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), Atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of MOS capacitor were studied at room temperature by applying the dc bias gate voltage swept from –3V to 3V for both, high and low-frequency operation on a probe station. The thermal stability of the MOS capacitor is of critical importance for use in the fabrication of electronics for deployment in extreme environments. Hence, the effects of post-deposition annealing (PDA) temperatures (200-1000 ºC) on the electrical properties of MOS capacitor have been investigated. MOS characteristics of $Ti/ZrO_2/SiC/Ti$ capacitor were correlated with structural and morphological properties of an insulating dielectric layer at different PDA temperatures. It has been observed that a synergetic contribution of lowest effective oxide charge, semiconductor-oxide interface-trap density and total interface-trap density improve the electric breakdown field of MOS capacitor for PDA samples.

10:20am **F4-1-8 On the Importance of the Energy of Negative Ions in Achieving Uniform and High-quality Magnetron Sputtered AZO Films**, ***Fanping Meng***, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences,, China

Spatial distribution of highly energetic negative ions inherent in magnetron sputtering of oxides has long made low temperature deposition unsuitable for high quality films uniform over relatively large areas. Here we examine the distributions of both structure and physical properties of magnetron sputtered Al-doped ZnO (AZO) films deposited at low temperatures (≤393 K) in which the bombardment from the negative oxygen ions was systematically studied by changing the discharge voltage (i.e., ion energy) and the substrate position (i.e., ion flux). The film structure was characterized by X-ray diffraction, Raman spectroscopy, and transmission electron microscopy; and the electrical and optical properties were obtained by a Hall system and Spectroscopic Ellipsometry. We found (i) that uniform yet high quality AZO films ($<4x10^{-4}$ Ω cm) can be obtained only when the energy of the negative ions was set below a threshold; (ii) that the ion flux exerted an ever-decreasing effect on the structural uniformity as the ion energy was reduced; and (iii) that a set of structural criteria, incorporating crystallite quality (orientations, size, lattice spacing) and point defects, were derived for low resistivity AZO films. The benefit of lowering the ion energy is then explained in terms of the favorable competition between radiation-induced defect generation and the subsequent dynamic annealing. These findings may pave a way for large-area coating of high quality AZO films at low temperatures.

11:20am **F4-1-11 Combinatorial Thin Film Materials Science: Limitations and Opportunities for Combining Experiments and DFT Based Theory**, ***Jochen M. Schneider***, RWTH Aachen University, Germany **INVITED**

The combination of modern electronic structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge based materials design of hard and wear resistant coatings, energy conversion materials as well as of thin film metallic glasses. Besides elastic properties and phase stability also the interaction of the coating with the ambient can be described based on quantum mechanics. In the talk predictions of the interaction of coated tool surfaces with gases contained in the atmosphere as well as materials to be formed are discussed. Hard coatings used for forming operations of Al and Polymers are investigated and experimental data characterizing these interactions will be discussed. Furthermore, the implications of the presence of point defect for the thermal stability of TiAlN [1] will be analyzed and hybridization implications for the damage tolerance of thin film metallic glasses will be presented [2]. Limitations and opportunities of combining modern electronic structure calculations with combinatorial thin film synthesis und spatially resolved characterization techniques will be discussed.

Surface Engineering - Applied Research and Industrial Applications
Room Sunset - Session G1

Advances in Industrial PVD, CVD, and PCVD Processes and Equipment

Moderators: Emmanuelle Göthelid, Sandvik Machining Solutions, Ladislav Bardos, Uppsala University, Sweden

8:00am **G1-1 Enhanced PVD Process Control by Online Substrate Temperature Measurement**, *K Bobzin, T Brögelmann,* ***Nathan Kruppe,*** RWTH Aachen University, Germany

In physical vapor deposition (PVD) processes pressure and temperature are of outstanding importance for process control and coating performance. The pressure measurement and its integration into the process control are state of the art in industrial coating units. In contrast, the precise determination of the substrate temperature $T_{Substrate}$ presents an unequally greater challenge. In PVD processes the temperature control has a great importance in two respects. On the one hand, the morphology of the coating as well as the adhesion between the coating and substrate directly depend on $T_{Substrate}$. On the other hand, the process temperature is limited by the maximum permissible temperature T_{Max} as for example of heat-treated steel. Exceeding can easily lead to a critical loss of hardness and size accuracy of the substrate and production reject. The online measurement of $T_{Substrate}$ using currently applicable systems such as drag pointer or pyrometer is either extremely complicated or simply not possible. This is particularly the case for large-volume industrial coating units with a rotating substrate table. Therefore, in coating processes, the influence of the different process parameters on $T_{Substrate}$ is ususally not quantified. Hence, $T_{Substrate}$ is often several tens centigrades below T_{Max}. Within the scope of this paper, a temperature sensor developed at the Surface Engineering Institute (IOT) of the RWTH Aachen University is used in an industrial coating unit with rotating substrate table. With this sensor, the online temperature measurement of rotating substrates is possible throughout the entire coating process, from the heating to the etching over the coating to the cooling process phase. The measuring accuracy is $\Delta T = \pm 1$ °C. In all four process phases, the influence of the heating power on $T_{Substrate}$ was analyzed and mathematically described. The results were used to improve the temperature management of an industrial coating process with regard to T_{Max}. Here the temperature difference between T_{Max} of the heat-treated steel and the realized $T_{Substrate}$ was reduced to a minimum over the entire process time. In addition, the influence of the cathode power and cathode number for direct current (dcMS) and high power pulsed magnetron sputtering (HPPMS) processes as well as for hybrid processes dcMS/HPPMS on $T_{Substrate}$ was quantified. For an hybrid six-cathode process, it was shown that an increase in the cathode power by 100 % results in an increase of $T_{Substrate}$ by approx. 17 %. Investigations on the compund properties show a considerably improved adhesion between coating and substrate.

8:20am **G1-2 A Compact, Symmetrical and Efficient Filtered Cathodic Arc Source that uses Permanent Magnets**, ***Paul Sathrum,*** Fluxion Inc., USA

A compact and symmetrical filtered cathodic arc source that uses no magnet coils is presented. The Radial Arc is described and compared to other filtered cathodic arc sources, including how permanent magnets are used instead of coils and how geometric factors promote efficiency. Compared to unfiltered cathodic arc, the Radial Arc is shown to retain many of its useful popular features such as simplicity and ease of maintenance and operation. Deposition rate profiles for metal and tetrahedral amorphous carbon (ta-C) films are given and show rates comparable to unfiltered arc.

8:40am **G1-3 HiPIMS Meets Diamond**, *T Leyendecker, O Lemmer, W Kölker,* ***Christoph Schiffers,*** CemeCon AG, Germany

This paper will introduce a visionary new class of coating materials with revolutionary properties. It creates added value by merging diamond – the hardest of all materials – with HiPIMS – smooth and dense thin films.

The exceptionally hard diamond layer provides the perfect foundation to the HiPIMS film. Diamond has an outstanding thermal conductivity and spreads the extreme heat that is generated in the cutting zone. Both effects, the unrivalled hardness and the heat spreading properties of diamond, avoid the typical egg-shell effect. The generally lower heat input into the carbide substrate and the avoidance of local overheating is an enormous plus when it comes to cutting of heat resistant superalloys.

HiPIMS is a vital contribution to this new material: HiPIMS films are dense and have thereby a high oxidation resistance. Quite a portion of the heat load during machining is transferred into the chips. The other beneficial effect of the HiPIMS part of the new material is its protection of the diamond against dissolution at high temperature in an oxygen atmosphere. The smooth, droplet-free surface of HiPIMS coatings reduces friction, heat generation and optimizes the running in process of the cutting tool.

Case studies like the machining of casted CrCo for medical implants and the milling of stacks with extra thick titanium layers show that the radically new materials concept HiPIMS meets Diamond is the answer to new business for cutting tools after the combustion engine.

9:00am **G1-4 Functional DLC by HiPIMS and Pulsed DC-magnetron Sputtering in an Industrial Coating System**, *I Fernandez Martinez, A Wennberg,* Nano4energy, Spain*; F Papa,* Gencoa, Ltd, USA, Spain*; J Santiago,* Nano4energy, Spain*; N Dams,* PVT GmbH, Germany*;* ***Herbert Gabriel,*** PVT Plasma und Vakuum technik GmbH, Germany

The demand for high-performance coatings for special tooling and component applications is increasing rapidly. The most prominent example for such coatings are Diamond-like carbon (DLC) coatings, due to their tribological, wear resistant and corrosion resistant properties. Due to the growing importance of such coatings in many industrial fields, the market for industrial coating systems is growing very fast.

In order to fulfil the future's demand of such coatings, efficient and highly productive coating systems are required. The consortium's approach is an advanced industrial vacuum coating system with a plasma volume of 350 × 650 mm (Ø × H) equipped with four large area magnetron sputtering-sources and the new hiPlus - positive pulsed technology from Nano4Energy. The magnetrons, manufactured by Gencoa Ltd, incorporate the VTR technology (Variable Magnetic Field) that allows to vary the balanced to unbalanced degree of the magnetron source during deposition, and thus, the ion bombardment of the growing film.

The plasma can be excited in both HIPIMS and DC-Pulsed mode, that in combination with an optimum adjustment of the magnetic field design, smooth coatings with high hardness and ideal adhesion can be produced efficiently. Detailed process description will be given.

The technology is very much up-scalable.

A wide variety of DLC coatings can be deposited in the system with hardness values up to HV 4000. This includes hydrogen-free amorphous carbon (a-C), hydrogenated amorphous carbon (a-C:H), tetrahedral amorphous carbon (ta-C) or Metal-doped DLC (such as Cr-doped DLC). Detailed information on coating properties will be given.

As a benefit, the design of the system allows the deposition of extremely smooth hard nitrides and carbo-nitrides, such as all standard multi-layered, nano-structured TiN, TiC,N, AlTiN, AlCrN and Si-doped coatings.

For industrial production purposes the system runs in a fully automatic mode. For R&D - applications the system can be operated in a complete manual mode.

9:20am **G1-5 Microwave Assisted PVD and PECVD Systems for Carbon-Based Nano Composites**, ***Sven Ulrich,*** *C Poltorak, M Rinke, H Leiste, M Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany **INVITED**

HiPIMS differs significantly from conventional d.c. magnetron sputtering, and together they cover a wide range of scenarios of deposition kinetics that are often critical for the characteristics of resulting coatings. In d.c. magnetron sputtering, particles sputtered from the target are mostly electrically neutral with low kinetic energies of only a few eV. In HiPIMS deposition, however, the particles sputtered from the target crossing the highly densed plasma are largely ionized and, therefore, their kinetic energy can be purposefully adjusted before arriving at the deposition surface via an appropriate substrate bias. Additionally a novel microwave plasma source designed for large-area industrial plasma surface processing and film deposition creates high density plasmas at low pressures even far from the source. A hybrid deposition method (HiPIMS, d.c. magnetron sputtering and microwave plasma source deposition) is developed for advanced carbon-based nanocomposites in the system Ti-Zr-C-N. The coating properties and microstructures were characterized and compared. The results will be discussed in this study and related to the strongly different deposition kinetics. The coatings were deposited from a segmented metallic Ti/Zr target in reactive mode with different Ar-N_2-CH_4 gas mixtures. Effects of thermal treatment were also examined on the deposited coatings. The chemical composition of coatings was analyzed by electron microprobe, the morphology by scanning electron microscopy

(SEM), and the microstructure by X-ray diffraction (XRD). The coating hardness as well as reduced elastic modulus was characterized by nano-indentation.

10:00am **G1-7 Correlation Between Plasma Nitriding of Several Steels and Active Nitrogen Concentration Correlated through Optical Emission Spectroscopy and Atomic Nitrogen Partial Pressure**, *F Papa,* Gencoa, Spain; ***Joaquin Oseguera,*** TRAMES S.A. de C.V., Mexico

Plasma nitriding of steels has been a very important industrial solution to attend solicitations that are produced on many tribo-mechanical applications. Nitrogen diffusion into the steel can be correlated to specific spectral lines obtained from optical emission spectroscopy in the plasma, active nitrogen can be identified through this technique. The correlation between parameters to produce nitrogen diffusion in the steel makes relevant to have a reference of the active species in the process. Analyses of spectral lines observed from the plasma indicate zones where the active nitrogen can produce diffusion into the steel. Through this work, several steels were treated in weak ionized plasma; active nitrogen identified from OES was correlated with atomic nitrogen partial pressures measured from remote emission spectroscopy, through the analysis of information a procedure to identify plasma parameters to produce nitrogen diffusion in steels is presented.

10:20am **G1-8 CVD Technology & Machinery – Tribological Applications and High Temperature Potential**, ***Hristo Strakov,*** *V Papageorgiou, M Auger,* IHI Ionbond AG, Switzerland

Hard material coatings deposited by thermal CVD have maintained their outstanding position for decades in the field of many tribological and high temperature applications. This success can be explained by the excellent mechanical properties at high temperatures and the thermochemical stability of the coatings. Through continuous further development of the materials and the coating machinery, today's coating products are adapted and optimized for the constantly growing demands on the composition and structural properties. Moreover, new CVD technologies are also being developed that address friction and wear improvements at elevated temperatures. Examples of these developments include high Aluminum content TiAlN. Optimized coatings can be produced through specific multilayers adaptations, coating material combinations, together with suitable substrate materials. Specific examples illustrating the influence of coating parameters and base material condition upon performance as well as the necessary equipment improvements are presented.

10:40am **G1-9 Vacuum Barrel Coating: An Opportunity to Performance Increase for Various Small Parts**, ***Heidrun Klostermann,*** *B Kraetzschmar, F Fietzke,* Fraunhofer FEP, Germany

Vacuum coating has found its way into many sectors of mechanical engineering due to the benefits of suitably coated surfaces in terms of wear resistance, corrosion protection and other value-added properties. Essential criteria for the implementation of a vacuum coating step in production are the technical, the economic and the ecological viability. The latter is a pro of vacuum coating processes, the other two challenge engineers as well as entrepreneurs. In the coating of three-dimensional parts, the handling of these represents a considerable fraction of the whole effort for coating. Handling individual parts, often in several process steps, is still mainly a manual task. It is not an option for a large quantity of small parts, which have to be handled as bulk goods.

Vacuum barrel coating seems to be an appropriate technique for the finishing of bulk goods that have to withstand severe load conditions in service. However, coating and process development for a variety of very different applications is a challenge for researchers and engineers. Fraunhofer FEP has pursued the objective of vacuum bulk coating for some years. In this talk, we want to share our experience regarding plasma activated high rate evaporation and magnetron sputtering in the barrel coating device ALMA 1000. Evaporated aluminum based coatings, sputtered coatings, as well as multilayers will be evaluated in the context of their respective field of application and an outlook will be given to further development options.

11:00am **G1-10 Scaling Up Graphene-like Carbon Film: Insights into the Deposition Process in a Roll-to-roll rf Plasma CVD System**, ***Majed Alrefae,*** *A Kumar, D Zemlyanov,* Purdue University, USA; *T Fisher,* UCLA, USA

Graphene and graphene-like-carbon films have found broad applications ranging from corrosion protection of metals to transparent conducting electrodes. Here, we study a high-throughput, roll-to-roll plasma chemical vapor deposition (CVD) of graphene-like-carbon film on Cu foil, particularly the related effects of heat transfer and web speed on film quality in combination with optical emission spectroscopy (OES) to study plasma composition during growth. Graphene-like carbon film is deposited on a moving copper foil using a custom-built roll-to-roll radio-frequency plasma CVD system. The carbon film is deposited on both sides of the substrate at a high speed of 300 mm/min. We find an asymmetry in the quality of the film on the two sides of Cu foil attributed to asymmetry in the plasma's sheath. Results from OES provide insights into the distribution of chemical species between the electrodes. Emission intensities from major plasma species (i.e., CH, C_2, H and H_2) show no dependence on web speed. However, the temperature of the Cu foil, estimated from its blackbody emission using OES, decreases with increased web speed. The Cu foil temperature is near 1000 K for plasma power of 1350 W. We also find that high web speed is necessary with high-energy plasma input to achieve an optimal dwell time and minimal defects in graphene-like carbon film. The results provide insights into roll-to-roll growth of graphene-like carbon film on Cu foil using heat transfer principles and establish the feasibility of the method for a large-scale production.

11:20am **G1-11 TAOS Based Cu/TiW/IGZO/Al_2O_3/Pt Bilayer CBRAM for Low-power Display Technology**, ***Kai-Jhih Gan,*** *P Liu, W Chang, D Ruan, T Chien, Y Chiu, S Sze,* National Chiao Tung University, Taiwan

Herein we report a Cu/TiW/IGZO/Al_2O_3/Pt bilayer CBRAM stack using amorphous InGaZnO, a TAOS material, as the resistive switching layer. The addition of a thin metal-oxide layer (5 nm-thick Al_2O_3) in the bottom of the IGZO memory stack significantly increases the R_{OFF} and the memory window. The a-IGZO bilayer CBRAM shows the excellent memory performances, such as low operation current (down to 10μA), high on/off resistance ratio (more than 10^3), high switching endurance (up to 10^3 cycles)and the capability of multi-level tuning have been demonstrated in our memory device. Meanwhile, high thermal stability was also achieved (two decades of window margin are constantly maintained beyond 10^4 s at 85 °C). This result has given a great potential for the TAOS based material utilizing in CBRAM stacks and integrating into the display circuit for future memory in pixel application.

Coatings for Use at High Temperatures
Room Royal Palm 1-3 - Session A3

Materials and Coatings for Solar Power Concentration Plants

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Gustavo García-Martín, REP-Energy Solutions

2:30pm **A3-4 Corrosion Impact Of Alkali Carbonate At 750°C On Nickel Base, Stainless Steel And Alumina Forming Ferritic Steels*, Christine Geers,*** Chalmers University of Technology, Sweden

A carbonate mixture containing equal amounts of lithium, sodium and potassium was investigated in respect to its corrosive impact on metallic materials at 750°C to meet the demand of increased operation temperatures in concentrated solar power plants. A constant carbon dioxide feed was applied to suppress salt decomposition during exposure. Rapid oxidation and internal corrosion by carburization are characteristic consequences of carbonates in contact with steel at high temperatures. Significant differences in oxide scale stability and carbon ingress have been found for the three alloy classes after a maximum exposure time of 740 h. Depending on which oxide scale is formed, chromia or alumina, the corrosion features change from general to local occurrences pointing towards a high permeability of the oxide scale in the case of chromia formers compared to alumina formers where only locally non-protective behavior was observed. These observations are in agreement with findings from experiments in “solar salt” where major differences between alloys was also coupled to different oxide species and characteristics formed at the surface, independent of the permeating species which was nitrogen in that case.

2:50pm **A3-5 Challenges of New Materials and Coatings for Solar Receivers and Reflectors in Concentrated Solar Power Plants*, Florian Sutter,*** German Aerospace Center (DLR), Spain*; Y Binyamin,* Brightsource Industries, Israel*; A Agüero Bruna,* Instituto Nacional de Tecnica Aeroespacial (INTA), Spain*; C Hildebrandt,* Fraunhofer ISE, Germany*; D Fähsing,* DECHEMA Forschungsinstitut, Germany*; A Morales, A Fernandez-Garcia,* CIEMAT, Spain*; F Pérez-Trujillo,* Universidad Complutense de Madrid, Spain **INVITED**

With increasing share of fluctuating wind and photovoltaic power generation, Concentrating Solar Power (CSP) technologies with thermal storage become more important due to their flexibility in dispatching power to the grid. The International Energy Agency envisions that the global electricity share of CSP systems will reach 11% by 2050, provided that the CSP technology achieves significant cost reductions. One approach to meet this goal is the use of novel materials and coatings to increase the plant efficiency and to enhance lifetime.

This work reviews several new materials with potential to be applied in future CSP plants. In the low temperature range, protective coatings to prevent silver corrosion of glass mirrors will be discussed. In addition, experimental results of anti-soiling coatings to reduce the soiling rates on the mirror surface will be presented. In the medium temperature range (up to 400°C), novel selective absorber coatings operating in air or vacuum are described, as well as anti-reflective coatings with increased abrasion resistance. In the high temperature range (up to 750°C) a set of new high solar absorptance coatings for solar towers will be presented, as well as protective coatings for stainless steels to prevent corrosive attack from molten nitrate salts used as heat transfer and storage medium.

The above described materials are undergoing severe accelerated lifetime tests to ensure that they meet the challenging and harsh operating conditions, which materials need to face in CSP plants. The performance and expected lifetime of the prototype materials is compared to the state of the art.

3:30pm **A3-7 Corrosion Testing of Diffusion-coated Steel in Molten Salt for Concentrated Solar Power Plants*, Diana Fähsing,*** *T Meissner, M Galetz,* DECHEMA-Forschungsinstitut, Germany

In the course of energy transition the development of sustainable technologies for power generation providing base load supply is of particular importance. In comparison to photovoltaics Concentrated Solar Power (CSP) Systems have great potential to fulfil this requirement by the use of thermal storage systems employing molten salt mixtures as heat transfer fluids. For this purpose, molten nitrates are frequently discussed due to their beneficial thermal and physical properties as well as high working temperatures. These fluids are circulated through the superheaters of the CSP receiver for heat absorption, which is subsequently transferred to a steam generator for power generation.

While the receiver tubing's external surfaces are exposed to dust erosion as well as to fluctuating high temperature profiles, its insides are attacked by mechanisms from molten salt corrosion. In order to protect the piping system from degradation coatings can be applied to the materials in use which are commonly steels or Ni-based alloys. The goal is to achieve cost reduction to ensure an even more competitive position of the CSP technology with respect to other renewable sources on the market.

In this study, the behaviour of coated and uncoated ferritic-martensitic steels of type T91 and VM12 in molten salt (mixture of $NaNO_3$ and KNO_3) has been investigated under isothermal conditions. The diffusion coatings are based on potentially protective elements such as Al, Si or Cr and were applied to the steels either by pack cementation or slurry aluminization. Characterization of the samples was conducted by means of optical microscope, EPMA and XRD analysis in order to gain deeper understanding of the occurring corrosion mechanisms and for the purpose of life expectancy analysis.

3:50pm **A3-8 High Temperature Molten Salt Corrosion Behavior of Aluminide and Nickel-aluminide Coatings for Heat Storage in Concentrated Solar Power Plants*, Pauline Audigié,*** *S Rodríguez, M Gutiérrez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; V Encinas-Sánchez, F Pérez-Trujillo,* Complutense University of Madrid, Spain*; A Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Thermal energy storage (TES) in concentrated solar power (CSP) plants is still a key issue as CSP plants are subjected to intermittency of the Sun. Using suitable TES systems is so of great interest. Currently, CSP plants use the so-called Solar Salt (60% $NaNO_3$ - 40% of KNO_3) as heat storage system which is considered to be stable, and has adequate heat storage and transfer capability. However, the maximum storage temperature is limited to 580ºC. New molten salt mixtures with higher temperature stability point are therefore required to increase the plants efficiency, all of this without increasing cost. In general, molten salts can be very corrosive to metallic components in direct contact with them and the corrosion resistance of the materials used for tanks or tubes depends on the formation of a protective oxide scale, which is similar to the protection mechanism occurring during oxidation in high temperature gaseous atmospheres. However, an important difference when using molten salts is that Cr, a protective oxide former, can be soluble in some salts mixtures preventing the formation of the oxide. This results in non-protective and/or fast-growing oxide formation and in the increment of material degradation due to higher corrosion rates. The use of coatings to prevent molten salt corrosion can be a solution. Slurry aluminide coatings are a low cost alternative that allows uniform coating of internal surfaces. Recent studies *[Dorched et al. 2016, Audigié et al. 2017]* have demonstrated the good behavior of these coatings but the protection mechanism is still not well identified. Moreover, since increasing nickel content in Ni-base alloys improved alloy corrosion resistance to molten nitrate-nitrite salt, newly developed nickel-aluminide coatings deposited on 9 wt.% Cr P91 were also tested in contact with molten salts. In this work, sprayed slurry aluminide and nickel-aluminide coatings deposited by means of electrodeposition and slurry application to 9 wt.% Cr P91 alloy have been characterized and both systems have been tested isothermally at 580ºC in contact with the Solar Salt and at 650ºC with a ternary molten salts mixture based on Na, K and Li carbonates. Both tests have been carried out under static and dynamic conditions. All the coated systems in contact with both salts up to 1000h performed much better than the uncoated material as they exhibited very slight weight variations and formed very thin Na or Li aluminates. On the contrary, the uncoated P91 developed a complex, fast growing multilayered oxide scales experiencing significant metal loss which was calculated after removing the corrosion products by chemical etching.

4:10pm **A3-9 High-Temperature Coatings for Protection of Steels in Contact with a Novel Molten Salt under Static and Flow-Accelerated Conditions for CSP Technology*, V Encinas-Sánchez, M Lasanta, M de Miguel, G García-Martín, Francisco Javier Pérez-Trujillo,*** Complutense University of Madrid, Spain

The dramatic increase in demand for energy independence and inclination towards renewable energy as a sustainable and green energy source have led research groups all over the world to concentrate their investigation on solar power. As renewable energy penetration grows, the need for utility-scale renewable generation with storage technology is increasingly important to mitigate intermittency problems, deliver power to peak demand periods and support transmission system reliability. Hence,

concentrated solar power has gained momentum as an attractive technology. Molten nitrate salts are currently considered ideal candidates for heat transfer and storage applications because of their properties. However, this technology is still expensive compared to other renewable sources, which lead to propose solutions for reducing costs, such as development of new mixtures with greater work-temperature range. This increase in temperature limits would strongly require the use of alloys known for their high cost compared to other steels, such as ferritic-martensitic steels. According to this scenario, the use of high-temperature corrosion-resistant coatings would be a very suitable option, even more if they were deposited on ferritic-martensitic steels. This solution not only would help to overcome the corrosion problems of using ferritic-martensitic steels at higher temperatures, but also would allow the CSP industry to improve the Levelized Cost of Energy by reducing Operating & Maintenance costs. In this respect, alumina-based and zirconia-based sol-gel coatings seems to be a great option, both from an operational and economical point of view.

In this work, sol-gel alumina-based and zirconia-based coatings deposited on P91 has been tested in contact with a proposed novel molten nitrate salts at 560°C, results being compared with the uncoated substrate. The study was developed up to 1000 h under static and flow-accelerated conditions, the latter being performed in a novel pilot plant facility, patented under the reference code WO2016102719. Samples were characterized via gravimetric, SEM-EDX, and XRD. Also corrosion was monitored by electrochemical sensors, patented under the reference code WO2017046427.

Results showed the good behavior of the coated substrates, with very little weight gain after 1000 h of test in comparison with the uncoated ones, which exhibited significant weight gain and spallation. The good behavior of the proposed coatings was also observed by SEM-EDX and XRD. Furthermore, corrosion monitoring system showed the protective behavior of the coatings, these being compared with the uncoated samples, where widespread corrosion was determined.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-4

PVD Coatings and Technologies

Moderators: Joerg Vetter, Oerlikon Balzers Coating Germany GmbH, Qi Yang, National Research Council of Canada, Jyh-Ming Ting, National Cheng Kung University

2:10pm **B1-4-3 Particles in PVD-Coatings: Imperfection or Functional Add-on Feature?**, ***Uwe Beck***, *J Baier, M Sahre, M Weise, G Hidde,* BAM Berlin, Germany

The application of PVD-coatings ranges from mechanical engineering, i.e. thicker tribological coatings, to precision optics, i.e. thinner optical coatings. For physical vapor deposition (PVD) technologies such as evaporation, sputtering, ion beam assisted/driven deposition, vacuum is a prerequisite for two reasons: at first process-related ones (evaporation source, plasma discharge, and mean free path) and at second coating-related ones (pure, perfect, and dense films). Usually, the goal is a homogenous coating of defined stoichiometry and micro-structure without any imperfection.

However, the implementation of micro- or nano-particles may occur accidentally or deliberately. Independent of the particle origin, there are two fundamental rules regarding coating functionality: at first, the larger the particle diameter to coating thickness ratio the more affected the functionality of the coating, and at second, the larger the material contrast in terms of the functional feature of interest the more affected the coating performance. Hence, embedded particles have to be avoided for the majority of thin films by all means. The unintended implementation of particles usually results in a malfunction of the coating from the beginning or is at least considered as a weak point of the coating creating a time-dependent defect under service conditions. The intended implementation of particles on surfaces and in coatings may create add-on features, topographic ones and functional ones, however, the facts mentioned hold true.

Examples of particle-initiated coating defects are demonstrated in dependence on the origin and the field of application. Strategies for deliberate attachment/embedding of particles on surfaces/in coatings are discussed regarding process compatibility and coating integrity. For industrial applications, both the validation of process compatibility of particle injection and the plasma resistance of particles under vacuum and plasma conditions have to be confirmed. Further points of interest are the homogeneity of particle distribution and the avoidance of particle agglomeration which is still a crucial point for dry dispersed particles. So far, technical applications are limited to PVD hybrid coatings, plasma dispersion coatings are still a challenge except for applications where homogeneity is not required as in case of product authentication.

2:30pm **B1-4-4 Gradient Coating for NIF Double Shell Targets**, ***Hongwei Xu***, General Atomics, USA

Double shell provides an alternative implosion platform for National ignition facilities (NIF). Double shell inner shell incorporates density graded layer to suppress Rayleigh-Taylor instability during implosion caused by inhomogeneity. We will report our efforts of fabricating density graded layers for double shell inner shell using magnetron sputtering and characterization of graded layers. The cold welding was observed for a lot of metals when deposited on a spherical mandrel, which seems correlated with material ductility. W-Be gradient layer was fabricated for double shell inner shell because of their large density difference and microstructure changes were revealed with varying composition. A W-Be amorphous phase was also discovered.

2:50pm **B1-4-5 Growth Morphology and Piezoelectric Properties of AlN Thin Films Deposited by Reactive DC Magnetron Sputtering**, ***Mathis Trant***, *M Fischer, K Thorwarth, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The piezoelectric properties of aluminum nitride (AlN) make it a good candidate for many applications in microelectronics, electroacoustic and optoelectronics. Magnetron sputtering is widely used to prepare AlN thin films so that they can easily be integrated into, for example, MEMS devices. However, controlling the microstructure and microchemistry, especially at low deposition temperatures, is crucial for a good performance. Ions impacting on the growing film can be used advantageously in magnetron sputtering to address these needs. We investigate the effect of low energy ion bombardment on the AlN thin film growth morphology and its correlation to piezoelectric properties.

An electromagnetic coil is used to generate a variable magnetic field that allows varying the ratio of ions and neutrals impacting on the growing film by more than one order of magnitude. With an increasing ion flux, the residual stress of AlN thin films changes from tensile to compressive. This evolution is compatible with a change in the growth morphology from open grain boundaries towards dense films. The piezoelectric properties of AlN thin films in the different growth regimes are discussed and possible applications for scanning probe microscopy are presented.

3:10pm **B1-4-6 Plasma Generation and Coating Composition from Ti-C, Ti-Al, and Ti-W Cathodes used in DC Vacuum Arc**, ***Igor Zhirkov***, Linköping University, Sweden; *P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J Rosen,* Linköping University, Sweden

Arc deposition from composite cathodes is a common method for synthesis of a wide range of functional coatings. A commonly used cathode element is Ti, which combined with different elements can deliver properties of coatings requiring in various applications. To understand the plasma generation from these cathodes is of importance for controlling the structural and compositional evolution of the coating of interest. In this work, we present the correlation between cathode, plasma and film composition for Ti-C, Ti-Al, and Ti-W composite cathodes of various stoichiometry used for DC vacuum arc depositions. The generated plasmas are characterized with respect to plasma chemistry and charge-state-resolved ion energy, and the intensity of the macroparticle flux is evaluated. The obtained results are compared to corresponding evaluation of elemental Ti, Al, C and W cathodes. We show that the plasma and film composition are in good agreement for the Ti-Al and the Ti-W cathodes, while for the Ti-C cathodes, there is a significant loss (~ 50%) of the light element. We also show, that the kinetic energies of ions from the Ti-Al and Ti-W cathodes are slightly different from those from the elemental cathodes, while the difference between the Ti-C and Ti cathode is more pronounced (Ti^{1+} average ion energy; ~ 90 eV and ~ 50 eV, respectively). The ion charge states are also found to be sensitive to cathode composition. The overall observations are explained by the cohesive energies and melting temperatures of the phases present at the cathode surface during arcing, while also considering transportation of ions of different mass within the generated plasmas. The systematic evaluation of general trends in properties of the generated material fluxes accompanying the addition of elements of different masses and chemical reactivity (C, Al, W) to a Ti cathode, contributes to an increased understanding of plasma

generation from a two element cathode, which in turn may provide guidance for selection of cathodes and experimental conditions for other material systems.

3:30pm **B1-4-7 Improved Adhesion Strength of the Gradient Zn-Mg Coating on TRIP Steel**, ***MyeonKyu Song***, *J La, H Kim, S Lee,* Korea Aerospace University, Republic of Korea

The high-strength steels (HSS) such as dual phase (DP) steel, transformation-induced plasticity (TRIP) steel, and twinning-induced plasticity (TWIP) steel have been used extensively in automotive industries to reduce the weight and to improve the safety of automobiles. To ensure the corrosion resistance of HSS, advanced coating material and process to replace conventional galvanizing coating and process are necessary. Zn-Mg coating is a strong candidate for the corrosion protective coating of HSS, and physical vapor deposition (PVD) process is a promising process for deposition of Zn-Mg coating on HSS. As reported in previous works, however, the Zn-Mg coating showed the insufficient adhesion strength compared to Zn coating due to the high brittleness of the Zn-Mg coating.

In this study, to improve the adhesion strength of the Zn-Mg coating, the Zn-Mg/Zn coatings were synthesized on TRIP steel substrate using evaporation deposition process, and the annealing heat treatment at 200°C in vacuum led to the gradient Mg content along the cross-section of Zn-Mg coatings. Microstructure, chemical composition depth profile, and adhesion strength of gradient Zn-Mg coatings were investigated by field emission scanning electron microscopy (FE-SEM), glow discharge optical emission spectroscopy (GDOES), and punch test, respectively. The gradient Zn-Mg coating was synthesized successfully by heat treatment of Zn-Mg/Zn coating. The gradient Zn-Mg coatings showed an improved adhesion of the coatings during adhesion test, and this indicated that the adhesion strength of Zn-Mg coating could be improved by the gradient Mg content. Detailed expereimental results will be presented.

Acknowledgement

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Hard Coatings and Vapor Deposition Technologies
Room California - Session B3

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa, Konrad Fadenberger, Robert Bosch GmbH

1:30pm **B3-1 Tribology of Diamondlike Carbons in Various Application Environments**, ***Gary Doll***, University of Akron, USA **INVITED**

Hydrogen free and hydrogen containing amorphous carbon materials are commonly referred to as diamondlike carbons. Due to the hardness and the ability to deposit coatings at temperatures compatible with most engineering materials, diamondlike carbons have become widely used as tribological coatings for addressing friction and wear in mechanical components. There are few if any intrinsic properties of these synthetic materials since their mechanical, structural, and compositional properties are strongly dependent upon the deposition process conditions. Furthermore, a high level of fundamental knowledge on how material properties relate to the tribological performances of diamondlike carbon coatings in various application environments has not been achieved. Application environments can be categorized by the type of tribological contact (rolling, sliding, mixed mode), lubrication condition, temperature, atmosphere, loading, and other items. This presentation shall discuss several examples where subtle differences in the deposition processes of diamondlike carbon coatings were responsible for transitioning unacceptable tribological performances in specific application environments to acceptable ones.

2:10pm **B3-3 Synthesis and Comparison of Highly Tetrahedral Amorphous Carbon by Arc-mixed HiPIMS and Arc-free HiPIMS Modes**, *H Hug,* ***Rajesh Ganesan***, *K Thorwarth,* EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *M Tucker, N Marks,* Curtin University, Australia; *M Stüber, S Ulrich,* Karlsruhe Institute of Technology (KIT), Germany; *D McKenzie, M Bilek,* The University of Sydney, Australia; *S Guimond, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Tetrahedral amorphous carbon films with high sp^3 content have been synthesized by high power impulse magnetron sputtering (HiPIMS) operated in an arc-free sputtering mode and in a mixed sputtering/arc mode. The properties of the films deposited in these both modes have been compared. In the mixed-mode, the presence of macroparticles in the deposited films were observed, though the amount and size of macroparticles are less than that of the ones in the films deposited by filtered cathodic arc vapour deposition. The short-lived cathode spots form in the magnetic racetrack and produce large numbers of carbon ions in the mixed-mode HiPIMS. In the arc-free HiPIMS, the macroparticle content in the films have been significantly reduced, however the deposition process has to be tuned for high degree of carbon ion production in order to compensate the loss of arc-facilitated carbon ion generation.

2:30pm **B3-4 Evaluation of Superhard ta-C Coatings for the Machining of Synthetic Materials**, ***Frank Kaulfuss***, Fraunhofer Institute for Material and Beam Technology (IWS), Germany; *D Hoesel,* Fraunhofer Institute for Machine Tools and Forming Technology (IWU), Germany; *V Weihnacht, A Leson,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

The superhard ta-C carbon coatings are outstandingly suited as friction-reducing protective coatings for lubricated and non-lubricated application conditions. They can be deposited on all kinds of tools and components with very good adhesion over a wide coating thickness range. The coating is applied with the Laser-Arc technology, particularly developed for ta-C coatings. In order to obtain a high ta-C coating quality with low defect densities, a plasma filtering technique is used. With hardness of up to 70 GPa, ta-C coatings nearly reach the hardness of nanocrystalline diamond coatings. This results in an unusually high resistance to abrasive wear, above all in the machining of challenging composite materials. At the same time, the carbon surface reduces adhesion of material and causes very low friction between the tool edge and the cutting chips. The combination of hardness and low friction provides ta-C coatings with a special advantage for the processing of composite materials.

2:50pm **B3-5 Selection of DLC Coatings for Application in Wrist-watch Mechanisms**, ***Steve Franklin***, Steve Franklin Consultancy, Netherlands

Traditionally, watch manufacturers use liquid lubricants, sometimes applied to up to 100 individual lubrication points, to achieve the required low and stable friction behaviour between components and sufficient lifetime performance. Despite the careful treatment of parts and use of specific (often customized) lubricants, after a few years, the effectiveness of the lubricants degrades through evaporation, (wear) particle contamination, etc., and as a consequences watches break down or do not perform as required. In addition, some lubrication points are very difficult to access.

The goal of this study was to evaluate whether, for certain watch components, solid-lubricating coatings can be used to replace liquid lubricants.

Eight different types of Diamond Like Carbon (DLC) coatings and a titanium-stabilized MoS_2 coating (all commercially available, different suppliers), which had been preselected from a wider range of possibilities, were evaluated in laboratory tribological tests. The tests were carried out in air under reciprocating sliding conditions using an uncoated steel ball (4.5 mm diameter) sliding on a coated steel plate at 2N load, 10 mm/s sliding speed and at two levels of humidity, 30% and 70% RH. These conditions were chosen in order to simulate the actual use conditions as closely as possible. All tests were carried out three times to gain insight into the repeatability of the results.

The friction force was recorded continuously as a function of sliding distance up to 720m, corresponding to a test duration of 20 hrs. The average wear rate of the coating was determined at the end of the test, based on surface profilometry. Scanning Electron Microscopy (SEM) was used to examine the coatings and associated steel balls after testing.

Clear differences were observed in the friction and wear behaviour of the different coatings but this did not correlate well with coating hardness.

Transfer layer formation from the coating onto the steel ball was observed in all cases and it is hypothesized that the formation of this layer is related to the running-in behaviour, i.e. the sliding distance needed in order to achieve a stable friction force. The characteristic appearance of the transfer layer, as observed using SEM, varied considerably between the coatings tested. Increasing the humidity from 30% to 70% had relatively small effects on the friction and wear behaviour.

Three coatings, Ti-MoS_2, a-C:H and Si-doped DLC, were found to exhibit the best performance in terms of tribological criteria specific to the application. These coatings were selected for further testing using actual watch components.

3:10pm **B3-6 The Role of HIPIMS and Discharges with a Positive Voltage Reversal on Coating Properties in Industrial Applications such as Hard Coatings and DLC***, **Ivan Fernandez**, A Wennberg, F Papa,* Nano4energy Sl, Spain*; G Eichenhofer,* HiP-V, Germany

HIPIMS (High Power Impulse Magnetron Sputtering) is a magnetron sputtering technology devoted to produce thin film coatings with enhanced properties. The technology offers advantages such as denser coatings, higher hardness values and smoother surfaces. This paper presents studies of the role the HIPIMS discharge, as well as an added positive voltage reversal pulse right after the negative HIPIMS pulse, have on coating properties and productivity in industrial applications.

The instant advantage is that the magnetron surface will be immediately discharged, which will reduce the tendency to arcing. However, there are several other effects observed during the performance of reactive sputtering, such as enhanced high energetic positive ion bombardment towards the substrate. Due to raise of the plasma potential, higher incorporation of reactive species into the depositing film, enhanced deposition rates and elastic hardness values, as well as crystallinity will be affected.

Measurements of the deposition rate, coating hardness and crystallinity have been performed for different metallic coatings (Ti, Al) as well as nitrides (TiN) and oxides (TiO2) deposited in reactive mode and more recently the effects that HIPIMS and positive voltage reversal plays on DLC coatings, in terms of adhesion as well as the functional layer.

3:30pm **B3-7 Towards New Horizon for DLC Coating Technology for Automotive Components***, **Tetsuya Takahashi,*** Kobe Steel, Ltd., Japan **INVITED**

Minimization of energy loss due to friction of sliding parts in automotive components becomes increasingly important to increase overall energy efficiency of vehicle. Surface engineering through application of DLC coating is effective to lead to enhancement of wear resistance and sliding property, and hence widely used in recent automotive industry. A product range of DLC coatings in automotive components includes, for instance, fuel injection system, valve lifter, rocker arm, piston ring, gears. Items for application have been expanding more and more in recent years. Depending on its application, suitable deposition techniques shall be selected and the process parameters including design of adhesion layer are optimized accordingly. In addition to conventional hydrogen containing DLC coatings, hydrogen free DLC having a high sp3/sp2 ratio, also referred to as ta-C (tetrahedral amorphous carbon), draws a great practical attention due to its unique features of high hardness >40 GPa and a possible superlubrication effect in a particular lubricating condition. Deposition of ta-C with the controlled property and ensured adhesion is of practically significance. A productivity of coating process, i.e., throughput, is equally important especially for an industrial mass production scale.

In this work we compare systematically various DLC coatings deposited by various industrial vacuum coating technologies of, for instance, unbalanced magnetron sputtering, cathodic arc, also referred to as arc ion plating, and plasma enhanced CVD process. These are presented with respect to the coating properties, applications, and productivity. Our particular interest is also placed on ta-C coatings deposited by cathodic arc. We have developed a round-bar type target specially designed for ta-C coatings for industrial scale. The target was a pure graphite with a typical diameter of 20 mm. A stable arc discharge was sustained at a target surface either in vacuum or in inert gas atmosphere. The coatings were characterized as a low hydrogen content of <1%, high sp3 fraction of >80%, and high hardness of up to 70 GPa. Also the coatings exhibited a relatively low surface roughness in as deposited condition, implying a less emission of macroparticles without any mechanical and/or magnetic filter. For better understanding of intrinsic mechanical properties of coatings, Micro Slurry Erosion (MSE) test was performed where erosion rate of material against blasting was quantitatively evaluated and served as a representative material parameter. The results of MSE of some selected coatings are discussed in relation to the material properties and respective coating parameters.

4:10pm **B3-9 DC/Pulsed Cathodic Arc Discharge for Deposition of ta-C Coatings***, **Xiubo Tian**, P Wan, H Liu, C Gong,* State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, China

The ta-C films have gained more interest in industrial applications due to excellent properties including good chemical stability, high hardness and wear resistance, good biocompatibility. Vacuum arc is an effective tool to deposit Ta-C films. To achieve better microstructure and surface properties, we have developed new power supply and system. The cathodic carbon arc may be driven by the specially designed power supply to produce required plasmas. With the assistance of external magnetic field, the plasmas near the samples may be optimized. In order to improve the adhesion between the film and substrate, the bottom layer and support layer were deposited. The processing parameters have to be optimized for the top ta-C coatings (thin and thick). A proper coil current (external magnetic field) was needed to achieve better adhesion of the films. A larger arc current was not favorable for better microstructure and surface properties. With the DC arc, the ta-C film possessed the nanohardness of 33.5GPa with a coil current of 0.1A. With the pulse work mode of arc power supply, a hardness of 45GPa was obtained with average current of 80A. The ta-C films have been utilized on surgical knives and cutting tools. The discharge of pulsed carbon arc, microstructure and surface properties of ta-c films will be presented.

4:30pm **B3-10 A General Engineering Applicable Superlubricity: Hydrogenated Amorphous Carbon Film Containing Nano Diamond Particles***, **Junyan Zhang**, Z Cao,* State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

Designing promising mechanical systems with ultra-low friction performance and establishing superlubricity regimes are desirable not only to greatly save energy but also to reduce hazardous waste emissions. However, very few macroscale superlubricity regimes for engineering applications have been reported. Here, we demonstrate that sustained superlubricity can be achieved at engineering scale when the contact pressure is higher than 2 GPa. Such engineering superlubricity originates from the in *situ* formation of curved graphene ribbons or onion carbon tribo-films at the sliding interface. Experimental data also demonstrate the wear of the amorphous carbon film containing some nano-diamond particles against Al_2O_3 ball is consistent with atomic attrition. A feasible two-stage mechanism is proposed to explain the friction and wear behaviors. This finding in amorphous carbon films will not only enrich the understanding of superlubricity behavior, but also be helpful to establish more superlubricity regime for more engineering applications.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Sunrise - Session C4

Energetic Materials and Microstructures for Nanomanufacturing

Moderators: Karsten Woll, Karlsruhe Institute of Technology (KIT), Ibrahim Emre Gunduz, Purdue University, USA

2:10pm **C4-3 High Surface Area Silicon Quantum Dots for Energetic Materials***, **Philip M. Guerieri**, N Piekiel, S Adams, M Ervin, C Morris,* U.S. Army Research Laboratory, USA

"On-chip" porous silicon has now been researched for a number of years as an energetic material to augment traditional electronics performance, or provide thrust or actuation in small-scale applications. On-chip porous silicon is ideal for these applications thanks to its high energy density and MEMS fabrication capabilities. However, when you consider that "on-chip" porous silicon is, by its nature, attached to a piece of silicon wafer, the effective energy density when including the mass of the energetic portion and the mass of the inert substrate base, is much lower than the energy density of the energetic material alone. In an attempt to obtain similar performance as on-chip porous silicon, we have fabricated silicon powders with a <5nm (quantum dots) primary particle size for use as a fuel in energetic materials. Initial results demonstrated that flame speed in open channels can eclipse 1 km/s and is comparable to on-chip porous silicon. This study further investigates flame speed characterization of these particles with various oxidizers, and explores mixture of this material with various binders for additive manufacturing applications. FTIR, EDS, TEM,

SEM, high speed imaging, bomb calorimetry have all been used to characterize the particles and/or energetic formulations.

2:30pm **C4-4 Investigating Transport Processes in Multilayer Films***, **David Adams**, M Abere, C Sobczak,* Sandia National Laboratories, USA

Metallic thin film multilayers that undergo rapid, self-propagating formation reactions are of interest for several applications including advanced joining technology. The development and optimization of new materials for these applications requires a detailed understanding of mass transport, chemical reactions, heat release and thermal transport processes. With this presentation, we focus on the thermal properties of produced multilayers. Thermoreflectance techniques have been used to characterize the thermal conductivity of different Pt/Al, Co/Al and Ni/Al multilayers. The bilayer thickness dependence of cross-plane thermal conductivity has been determined for various multilayers. The results are examined in terms of conductivity through the reactant layers and the role of interfaces. The interfacial structure and composition of each system has been mapped by cross section transmission electron microscopy. The measured properties are compared with estimates derived from analytical modeling of self-propagating formation reactions. The model developed by Mann et al. (J. Appl. Phys. 1997) to predict how measured flame speeds vary with multilayer design is used to estimate the thermal and mass transport characteristics. This analytical model accounts for reactant layer thicknesses, compositional profiles near interfaces, flame temperatures, measured heats of reaction, measured activation energies, and adiabatic temperatures.

This work was supported by a Sandia Laboratory Directed Research and Development (LDRD) program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

2:50pm **C4-5 Analytical Modelling of Propagation Velocity in Non-stoichiometric and Impact Compressed Nanolaminates***, **Michael Abere**, D Adams,* Sandia National Laboratories, USA

The ignition of sputter deposited bimetallic nanolaminate films results in rapid, self-propagating reactions. Analytical models of the measured propagation velocities have been typically performed using a framework developed by Mann et al. (J. Appl. Phys. 1997). This work seeks to expand upon this model to handle bimetal systems such as Al/Pt in which the lateral and transverse thermal conductivity are highly anisotropic. A thermal circuit model is thus employed that is shown to hold for both equimolar and non-stoichiometric compositions of Al/Pt. Furthermore, this work utilizes cross-sectional scanning transmission electron microscope energy-dispersive X-ray spectroscopy data to calculate the Fourier coefficients in the Mann et al. model from the physical composition profile in the intermixed region. The same framework can also be applied to determine the magnitude of plastic deformation necessary after laser flyer impact to produce observed propagation velocities as much as a factor of two above the steady state velocity of NiV/Al within the impacted zone.

3:10pm **C4-6 On the Fly Mixing and 3D Printing of Al/CuO Thermite for Controlling Reactivity***, **Alexandra Golobic**, M Durban,* Lawrence Livermore National Laboratory, USA*; E Duoss,* Lawrence Livermore National Laboratory, USA, US*; A Gash, K Sullivan,* Lawrence Livermore National Laboratory, USA

The ability to spatially control the behavior of reactive materials *within* a part is now a reality with advances in 3D printing. This vastly opens up the design space for rapidly deflagrating materials, such as pyrotechnics or thermites, to yield a precise property or dynamic performance. In order achieve this goal, a mixing print head was used to mix an aluminum and a copper oxide ink on the fly. The mixing and printing parameters were first investigated for a stoichiometric mix of fuel and oxidizer to determine at what point the material can be assumed well-mixed. The equivalence ratio was then changed, and the critical mixing parameters established. The reactivity was characterized by printing a strip of material, then initiating the thermite and measuring the propagation velocity with a high-speed camera. Once the velocity reached a plateau, we considered the system well mixed. 3D printing was then used to make parts where the local stoichiometry, which corresponds to performance, is spatially varied. Collective effects of having incorporated features with differing reactivates were investigated.

3:30pm **C4-7 Tin-based Composites Combined with Reduced Graphene Oxide via a Simple Chemical Treatment as Anode Material for Rechargeable Lithium Ion Batteries***, **Yi-Zhu Wu**,* National Cheng Kung University, Taiwan*; C Chang,* National University of Tainan, Taiwan*; S Brahma, J Huang,* National Cheng Kung University, Taiwan

We successfully synthesize the reduced graphene oxide/SnO_x (RGO/SnO_x) composites via a one-step chemical treatment with low cost and low toxicity at room temperature. In this procedure, we use the $Sn(BF_4)_2$ as the precursor and $NaBH_4$ as the reducing agent to deposit the tin onto reduced graphene oxide and utilize the composite as anode material for lithium ion batteries. With different concentration of reducing agent, we can control different reduction degree of composites. This study shows that reductant concentration significantly affect the density and agglomeration of nanoparticles over the GO sheets. The average size of the nanoparticles in the composites is approximately 5 nm. The observed electrochemical performance of RGO/SnO_x composite shows improved capacity (937.9 mAh/g for first cycle discharge) and good cycling ability (824.0mAh/g with 88% retention after 50 cycles.).

3:50pm **C4-8 Additive Manufacturing of a Composite Solid Propellant with High Solids Loadings***, **Monique McClain**, I Gunduz, S Son,* Purdue University, USA

Solid propellant performance is strongly dependent on the manufacturing process. The traditional method of casting propellant limits the ability to locally vary geometry and reactivity throughout the grain and could lead to the creation of defects. Additive manufacturing (AM) has been effectively demonstrated as an alternative manufacturing process for complex hybrid propellant grains. However, methods such as jet printing, stereolithography, and fuse deposition modeling are limited by the materials that can be printed. Conventional printable materials are less reactive than baseline fuels, such as hydroxyl-terminated polybutadiene (HTPB), and high solids loadings have not been achieved, rendering the printing of high performing solid propellants unobtainable. In this work, an AM method developed in our lab was used to print ammonium perchlorate (AP) composite propellant strands at 85% solids loading. The viscosities of AP propellant mixtures were characterized to quantify printing parameters and the integrity of the samples were investigated with X-ray tomography scans. The printed AP propellant strands were burned at high pressure to determine the burning rate and were compared to cast samples with the same formulation. It was demonstrated that AM could be used to manufacture solid propellants at a solids loading comparable to current industry standards.

4:10pm **C4-9 Manufacturing and Characterization of Nanocomposite WC-based Powders***, **Abdulsalam Alhazza**, L Al-Hajji, S El-Eskandarani, A Al-Rowayyeh,* Kuwait Institute for Scientific Research, Kuwait

In the present work, the structural, mechanical, chemical, and morphological characterizations of the synthesized powders and their consolidated buttons was investigated. The synthesized powders are mechanically-induced solid state mixing or synthesizing of nanocomposite WC-Co-metal oxide (Al_2O_3, MgO, SiO_2, and ZrO_2) s uperhard material powders.

During the consolidation and manufacturing process, the nanocrystalline characteristic of the nanocomposite should be noticed and maintained to take advantage of the unique properties of the synthesized nanocomposites.

The consolidation of the nanocomposite powders will lead to the manufacturing full dense buttons with a very high hardness, fracture toughness, and wear resistance by synthesizing a nanosized powders and advent of fast sintering techniques.

4:30pm **C4-10 Ternary Reactive Ru/Al/X Multilayers - The Effect of Stacking Sequence on Ignition, Propagation and Microstructure Evolution***, **Christoph Pauly**,* Saarland University, Germany*; K Woll,* Karlsruhe Institute of Technology (KIT), Germany*; I Gallino,* Saarland University, Germany*; M Stüber,* Karlsruhe Institute of Technology (KIT), Germany*; F Mücklch,* Saarland University, Germany **INVITED**

To date, self-propagating reactions in PVD multilayers have been extensively studied regarding their underlying mechanisms and applications. Adjusting the reaction behavior to meet the demands of an application requires a fundamental understanding of the mechanisms and transformations on the micro- and nanoscale. Interfacial reactions are found to play a key role in determining reaction parameters such as front propagation, heat release over time and ignition behavior. The majority of studies use binary samples consisting of elemental or alloyed layers where

the bilayer thickness is the main design parameter while the material combination at the interface remains unchanged. By introducing a third kind of layers, the stacking sequence becomes an additional design parameter allowing us to define type and density of the interfaces.

In this study, we designed ternary reactive multilayers based on Ru/Al by partially substituting either Ru or Al for selected elements which allows us to retain the B2-structure of the product phase. The system Ru/Al shows a heat of formation and propagation velocity comparable to that of Ni/Al, however, its temperature of reaction and ignition are higher. We present how stacking sequence and ternary additions affect the properties of the self-propagating reaction. The role of interfacial solid state reactions on ignition is discussed and how this can be used to modify ignition temperatures. Strong effects of composition and stacking sequence on net propagation velocity are observed and discussed with the help of microstructural analysis of quenched reaction fronts.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Royal Palm 4-6 - Session E3

Tribology of Coatings for Automotive and Aerospace Applications

Moderators: Sebastien Guimond, Oerlikon Balzers, Oerlikon Surface Solutions AG, Nicolas Argibay, Sandia National Laboratories, Christian Greiner, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM)

2:10pm **E3-3 Cladding Tribaloy T400 on Steel Substrates using a High Power Nd:YAG Laser***, **Wei Ya**, B Pathiraj, D Matthews,* University of Twente, Netherlands*; M Bright,* Tata Steel, Netherlands*; S Melzer,* Tata Steel Research & Development, Netherlands

Tribaloy T-400 is a Cobalt and Molybdenum based alloy, which has been developed for the resistance to high temperature wear, galling and corrosion. Its hardness is provided by a hard inter-metallic Laves phase, dispersed in a tough matrix of eutectic or solid solution. However cracking during processing limits its application such as hard facing using laser surface cladding/coating, especially when a Nd:YAG laser is applied as is commonly available in industry. The primary aim of this work is accomplished by laser cladding crack-free Tribaloy T-400 layers using a high power Nd:YAG laser. The optimal process conditions of cladding crack free Tribaloy T-400 coating on different steel substrates (st355J2 steel plates and AISI 316 steel bar) were obtained. The dilution effects on the hardness of cladded Tribaloy T-400 coating are investigated. Microstructures of the clad layer produced with optimal process parameters with and without preheating substrate were analysed by using Scanning Electron Microscope (SEM). The chemical compositions of different phases in the clad were analysed by using Energy Dispersive X-ray Spectroscopy (EDX). The resulting Austenite, Ferrite and Laves phases present in the clad were analysed by using X-ray Diffraction (XRD). The residual stress in the clads were evaluated by using hole drilling and XRD techniques. The correlation between the process conditions and resulting microstructures are discussed to provide guidelines for further up-scaling of laser clad crack-free Tribaloy T-400.

2:30pm **E3-4 Tribological Properties of HVOF-Sprayed WCCoCr Coatings for Applying to Sliding Rings of Mechanical Seals***, **Aleksander Iwaniak**,* Silesian University of Technology, Poland*; G Wieclaw,* Certech Sp. z o.o., Poland*; L Norymberczyk,* ANGA Sp. z o.o., Poland

The critical elements of mechanical seals are sliding rings. In almost all applications constructions, at least one of these rings is made of tungsten carbide or silicon carbide, usually in the form of a solid ceramic. The paper presents the results of research on the development of a new generation of sliding rings with a metallic core and a working face covered with coating using HVOF thermal spray technology with the use of WCCoCr ultra fine powder. The metallic core of the ring provides very good mechanical properties, including impact resistance, while the heat-sprayed carbide coating allows for wear resistance comparable to that made of solid ceramic. The tests were conducted with the "ring on ring" method for time 400 hours. The specimens "ring" were made of various materials: carbon-graphite material and a tungsten carbide. The condition of the top layer of the specimens was determined after the friction tests (3D profilometry, SEM). Laboratory tests of the new generation of slip rings and preliminary tests in industrial conditions have shown that the developed solution is characterized by high durability and has high application potential.

Financial support by The National Centre for Research and Development (NCBiR) in Warsaw, Poland - Project No INNOTECHK2/IN2/2/181798/NCBR/13 is gratefully acknowledge.

2:50pm **E3-5 The Effects of Relative Humidity on Fretting Corrosion Behaviors of Silver-plated Electrical Contacts***, **Florent Pompanon**, S Fouvry,* LTDS, CNRS UMR 5513, Ecole Centrale de Lyon, Ecully, France*; O Alquier,* PSA, Vélizy – Villacoublay, France

During the last decades, the use of connectors in electrical devices for automotive has increased significantly. This raise in the number of electrical and electronic devices on board cars has led to a growing number of breakdowns. Indeed, this connectors need to keep a low and stable electrical contact resistance (ECR) otherwise micro-interruptions of signal may occur. Due to their work environment (car engine) they are subjected to vibrations inducing fretting in the contact.

Fretting occurs at the interface of materials in contact and refers to small oscillatory motion between the two surfaces. This phenomenon induces wear and the formation of oxide debris layer (third body) in the contact area increasing the electrical contact resistance.

The damaging effect on electrical contacts has been widely studied, a lot of studies have been conducted on non-noble materials (such as tin-plated contact) and noble materials (gold-plated and silver-plated contact) to determine the mechanisms of electrical contact damage and predict the electrical contact resistance endurance (ECR endurance)[1], [2].

The aim of this study is to consider the effect of the relative humidity rate on fretting behavior of silver-plated electrical contact. A climatic generator is used to work in a range of relative humidity (RH) from 10 % to 90 %.

The results show that the relative humidity rate impact the electrical contact resistance endurance. The number of cycles to reach the electrical failure (Nc) of the contact increase substantially, and especially when the relative humidity is above 50 %. Two behaviors can be highlighted, a threshold RH_{th}=50% as been established marking the transition between the two regimes :

- When RH < 50% :

- A rather constant evolution is observed, the ECR endurance remains stable.

- The third body layer is formed of pulverulent oxides displaying a low current conductivity . They are easilly ejected from the interface. This implies a high wear rate and a low ECR endurance.

- When RH > 50% :

- The ECR endurance strongly increases : the larger the relative humidity the large the ECR endurance (linear increase).

- The formation of oxide – hydrate is activated. The third body is more compacted and adherente to the interface (uneasy third body ejection), the wear rate is decreased. Moreover, hydrates displays a lower coefficient of friction and high current conductivity extending the ECR endurance.

These hypotheses are discussed regarding the mechanical, chemical and electrical characterization of the debris layer.

References:

1. S.Fouvry, P. Jedrzejczyk, P. Chalandon, Wear 271, 2011, 1524-1534

2. J.Laporte, O. Perinnet, S. Fouvry, Wear 330-331, 2015, 170-181

3:10pm **E3-6 Evaluation of Solid Particle Erosion Resistant Coatings for Gas Turbine Engine Applications***, **Qi Yang**,* National Research Council of Canada, Canada

Aircrafts, when operating in a sandy environment , can experience severe erosion damage to gas turbine engine components, such as compressor blades, vanes and impellor blisks/wheels, due to sand particle ingestion. As erosion progresses, a significant amount of material removal not only leads to significant aerodynamic losses, but results in the structural weakening of blades as well. Applying erosion resistant coatings on airfoil surface has been proven effective in extending the serviceable life of engine components. In the course of coating development, the adequate erosion testing techniques have to be applied in order to identify potential candidates economically and under representing conditions. From this perspective, various erosion testing techniques are first reviewed for their pros and cons. Then, proper testing protocols and evaluation methods of

erosion resistance are elaborated based on testing results of TiN coating and another proprietary erosion resistant coating using gas jet apparatus. Taking the consideration of aerodynamic factors to erosion performance, wind tunnel sand erosion testing is also performed on the coatings. The results of gas jet and wind tunnel erosion testing are compared and discussed. Furthermore, several technical concerns related to erosion resistant coatings are deliberated.

3:30pm **E3-7 Influence of Sliding Induced Defects on the Frictional Properties of Molybdenum Disulfide (MoS_2) and Graphene**, ***Zaixiu Yang***, *S Bhowmick, G Sun,* University of Windsor, Canada*; F Sen,* Argonne National Laboratory, USA*; A Alpas,* University of Windsor, Canada

2D-layered structures MoS_2 and graphene show low coefficient of friction (COF) during initial sliding contact (running-in period), but their long-term tribological performance depend on the moisture in the testing environment. Sliding induced defects contribute differently to frictional properties of MoS_2 and graphene under humid environments. Micro-Raman spectroscopy indicated that sliding induced structural defects in graphene, but graphene showed a low friction under humidity while a higher friction in dry N_2. Using van der Waals interaction incorporated Density Functional Theory (DFT) calculations, it was found that dissociative adsorption of water molecules at a mono-vacancy site of the graphene led to the increase in the graphene layer spacing and reduced interlayer adhesion energy, and thus contributed to the reduced COF. Meanwhile, the MoS_2 tested under humid environment showed a high friction whereas a low friction in dry N_2 was observed. Results of DFT calculations suggest the possibility of formation of Mo-O-Mo by the dissociated water molecules at triple vacancy site, resulting in the increase in COF as will be discussed in the conference.

3:50pm **E3-8 Analysis of Tribo-mechanical Behavior of a Low Temperature Plasma Nitrided Austenitic 316L Stainless Steel**, *J Oseguera,* ITESM-CEM, Mexico*; R Meza,* TEROMOINNOVA, Finland*;* ***Fernando Santiago***, ITESM-CEM, Mexico

Microstructure of AISI 316L nitrided steel, treated by a weak ionized plasma process, using N2,H2 and Ar gas mixtures, was analyzed. Active nitrogen in the plasma that correlates to the diffusion of nitrogen in the steel is identified by optical emission spectroscopy. The kinetic evolution of expanded austenite was identified by treatments developed at low temperatures bellow the eutectoid transformation temperature. Phases obtained on surface were identified by XRD, from cross sectional views obtained by optical microscopy the thickness of expanded austenite was measured. Vickers hardness profile from surface was measured. Analyses of tribo-mechanical behavior of steel in a pin-on-disk system, for nitrided and non-nitrided steels samples, were used to contrast friction coefficients. The response of the tribo-mechanical system was interpreted through the structural characterization of the steel.

4:10pm **E3-9 Tribological Systems Solutions for Gas Turbine Engines**, ***Pantcho Stoyanov***, *A Wusatowska-Sarnek, T Kasprow,* Pratt & Whitney, USA **INVITED**

The advancement of durable gas turbine engine components depends heavily on the development of high-performance materials, which can withstand extreme environmental and contact conditions (e.g. large temperature ranges, high contact pressures, and continuous impingement of abrasive particles, all of which degrade the physical properties). In particular, due to the large number of complex contacting and moving mechanical assemblies in the engine, the lifetime of certain structures is limited by the tribological performance of the employed materials and coatings. This talk will provide an overview of tribological solutions employed in several sections of gas turbine engines. After a general review of aircraft engine tribology, the talk will focus on coatings used for clearance control (i.e. abradable air seals) as well as tribological materials used to minimize fretting type of wear. More specifically, a study will be presented on the influence of self-lubricating hexagonal boron nitride (hBN) on the erosion and abradability of Ni-based abradable coatings. Subsequently, a series of studies on the friction and wear behavior of Ni-based and Co-based superalloys at elevated temperatures will be presented. Emphasis will be placed on the correlation between the third body formation process (e.g. oxide layer formation, transferfilms) and the tribological behavior of the superalloys. This talk will conclude with a discussion of the needs for tribological coating solutions in gas turbine engines.

4:50pm **E3-11 The Friction and Wear Performance of DLC Coatings Deposited on Plasma Nitrided AISI 4140 Steel by Magnetron Sputtering under Air and Vacuum Conditions**, ***Halim Kovacı***, Atatürk University, Turkey*; O Baran,* Erzincan University, Turkey*; A Yetim,* Erzurum Teknik University, Turkey*; Y Bozkurt, L Kara,* Erzincan University, Turkey*; A Çelik,* Atatürk University, Turkey

Diamond-like-carbon (DLC) coatings with high hardness and low friction coefficient exhibit excellent tribological performance under air and vacuum conditions. However, adhesion and cold welding problems in vacuum conditions lead to increase friction coefficient values. These negative effects can be eliminated by different methods such as forming interlayers between coating and substrate or ion treatment of the substrate. In this work, DLC coatings were deposited on untreated and plasma nitrided (at 400 °C, 500 °C and 600 °C for 1h and 4h) AISI 4140 steel substrates by magnetron sputtering technique. The effects of plasma nitriding treatment on the friction and wear properties of DLC coatings under air and vacuum conditions were investigated. The structural and mechanical properties of DLC films were examined by XRD, SEM, and microhardness tester, respectively. The friction and wear properties were determined by a tribotester under air and vacuum conditions. The microhardness of samples increased after surface treatments and the highest value was obtained from the sample plasma nitrided at 600 °C for 4h plus DLC coated sample. The wear resistance of samples increased with increasing plasma nitriding time and temperature. Also, it was observed that the samples tested under vacuum condition showed better wear resistance than the samples tested under ambient air. Furthermore, increasing plasma nitriding time and temperature improved the wear performance of the material regardless of the test environment.

New Horizons in Coatings and Thin Films
Room San Diego - Session F4-2

Functional Oxide and Oxynitride Coatings

Moderators: Jörg Patscheider, Evatec AG, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, Marcus Hans, RWTH Aachen University

1:50pm **F4-2-2 On the Thermal Stability of Cathodic Arc Evaporated ($Al_{1-x}Cr_x)_2O_3$ Thin Films**, ***Valentin Dalbauer***, CDL-AOS at TU Wien, Austria*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C Koller,* CDL-AOS at TU Wien, Austria*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

The thermo-mechanically excellently performing α-alumina (corundum-type) is a perfect candidate to protect tool or component surfaces suffering from mechanical loads in hazardous atmospheres. Thus α-alumina protective coatings significantly extend the tool-lifetime especially in oxidising environment and at high temperatures. However, a major concern is the formation of amorphous phase fractions and/or metastable Al_2O_3 polymorphs during low-temperature physical vapour deposition, which can effectively be counteracted by alloying with Cr, where the phase composition of $(Al_{1-x}Cr_x)_2O_3$ coatings strongly depends on the Cr content.

With respect to industrial application, the knowledge about structure-property-relationships of $(Al_{1-x}Cr_x)_2O_3$ as a result of thermal exposure is of utmost importance. We therefore study the structural evolution of arc evaporated $(Al_{1-x}Cr_x)_2O_3$ coatings, which have been prepared by $Al_{0.75}Cr_{0.25}$, $Al_{0.70}Cr_{0.30}$, $Al_{0.50}Cr_{0.50}$, or $Al_{0.25}Cr_{0.75}$ cathodes.

The Cr-rich $(Al_{0.49}Cr_{0.51})_2O_3$ and $(Al_{0.23}Cr_{0.77})_2O_3$ coatings crystallise in a single-phase corundum-type structure (α-$(Al,Cr)_2O_3$) with pronounced columnar and facetted growth. Contrary, the Al-rich $(Al_{0.72}Cr_{0.28})_2O_3$ and $(Al_{0.69}Cr_{0.31})_2O_3$ coatings are multi-phased with a large metastable cubic-structured phase fraction and α-$(Al,Cr)_2O_3$.

Upon annealing to 800 and 950 °C, the metastable phases transform into a γ-type phase—with only minor indications for an intermediate θ-structure— and further to an α-type solid solution for temperatures above ~1080 °C. This structure stays stable up to the highest temperature tested, 1500 °C. The accompanied formation of bcc Cr phases indicates the decomposition of metallic droplets with—depending on the annealing conditions—subsequent oxidation of Al. Annealing within the spinodal-regime up to 6 h did not result in any phase separation towards α-Al_2O_3 and α-Cr_2O_3.

Thermo-mechanical properties of $(Al_{1-x}Cr_x)_2O_3$ show a stronger dependence on the microstructure than on the crystal structure of the as-deposited

coatings. Although exhibiting a multi-phase constitution, Al-rich coatings demonstrate higher hardness than the single-phased α-$(Al_{0.23}Cr_{0.77})_2O_3$ coating, which consists of tapered crystallites. Highest H and E values of ~22 Gpa and ~300 Gpa are obtained for $(Al_{0.49}Cr_{0.51})_2O_3$, which combines a dense microstructure with a dominant α-character. Upon vacuum annealing—and therewith associated structural transformation and densification—H and E of the Al- and Cr-rich coating compositions converge with peak values of H ~27 Gpa and E ~450 Gpa at 1050 °C.

2:10pm **F4-2-3 Phase Evolution of RF Magnetron Sputtered Cr-rich $(Cr,Zr)_2O_3$ Coatings Studied by *In-Situ* Synchrotron Experiments during Annealing in Air or Vacuum Conditions***, Ludvig Landälv,*** Linköping Univ., IFM, Thin Film Physics Div. and Sandvik Coromant R&D, Sweden*; J Lu,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; D Ostach,* Zentrum für Material- und Küstenforschung GmbH, Germany*; M Ahlgren, E Göthelid,* Sandvik Coromant R&D, Sweden*; B Alling,* Linköping Univ., IFM, Theoretical Physics division and Zentrum für Material- und Küstenforschung GmbH, Sweden*; L Hultman,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; M Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; J Birch, P Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited binary oxide alloy hard coatings draw increasing attention, often focusing on the Cr-stabilized corundum α-$(Al,Cr)_2O_3$ phase by means of a template growth or alloying; Cr forms escolaite Cr_2O_3 that is isostructural with corundum [1,2]. A new and interesting oxide is obtained by exchanging Al with Zr in the Cr-Zr-O system. Spitz *et al.* explored (Zr,Cr)O phases with respect to the Cr/Zr metal ratio in coatings prepared by reactive RF-magnetron sputtering, e.g., a solid solution α-$(Cr,Zr)_2O_3$ corundum structure at low Zr-content (< ~12 at %), a cubic-$(Zr,Cr)O_2$ based solid solutions at ~18 at % Zr, and a monoclinic/tetragonal solid solution $(Zr,Cr)O_2$ for higher Zr-content [3]. The as-deposited corundum structured coating from this study was the focus of an isothermal annealing study performed in vacuum with posterior HR TEM-characterization. It showed decomposition of a α-$Cr_{0.28}Zr_{0.10}O_{0.61}$ coating into tetragonal ZrO_2 and bcc chromium upon loss of oxygen [5]. In another study on the Cr-rich part of the (Cr,Zr)O-system, as-deposited amorphous coatings were investigated by means of *in-situ* synchrotron X-ray diffraction during annealing in vacuum. This showed the increase in crystallization onset temperature for both α-$(Cr,Zr)_2O_3$ and tetragonal phases $(Zr,Cr)O_2$ with increasing Zr content (3-15 at %) in the as deposited coatings [4]. The phase-stability of such coatings are, however, expected to depend also on ambient atmosphere during service.

In order to study the effect of annealing atmosphere on the phase evolution of α-$(Cr,Zr)_2O_3$ coatings, we use *in-situ* synchrotron radiation experiments performed in air and in vacuum. We find that the phase evolution in α-$(Cr,Zr)_2O_3$ coating samples differs significantly depending on annealing atmosphere conditions: with retained α-Cr_2O_3 after air annealing with accompanying formation of tetragonal ZrO_2, and decomposition of the α-Cr_2O_3 structure if annealed in vacuum with formation of tetragonal ZrO_2 and possible monoclinic ZrO_2 after cooling to room temperature. The difference in phase evolution results in significant nano hardness difference ~22 and 8 GPa respectively and a largely changed microstructure observed with posterior HR-TEM characterization.

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2:30pm **F4-2-4 Thick HS-PVD γ-Al_2O_3 Coatings for Challenging Cutting and Die Casting Applications***, K Bobzin, T Brögelmann, C Kalscheuer,* ***Martin Welters,*** Surface Engineering Institute - RWTH Aachen University, Germany

In the last decades crystalline physical vapor deposition (PVD) Al_2O_3 coatings offered their great potential due to outstanding properties such as high hot hardness, high oxidation resistance and high wear resistance, especially concerning cutting and die casting applications. However, the properties of alumina strongly depend on the formed crystallographic phase. Thereby, the thermodynamically stable α-Al_2O_3 phase is the technical most interesting, exhibiting superior mechanical properties. The deposition of α-Al_2O_3 by chemical vapor deposition (CVD) is well-established, but requires high process temperatures. Thus, the deposition of α-Al_2O_3 on temperature sensitive-materials is not possible. Another promising candidate concerning cutting and die casting applications is γ-Al_2O_3. Depending on the initial conditions, the formation of the γ-Al_2O_3 phase starts at T ≥ 450 °C, allowing lower deposition temperatures. Regarding the wear protection of turning tools, a higher coating thickness (s ≥ 10 µm) and thus a larger wear volume are beneficial. However, this requirement is hard to fulfill by typical PVD processes. A possibility to deposit thick PVD alumina coatings is the High-Speed PVD (HS-PVD) technology. In the present work thick, s ≥ 20 µm, γ-Al_2O_3 films are deposited on cemented carbides at a substrate temperature range between T = 500 °C and T = 850 °C, by means of HS-PVD. A thick, metallic (Cr,Al) bond coat was employed to improve the adhesion of γ-Al_2O_3. In order to analyze the influence of the bond coat regarding the adhesion of the coatings, scratch tests were conducted, as it is important regarding cutting and die casting operations. For determining the coating morphology and thickness, scanning electron microscopy (SEM) was used. Phase analysis was carried out by X-ray diffraction spectroscopy (XRD). The mechanical properties universal hardness (HU) and indentation modulus (E_{IT}) were determined by means of nanoindentation. Furthermore, thermal stability of the coatings was investigated via thermal exposure tests. Regarding the use in high temperature applications, especially the formation of γ-Al_2O_3 at substrate temperatures of T ≈ 850 °C indicates that the use of the coatings is possible at equal high temperatures without phase transformation. The HS-PVD γ-Al_2O_3 coatings were compared to thin γ-Al_2O_3 films deposited by magnetron sputtering (MS), as they are state-of-the-art in industry. The comparison emphasizes the advantages of the coatings deposited by means of HS-PVD.

2:50pm **F4-2-5 HiPIMS Deposition of Ta-O-N Coatings for Water Splitting Application***, Jiří Čapek, Š Batková, J Houska, S Haviar,* University of West Bohemia, Czech Republic*; T Duchoň,* Charles University, Czech Republic

As reported in [1], Ta-O-N material can provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). This could bring a great possibility to convert the solar light into a useful chemical energy. However, it is still a big challenge to prepare Ta-O-N electrodes exhibiting efficient water splitting performance.

In this work we first demonstrate that high-power impulse magnetron sputtering is a suitable technique for low-temperature (less than 250 °C) deposition of Ta-O-N coatings with a controllable oxygen to nitrogen (O/N) ratio and thus their properties. The band gap width of the coatings can be tuned for an effective visible light absorption at preserved proper alignment of the band gap with respect to the water splitting reactions. Subsequently, we focus on an optimization of the structure of the coatings with respect to the transport of the generated electron-hole pairs. For this purpose, the Ta-O-N coatings were either prepared at an elevated substrate temperature (up to 850 °C - limit of the substrate heater) or annealed in a vacuum furnace (up to 900 °C) after the deposition. The carried out X-ray diffraction analyses indicate that the coatings prepared at the elevated temperatures consist of a mixture of oxides and/or nitrides, while the annealed coatings (with a proper O/N ratio) are characterized by a single TaON phase. Moreover, the resulting TaON phase can be highly textured when a proper seeding layer (e.g., Pt) is used. This structure is very promising for the water splitting application due to a possibly reduced recombination rate of photogenerated electrons and holes.

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3:10pm **F4-2-6 Evolution of Microstructure and Mechanical Properties of Graded TiAlON Thin Films Investigated by Cross-sectional Characterization Techniques***, Nina Schalk,* M Tkadletz, V Terziyska, Montanuniversität Leoben, Austria*; M Deluca,* Materials Center Leoben Forschung GmbH, Austria*; J Keckes, C Mitterer,* Montanuniversität Leoben, Austria

In the last years, oxynitrides have emerged as a new class of materials due to their tunable properties. Within the present work, a graded TiAl(O)N film was grown by magnetron sputter deposition, using TiAl targets with an Ti/Al atomic ratio of 40/60, constant nitrogen and stepwise increasing oxygen partial pressures over the film thickness. The microstructural evolution of the film was investigated by transmission electron microscopy and synchrotron X-ray nanodiffraction. The first layer, grown without the addition of oxygen, showed a dual phase structure consisting of a prevalent wurtzite phase fraction and a subordinate face centered cubic (fcc) phase fraction. The addition of small amounts of oxygen resulted in the stabilization of the fcc phase and the wurtzite phase vanished. With increasing film thickness and thus, increasing oxygen content, the texture of the fcc phase changed from dominating (111) to (100). Further, with increasing oxygen content increasing amounts of an additional amorphous

phase fraction were observed. In the first layers, tensile residual stresses in the range of 1 – 2 GPa were determined, which turn compressive towards the film surface. Cross-sectional nanonindentation revealed increasing hardness and elastic modulus with increasing oxygen content in the first layers, however, towards the film surface the hardness decreases, which can be related to the increasing amounts of an amorphous phase fraction.

3:30pm **F4-2-7 Hard Transition Metal Oxynitride Thin Films: From Synthesis to Applications**, ***Filipe Vaz***, *J Borges,* Minho University, Portugal **INVITED**

The aim of this talk is to focus on the design, synthesis, properties and applications of different types of oxynitride protective and functional thin films and coatings. Multifunctional stable and metastable oxynitride coatings are expected to fill a gap between nitride and oxide based coatings. Therefore, they are considered to be of unique interest in fundamental research. Moreover, due to their combination of high oxidation resistance, chemical inertness, good mechanical properties at elevated temperatures and friction behavior, they have a wide application field. In fact, oxynitride thin films are rapidly emerging from the research laboratory, and there are actually several examples of successful industrial applications. Protective applications, decorative coatings for high-quality consumer products, gas barriers, optoelectronics, microelectronics, solar cells, are among the most important areas in which oxynitrides are revealing promising results.

Nevertheless, there is still a huge need for a comprehensive discussion of their fundamental properties and in-service response as a function of the different designs and basic characteristics.

This talk is focused on the development and understanding of the materials themselves and on relationships and knowledge-based correlations between process parameters, synthesis and growth, micro structure evolution and properties, providing a forum to discuss current and future applications of this class of thin films and coatings.

Surface Engineering - Applied Research and Industrial Applications

Room Sunset - Session G5

Hybrid Coatings and Hybrid System Processes

Moderators: Hana Barankova, Uppsala University, Sweden, Sang-Yul Lee, Korea Aerospace University

1:50pm **G5-2 Propagation of Electric Field Waves in a DC Magnetron Plasma**, ***Rachel Broughton***, *S Kirkpatrick,* Rose-Hulman Institute of Technolgy, USA

Arcing is an issue that extends throughout the field of plasmas that can cause expensive damage to industrial equipment. In magnetron plasmas, arcing is usually avoided by employing a preventative method, such as pulsed DC sputtering. This work superimposes a small AC signal onto the high voltage supplied to the DC cathode to observe the effects within a magnetron plasma. A Langmuir probe was inserted into an argon DC plasma formed by a two-inch magnetron gun. The voltage from the probe was read on an oscilloscope not only in the time domain to obtain the appropriate IV-curve, but also in the frequency domain to observe if the driven frequencies were able to propagate through the plasma. An 8 mm by 8 mm square probe was employed both parallel and perpendicular to the surface of the cathode. Variations depending on orientation were noted in the measured plasma temperature and density where typical density values of the observed plasmas were on the order of 10^{10} cm^{-3}. The applied AC signal was detected in the time domain measurements of the Langmuir probes only from probes oriented perpendicular to the surface of the cathode.

2:10pm **G5-3 From Surface to Coating - Tools for Surface Engineering**, ***Frank Papa***, Gencoa Ltd, USA, Spain*; V Bellido-Gonzalez,* Gencoa Ltd, UK*; I Fernandez Martinez,* Nano4energy SLNE, Spain*; F Meyer, H Li, D Monaghan, T Sgrilli,* Gencoa Ltd, UK **INVITED**

Surface engineering has been an area of interest for many decades. Initially, hybrid processes such as nitriding, anodizing and plating were applied to improve the surface properties of engineering materials such as steels and aluminum. Today, we are faced with many surface engineering challenges as the number of advanced materials increases and the "functionality" requirements of surfaces become more demanding. From metals to plastics to ceramics, the types of surface treatments and coatings are varied. For surface preparation, the energy and type of ion needed (etching/functionalization/cleaning) will vary with the application. Likewise, the properties of coatings and surface coating interfaces depend strongly on the type of impinging particles and their energies and reactivity. Several tools are available for "hybrid" processes where the energy and type of ions reaching a surface need to be controlled. Ion sources are typically used for pre-treatment of substrates, but sputtering magnetrons themselves can also be turned into sources of ions. Conversely, both can be used for depositing coatings. Advanced tools for surface engineering in today's world involve an understanding of how sources can be driven (power supplies) and how combinations of technologies, both active (anode layer ion sources) and passive (anodes), allow us to change interfaces and coating properties. In this talk, we'll explore such applications in the areas of glass coating, hard coatings and on polymers. We'll discuss the combined used of secondary sources to boost and to decrease plasma density as well as the effects of adding positive pulses to traditional HIPIMS processes. With such positive pulses, the ion flux and energy can be controlled to the growing film after each negative pulse (deposition). The successful implementation of hybrid processes for coatings such as AlCrN, ITO, DLC and functionalized Ag will be presented.

2:50pm **G5-5 Nb – Doped TiO_2 Deposited by Hybrid HIPIMS – CVD Process**, ***Justyna Kulczyk-Malecka***, Manchester Metropolitan University, UK*; D Donaghy,* University of Liverpool, UK*; B Delfour-Peyrethon,* Manchester Metropolitan University, UK*; P Chalker, J Bradley,* University of Liverpool, UK*; P Kelly,* Manchester Metropolitan University, UK

Novel methods for the deposition of thin functional coatings, such as hybrid CVD – PVD technologies have the potential to become an important means of overcoming the limitations of current processes, such as low deposition rates, associated with some sputtering processes or limited material/precursor choices, associated with CVD processes.

In this work we are combining PECVD with a magnetron sputtering source driven by a HIPIMS power supply to assist the deposition of functional oxides for TCO applications. Although, other PVD – CVD hybrid systems have been developed, each process requires its own power supply. However, combining the processes in this way means that only one power supply is required. Thus, niobium – doped titania coatings were deposited on glass and Si wafer substrates by this hybrid HIPIMS – CVD technique. The TiO_2 coatings were deposited by CVD from a TTIP precursor via the vapour drawn method. The HIPIMS process provided not only the source of Nb metal dopant to the functional films, but sustained the low temperature CVD process by the means of a highly energetic plasma. Furthermore, since HIPIMS deposition rates are very sensitive to magnetic field strength and the degree of unbalance, by using a magnetron with variable magnetic field strength, it was possible to adjust the dopant content of the film without adjusting the power applied to the magnetron target.

The effect of processing parameters (pulse frequency, peak powers, precursor flow rates, operating pressure, etc.) on generating a stable HIPIMS plasma across the process envelope has been studied in this work. The composition, microstructure and electrical properties of the deposited coatings have been investigated, in respect to variable process parameters, such as substrate temperature and operating pressure.

3:10pm **G5-6 Potential of Sequent and Simultaneous PVD PeCVD Hybrid Technology Combination. Investigations Aside Well-known Technologies in Duplex DLC and Co-deposition by Simultaneous Arc, Sputtering Evaporation**, ***Pierre Collignon***, *R Scheibe,* PD2i Europe GmbH, Germany

As Hybrid technology , the Combinations of different PVD and PeCVD technologies like WC/C or Cr-DLC are state of the art technologies that are well established and industrialized but there are more possible idle technological combinations . Research was concentrated on two specific technology combinations:

1) Further investigations in DUPLEX DLC, an upstream NITRATION to increase surface hardness and increased resistance against plastic deformation with a subsequent tribological DLC coating reducing the coefficient of friction in one batch (INSITU). Goal of the study is discovering the properties (adhesion , friction coeff , corrosion) but also the potential to what extent existing sequent processes can be substituted and further, the feasibility of substituting used material / surface treatment combinations.

2) Co-deposition a simultaneous ARC and sputtering evaporation to combine the advantage of high adhesive hard coatings with embedded lubricant / tribiological nanoparticles. Today's weakness in multi layered lubricant thin films are the limited working temperature of 300 °C and the fast elimination of the weak functional trobological layers by wear. Target of the test series is to figure out if lifetime can be increased significant by

embedding lubricant particles into the hard coating by simultaneous evaporation of a different hard coatings (e.g. AlTiN) via ARC and materials with low friction coefficient (e.g. WC/C) via sputtering evaporation.

3:30pm **G5-7 TiN Deposition using the Magnetized Hollow Cathode Activated Magnetron***, H Barankova,* ***Ladislav Bardos,*** Uppsala University, Sweden

A new type of the magnetron, Magnetized Hollow Cathode Activated Magnetron with the target coupled with the hollow cathode magnetized by the magnetic field of the magnetron was tested in the reactive process of TiN deposition. Increased deposition rate compared to the Ti metal deposition rate was confirmed. The depositions as well as optical measurements were performed at several pressures in the reactor. The results of the TiN reactive deposition are presented and discussed, including the TiN deposition in pure nitrogen.

3:50pm **G5-8 Structural and Tribological Properties of Mixed Iron-titanium Borides Produced with Cathodic Arc Assisted Alloying and Electrochemical Boriding***,* ***Erkan Kacar****, C Yelkarasi, S Timur, M Urgen,* Istanbul Technical University, Turkey

Borides of transition metals are very promising materials for a wide range of applications due to their high hardness, excellent wear, high temperature oxidation resistance and high thermal/electrical conductivity. Most widely used borides are iron and titanium borides. Iron borides are produced with diffusion based processes applied to iron and steel alloys. On the other hand titanium borides are produced either by boriding titanium or as coatings on different substrates using PVD or CVD methods. In this study we aimed to produce complex borides composed of Fe and Ti borides using hybrid process. For achieving this aim, low carbon steel substrates are alloyed with titanium using cathodic arc assisted process to produce iron-titanium alloy on the surface. This alloy is then borided using electrochemical boriding method. Produced mixed boride is characterized with respect to its structure, morphology and mechanical properties using XRD, SEM, FIB and ultra microhardness measurements. Tribological properties of the layers are determined using reciprocating wear tests against alumina balls. Results of the investigation revealed that it is possible to produce ultra hard surface layers (hardness above 40 GPa) by this hybrid method with excellent wear resistance.

Bunshah Award Honorary Lecture
Room Town & Country - Session HL

Bunshah Award Honorary Lecture

5:45pm **HL-1 A Retrospective View of Plasma-assisted PVD Innovations Since the 1960's*, Allan Matthews,*** University of Manchester, UK **INVITED**

Since the first plasma-assisted PVD processes for the deposition of engineering coatings first became available in the 1960's, there have been several distinct waves of development, created by innovators whose work opened-up new possibilities for these processes. The first systems were DC diode type "ion plating" processes for the production of metallic coatings, used mostly for corrosion and wear protection. The next wave involved enhanced plasma systems which augmented the diode systems with ionisation-enhancing modifications and permitted the deposition of ceramic coatings as well as improved metallic ones. The third wave involved additional ion and vapour source developments to further optimise processes, especially for multi-component, layered, nanocomposite and duplex systems. We have now entered the fourth wave, led mostly by development teams at companies, who are designing deposition systems to meet the challenges posed by the need to coat commercial products for industrial applications in a manufacturing world which is becoming increasingly digitalised. This often requires high-volume continuous and semi-continuous coating processes, with enhanced process monitoring and control. This talk will be a personal perspective on some of the key innovations throughout these four waves of development, concentrating on the first three and highlighting some of the many individuals who have led the innovations and the key ideas which they brought forward, drawing from the speaker's own experience over the period, including his interactions with some of those innovators.

Special Interest Talk

Room California - Session A1-1

Coatings to Resist High Temperature Oxidation, Corrosion, and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Shigenari Hayashi, Hokkaido University, Sebastien Dryepondt, Oak Ridge National Laboratory, USA

8:00am **A1-1-1 Degradation of Protective Coatings at High Temperatures**, ***Michael Schütze,*** DECHEMA-Forschungsinstitut, Germany **INVITED**

The potential of high temperature materials can only fully be exploited if protective surface coatings are being used. These can offer protection against abrasion and wear, and can reduce heat transfer in the form of thermal barrier coatings, but the most widely used function of such coatings is their capacity for high temperature corrosion protection. The life-time and the protective effect of the coatings plays a crucial role for material and component performance, therefore a strong focus has always been directed towards the degradation mechanisms of coatings. These can be of chemical, mechanical and thermomechanical nature and are strongly dependent on the type of coating. The paper aims at giving an overview on the types of high temperature coatings commonly used together with the respective degradation mechanisms that determine their performance. Furthermore, it will be examined in how far quantitative models and assessment procedures exist allowing prediction of coatings behavior. Finally some thoughts will be given to the future needs in research in this area.

8:40am **A1-1-3 Development of a New Slurry Coating Design for the Surface Protection of Gas Turbine Components**, ***Benjamin Grégoire,*** *G Bonnet, F Pedraza,* University of La Rochelle, France

With the overall increase of the working temperature in gas turbine engines, the colder parts of the turbine (low stages), which used to experience little degradation, start to become sensitive to high-temperature corrosion. Consequently, this broaden the use of protective coatings to these stages to increase the surface stability of gas turbine components (surface engineering). Current industrial processes to produce protective coatings are based upon complex and expensive techniques (e.g. EB-PVD, APS) and put in order hazardous chemicals (e.g. CVD-related techniques). Therefore, cost-effective and environmentally friendly slurry coatings recently came up as a convincing alternative allowing the formation, from Al microparticles, of a complete thermal barrier system in a single step process [1-3].

In this work, a new slurry coating design was developed for the surface protection of nickel-based superalloys (CM-247 LC, DS200 and IN100 superalloys). The addition of Cr microparticles in the water-based slurry compositions was found to decrease the activity of Al upon aluminizing by forming Al_xCr_y phases in the slurry deposit [4]. With further annealing at high temperature (i.e. 1080°C), interdiffusion between the nickel-based substrate and the synthesized Al_xCr_y phases was promoted. The initial contents of Al and of Cr of the slurry deposit allowed to control the coating growth direction (inwardly or outwardly grown coatings as reported for state-of-the-art CVD aluminide coatings). Consequently, different coating microstructures were produced on nickel-based superalloys by adjusting the initial contents of Al and of Cr. It was therefore possible to design, in a single heat treatment, the coating to fight against oxidation and/or hot corrosion.

The present coating design is also expected, in light of the SEM/EDS and XRD characterization, to allow the surface protection of metallic substrates with complex geometry such as gas turbine blades.

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9:00am **A1-1-4 Slurry Formulation for Industrial Large Scale Aluminum Diffusion Coatings**, *M Kimmich,* Fraunhofer ICT, Germany; ***Vladislav Kolarik,*** Fraunhofer Institute for Chemical Technology ICT, Germany; *J Bermejo Sanz, M Juez Lorenzo,* Fraunhofer ICT, Germany

Diffusion aluminide coatings, deposited as Al slurries, are an efficient and economic technique to protect ferritic steels, against oxidation and corrosion at high temperatures. In the international business the transport of liquid Al slurry paint to the application site is often preferred to the transport of high purity Al micro-powders due to legal regulations. The Al slurry paint has to possess appropriate viscosity and rheology, it has to be suitable for storage, transportable and not hazardous for health and environment.

Three slurry formulations were prepared with spherical high purity aluminum particles with an average diameter of 15 µm: formulations SMK1 and SMK2 using a composition of isopropanol and butanol as dissolvent and polyvinylbutryal 30 as binder and slurry formulation SMK3 using aceton and butanol as dissolvent and the commercial Paraloid B72 as binder. Commercially available rheology modifiers were applied to adjust the slurry properties.

To investigate the wet slurry thickness, from which sagging will occur the Anti-Sag-Index was determined according to ASTM 4400-99. Critical wet slurry thicknesses about 200 µm were found for the studied slurry formulations, adjustable by the portion of rheology modifier. Grindometer tests revealed a maximum grain size of 32 µm, which corresponds to the maximum particle size indicating small agglomerates and thus good dispersion and low sedimentation. Plotting shearing stress versus the rate of shearing strain all three formulations exhibit a shear thinning behavior, more pronounced for SMK2 and SMK3.

To simulate the spray process with high shear rates during spraying, the low-high-low shear rate test was applied, measuring the viscosity as a function of time. The slurries show different viscosities in the first low shear rate period. With the high shear rate in the second period the viscosity decreases close to 0 Pa*s for all three formulations. Reducing the shear rate subsequently, it increases to values about 750 Pa*s for SMK1 and SMK2 and to 8000 Pa*s for SMK3. With this behavior SMK3 would be more suitable for a spray process, since it would exhibit a very low viscosity during spraying, which would rapidly increase after deposition and avoid sagging.

The diffusion aluminide coatings prepared with the three slurry formulations showed the same phase structure composed of Fe_2Al_5 and FeAl and a comparable oxidation behavior at 650°C in air. The principal wet slurry thickness notably influences the phase structure of the diffusion aluminide coating and its evolution with the time. An appropriate slurry formulation contributes significantly to adjust a homogeneous wet slurry thickness.

9:20am **A1-1-5 Structural Properties of Hybrid Sol-gel Coatings for Corrosion Protection of Low-carbon Steel**, ***Marie-Joëlle Menu,*** CIRIMAT, Université de Toulouse UPS INP CNRS, France; *C Lavollee, R Noiville, M Gressier,* CIRIMAT, France; *J Garcia, J Sobrino,* CETIM, France

This work focuses on the development of hybrid sol-gel coatings for corrosion protection of low-carbon steel. The studied material is a DC04 laminated carbon steel, very sensitive to corrosion and with an uneven topography. Feasibility of the development of an architectured hybrid coating prepared by a sol-gel route on the DC04 steel has been demonstrated.

The architecture is based on a gradient of concentration of unloaded and loaded hybrid layers of zirconia nanoparticles imbedded in a hybrid matrix. The resulting coating is adherent, covering, leveling and presents high-performance anticorrosion properties. Architectured systems were assessed combining microstructural observations, electrochemical impedance spectroscopy analysis and solid state NMR. ^{13}C, ^{29}Si and ^{27}Al NMR spectroscopies have highlighted the importance of controlling both the inorganic and organic polymerisation reactions to obtain efficient anticorrosion coatings. Moreover, these results demonstrate that the modification of the organic-inorganic hybrid matrix structure allows the insertion of a higher amount of cerium without damage for the anticorrosive properties of the coating.

9:40am **A1-1-6 Diffusion Coatings for Corrosion Protection of Ferritic-martensitic Steels for Co-firing Combustion Plants**, ***Tobias Meissner,*** *D Fähsing, M Galetz,* DECHEMA-Forschungsinstitut, Germany

In the course of energy transition the use of existing power plants for co-firing with biomass plays a substantial role in terms of base load supply.

While co-firing reduces the CO_2 footprint of the plant, it also leads to higher amounts of corrosive species within the system such as chlorine and sulfur. Consequently, higher corrosion rates and material losses are observed in the firing chamber components. In particular, superheater tubes are subjected to increased corrosive attack and are prone to early replacement. Thus, co-firing is commonly limited to temperatures below 500°C and low biomass-to-coal ratios (10%).

The heat resistant ferritic-martensitic steel X20CrMoV12-1 is of great interest as a material for superheaters because the steel exhibits much better heat transfer behavior and a lower coefficient of thermal expansion, as well as lower costs in comparison to austenitic steels. However, corrosion resistance in the combustion gas atmospheres of biomass power plants is not sufficient.

Therefore, different corrosion protection systems have been developed in order to make ferritic-martensitic steels usable at temperatures above 500°C in such combustion gases. The first step was to apply a thin nickel layer. This interlayer serves as a nickel reservoir for the subsequent diffusion process of potentially protective elements such as Al, Cr and Si.

Coated and uncoated X20 samples as well as austenitic steel DMV 310 N samples were tested in a fireside corrosion atmosphere of N_2-O_2-H_2O-CO_2-SO_2-HCl at 650°C under an ash deposit containing sulfates and chlorides. This paper highlights the improved corrosion behavior of the ferritic-martensitic steel through the coatings even in this very harsh environment.

10:00am **A1-1-7 Biomass Corrosion Behavior of Steels and Coatings in Contact with KCl/K_2SO_4 at 550°C: a Screening Laboratory Test**, *M Gutiérrez,* ***Alina Agüero Bruna,*** *I Baraibar,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; M Hernández,* Instituto Nacional de Técnica Aeroespacial (INTA),, Spain*; R Muelas Gamo, S Rodríguez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Increasing the operating temperature in biomass-fueled power plants is a very difficult task when compared to plants operating with traditional fossil fuels in particular under an oxyfuel combustion atmosphere. The corrosion generated by alkaline deposits and chlorine present in biomass will dramatically increase with increasing temperature, and the presence of a higher content of water vapor and SO_2 characteristic of oxycombustion will likely further increase the corrosion rate. The alloys and coatings used until now will have to be modified due to the change in corrosion mechanisms. Due to these aggressive conditions, it is very important to develop a laboratory testing facility which allows to evaluate the viability of using new materials as well as to predict the useful life for those already in used, in particular if the operating parameters change. In the literature, ferritic-martensitic steels and several coatings were studied employing conditions similar to those found in a biomass power plant and it was observed that the presence of chromium in both the substrates and the coatings seems to increase the degradation *(S. Kiamehr, K.V. Dahl, M. Montgomery and M.A. J. Somers, Mater. Corros. 2015, 12, 66)*. Aluminum coatings with low chromium content appear to perform better in these alkaline enviroment. In this work, laboratory testing was carried out to evaluate the effects of salt deposits, as well as the effect of different coating composition and substrates on the corrosion mechanism. Exposure was performed at 550°C for more than 600h in a flowing model biomass oxycombustion atmosphere containing 60%CO_2, 30%H_2O, 8%O_2, 2%N_2 (Vol %), 400 vppm HCl and 2 vppm SO_2. The samples were covered with KCl + K_2SO_4 prior to be exposure. The present study compares the corrosion behavior of three steels (P92, T22 and SANICRO28) uncoated and coated in the above described biomass model atmosphere. The coatings include slurry applied diffusion aluminide and Cr aluminide coatings as well as Ni20Cr, Fe50Cr and a modified super hard steel (SHS) deposited by HVOF thermal spray. FESEM and XRD analysis were performed to identify the corrosion products and to determine the mechanism of corrosion. The developed test allows a meaningful ranking of the studied materials. The observed corrosion rate tendency based on the mass variations is as follows: T22>P92>Ni20Cr»modified SHS»Cr Aluminide>SANICRO28>Fe50Cr>Aluminide.

10:20am **A1-1-8 In-situ Post-Annealing of Si-Al Coatings for the Oxidation Protection of γ-TiAl**, *K Bobzin, T Brögelmann, C Kalscheuer,* ***Tiancheng Liang,*** Surface Engineering Institute - RWTH Aachen University, Germany

Many attempts have been made to extend the service temperatures of lightweight materials based on γ-TiAl alloys due to their insufficient oxidation resistance at T > 850 °C for turbine applications. Among them, deposition of high-temperature oxidation protective coatings has been proved to be a promising approach. The key purpose hereby is the formation of protective oxide scales such as Al_2O_3, Cr_2O_3 and SiO_2, which offer a barrier against diffusion of oxygen into the bulk material. Besides, a dense microstructure for a suppressed interdiffusion and an adequate coating-substrate adhesion in terms of the chemical compatibility and the similarity of the coefficients of thermal expansion are indispensable.

In the present work, an innovative in-situ plasma-assisted post-annealing combined with pre-oxidation for Si-Al coatings, carried out immediately after the deposition process by high-speed physical vapor deposition (HS-PVD) technology, was developed. The post-annealing aimed at the formation of a protective oxide layer consisting of Al_2O_3 or SiO_2 on the Si–Al coating surface and a refinement of the microstructure for the reduction of interdiffusion, to enable the application of Si-Al coated γ-TiAl in air up to T = 950 °C.

In a first step, three Si-Al coating systems with different Si:Al ratios were deposited on γ-TiAl substrate by HS-PVD, which offers high deposition rates owing to hollow cathode discharge (HCD) and gas flow sputtering (GFS). Subsequently, the coatings were annealed in the coating chamber with different oxygen flow Q_{O2} and bias voltage U_{bias}. Such kind of in-situ post-annealing, combining pre-oxidation and simultaneous argon plasma induced ion bombardment has not been reported elsewhere.

Both, post-annealed and as-deposited coatings were characterized with regards to their coating thickness, morphology, roughness and phase composition. Subsequently, isothermal oxidation tests were carried out at T = 950 °C in air. Weight changes and cross-sections were analyzed at certain annealing time intervals. The results confirm the high oxidation resistance of the post-annealed Si-Al coatings compared to the as-deposited coatings and the uncoated γ-TiAl substrates. Moreover, cross-sectional images and phase analyses of the coating surfaces indicate that the interdiffusion of Ti between coating and substrate can be effectively reduced due to the refined microstructure in the post-annealed coatings. The results of the conducted research reveal a high potential of the post-annealed Si-Al coatings for the oxidation protection of γ-TiAl at T > 850 °C in turbine applications.

10:40am **A1-1-9 Fatigue Performance of Bare and Coated 31V Alloy**, ***Sebastien Dryepondt,*** *B Armstrong,* Oak Ridge National Laboratory, USA*; Y Zhang,* Tennessee Technological University, USA*; S Sampath,* Stony Brook University, USA*; J Haynes,* Oak Ridge National Laboratory, USA

Diffusion aluminide and MCrAlY overlay coatings have been used for decades in the gas turbine industry to protect components against oxidation and hot corrosion. Due to increasing temperature in light and heavy duty internal combustion engines, corrosion-resistant coatings might be required to maintain or even improve the in-service lifetime of hot components such as valves. The coating impact on the valve alloy mechanical properties needs, however, to be assessed. ~50um thick slurry and pack aluminized coatings, as well as a NiCoCrAlY overlay coating, were therefore deposited on alloy 31V (57Ni-23Cr-13Fe-2Mo-2.3Ti-1.3Al-0.9Nb) fatigue specimens. The high cycle fatigue (HCF) behavior of the coated specimens at room temperature and 500º C was similar to the fatigue behavior of bare 31V specimens exposed to the coating heat treatments. Cracks in the coating were only observed close to the fracture surface and the cracks did not propagate in the substrate. Optimization of the coating processes to improve the HCF behavior of coated 31V will be discussed.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-1-1 Contact Fatigue Performance of Cobalt Boride Coatings**, *A Meneses-Amador, D Sandoval-Juárez, G Rodríguez-Castro, D Fernández-Valdés, I Campos-Silva,* IPN, Mexico*; A Mouftiez,* ICAM Lille, Matériaux, France*;* ***JoséLuis Arciniega-Martínez,*** IPN, Mexico

In this work, an experimental and numerical study of the contact fatigue test on cobalt boride (CoB/Co_2B) coatings is presented. The boride layers were formed at the surface of Co-Cr-Mo alloy using the powder-pack boriding process at temperatures of 1123 K for 3 h and 1223 for 1 and 5 h of exposure times in order to obtain three different thicknesses. From the set of experimental conditions of the boriding process, contact fatigue tests were performed with a servo-hydraulic universal testing machine by repetitive impact of a sphere on the layer-substrate system. The

methodology of the contact fatigue test consisted of two main stages. First a static critical load was determined, where radial cracks were considered as the failure criterion afterward fatigue conditions were conducted in low-cycle (n < 100,000) using sub-critical loads with a frequency of 6 Hz. The test results indicate that the thinner coating exhibited improved resistance to fatigue. In order to evaluate the stress field generated in the boride coating during the application of static and dynamic loads, a numerical simulations based in the finite element method was developed.

8:20am **B4-1-2 Revisiting the Nanocomposite Structure of Sputtered TiSiN Films**, *F Fernandes,* University of Coimbra, Portugal*; S Calderon, P Ferreira,* International Iberian Nanotechnology Laboratory, Portugal*;* ***Albano Cavaleiro****,* University of Coimbra, Portugal

TiSiN coatings with nanocomposite structure have been one of the most studied systems in the field of hard coatings with a large application in advanced machining and other high temperature cases due to their excellent mechanical, thermal and tribological properties. In a recent publication (F. Fernandes et al., SCT 264(2014)140), the authors have shown that the nanocomposite structure of these films can be easily achieved and tailored by changing relevant parameters during the deposition using the emergent HiPIMS technology (high power impulse magnetron sputtering), without requiring heating of the substrate. Here, we evaluate the effect of increasing the peak power on the nanocomposite structure of the TiSiN films and its correlation with their mechanical properties. For comparison purposes a TiSiN film deposited by direct current magnetron sputtering (DCMS) was also deposited, without substrate heating. The structure of the films was fully characterized by transmission electron microscopy (TEM) and X-ray diffraction. High-resolution plan-view and cross-sectional TEM, electron SAED patterns and EEELS / EDS chemical analyses were performed to understand the elemental distribution and the phases presented in the films. The results revealed that, independently of the deposition process and deposition conditions, Si segregation was always observed. However, the coatings deposited by DCMS, or HiPIMS with low peak power, showed much more Si content in solid solution in the TiN lattice than the films deposited with higher adatom mobility (HiPIMS with high peak power). In the former, an extremely high number of dislocations are forming a network inside TiN grains that seems to be related to Si segregation. This distribution could evolve to a tenuous nanocomposite structure, which is clearly visible in the last ones, as usually encountered in high adatom mobility depositions of this system, TiN grains surrounded by a Si-N amorphous layer. The high number of dislocations can justify the hardness improvement of the coatings in relation to single TiN.

8:40am **B4-1-3 Nanostructured Functional Coatings – From Process Diagnostics in High Power Pulsed Plasmas to Coating Properties and Performance**, ***Tobias Brögelmann****, K Bobzin, N Kruppe, M Arghavani, M Engels,* Surface Engineering Institute - RWTH Aachen University, Germany **INVITED**

The sustainable conservation of resources, the protection of environment, and the demand for increased productivity in manufacturing processes are the key drivers behind the design of physical vapor deposition (PVD) functional coatings that combine a low coefficient of friction and a low wear rate over a wide range of working environments. This applies in particular to industrial applications like forging and metal cutting. The measures to increase productivity and sustainability of machining, such as high speed cutting, high performance cutting, and dry machining sharpen the demands on cutting tools. As a result of advanced cutting parameters in combination with the continuous development of new workpiece materials, nanostructured PVD coatings reach a 15 % share of the world market of hard and super-hard cutting materials in 2013, and will acquire an even stronger role in future tool development. Nanostructured functional coatings based on a nanocrystalline, -laminate, or -composite structure open a new path to the design of coatings with tailor made properties. High performance plasmas, such as high power pulsed magnetron sputtering (HPPMS) provide a complex deposition parameter set to control the structure on a nanometer scale and adjust the coating properties. However, reaching the full potential of the process technology and the nanostructured coating requires fundamental understanding and full control of the deposition process, in particular when using an industrial scale coating unit with a multi-fold rotating substrate holder.

In this talk, highlights of research and development at Surface Engineering Institute of RWTH Aachen University on nitride based nanolaminate and -composite PVD coatings for use in forming and machining processes will be presented. The plasma in reactive HPPMS and dcMS/HPPMS hybrid processes is investigated by space- and time-resolved plasma diagnostics. Further investigations are focusing on the relationship among pulse parameters and coatings properties, such as chemical composition, intrinsic stress and elastic-plastic behavior. Correlations between the plasma properties, the pulse parameters, such as pulse length, frequency, and pulse power, and the coating properties are the basis for process and coating adjustment to the demands in forging and machining. Due to highly non-linear or multidimensional cause-effect relations artificial neural networks (ANN) are trained with extensive data sets to link the process parameters to the coating properties. This comprehension-oriented approach will contribute to overcome the empirical approach on the synthesis path of nanostructured coatings in high performance plasmas.

9:20am **B4-1-5 Mechanical and Tribological Properties of Gradient and Multilayered CrVN/CrMoN Coatings**, *Y Chang,* ***Chih-Cheng Chuang****,* National Formosa University, Taiwan

Transition metal nitride coatings have been used as a protection of cutting and forming tools for several decades. To extend the lifetimes of these protective nitride coatings, numerous efforts have been made on enhancing hardness and oxidation resistance by incorporating elements such as Al, Mo, V and Si etc. into CrN and TiN to form gradient and multilayered coatings. Vanadium nitride (VN) is easily oxidized to form vanadium oxides and becomes lubricious under stress. In this study, gradient and multilayered CrVN/CrMoN coatings were synthesized by cathodic-arc evaporation. During the coating process of CrVN/CrMoN, CrN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. By controlling the different negative bias voltages and cathode currents, the CrVN/CrMoN possessed different microstructures and mechanical properties. The microstructure of the deposited coatings were investigated by field emission scanning electron microscope (FE-SEM) and field emission gun high resolution transmission electron microscope (FEG-HRTEM), equipped with an energy-dispersive X-ray analysis spectrometer (EDS). Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the films. The hardness of coatings was evaluated using nanoindention and Vickers hardness measurement. Ball-on-disc wear tests were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. To evaluate the impact fracture resistance of the coatings, an impact fatigue test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. The combination of CrMoN and CrVN provides an alternative for a hard and lubricious coating. The design of gradient and multilayered CrVN/CrMoN coatings is anticipated to be advantageous in applications to enhance the machining quality of the cutting tools and life of mechanical parts.

9:40am **B4-1-6 Synthesis and Characterization of Multilayered Coatings in the Ti-Al-N System by a Reactive Gas Pulsing Process**, ***Ahmed El Mouatassim****, M Pac, P Henry,* LPMT, France*; C Rousselot,* FEMTO-ST, France*; C Tromas, F Pailloux, T Cabioc'h,* SP2MI, France

Nanostructured coatings of metallic nitrides are commonly used in the industry as protecting coatings for cutting tools due to an excellent combination of properties including a high hardness, improved wear properties and oxidation resistance. To improve their functionality towards various applications, it is necessary to test new deposition techniques beyond the conventional PVD techniques such as magnetron sputtering. The coatings here studied are synthesized by using a "Reactive Gas Pulsing Process" (RGPP) which is a promising new technique allowing one to obtain multilayer compositionally modulated coatings with potential excellent mechanical properties.

$Ti_xAl_{1-x}N/Ti_{x'}Al_{1-x'}N_y$ ($x \approx x' \approx 0.5$; $0 \le y \le 0.8$) multilayers were synthesized, cyclical variations of the nitrogen flux being imposed during the deposition process to obtain a stacking of bilayers (thickness in the range 12-36 nm) for a total thickness varying from 400 nm to 2 mm. The coatings were characterized by using mechanical testing (friction test, scratch test, nanoindentation) and structural characterization techniques (X-Ray Diffraction (XRD), Scanning and Transmission Electron Microscopy (SEM, TEM), Electron Energy Loss Spectroscopy (EELS),…

Very different mechanical properties were obtained for coatings made of ceramic/ceramic bilayers ($y^3 0.4$) and those with ceramic/metal bilayers ($y \ge 0.4$) and those with ceramic/metal bilayers ($y=0$), the latter being softer with very poor tribological properties due to the presence of the TiAl phase. Very different internal stresses were also found for ceramic/ceramic and metal/ceramic multilayers. Observations in a TEM (HR, HAADF, SAED,…) combined with EELS experiments allowed to discuss the evolution of the microstructure and of the stoichiometry of the multilayer during the

growth process. Complex phenomena like nitrogen interdiffusion and poisoning effect of the target during the deposition process have to be taken into account to discuss nitrogen amount and environment.

10:00am **B4-1-7 Tribological Behavior of Transition Metal Nitride Films with Crystalline and Noncrystalline Tailored Multilayer Structure**, *Z Lin, **Fan-Bean Wu**,* National United University, Taiwan

The transition metal nitride, TMN, films, including TaN, HfN, and MoN, were fabricated by RF magnetron sputtering with various microstructure features through input power and gas flow ratio control. With Ar/N_2 gas ratios and RF input powers from 8/12 to 18/2 and 75 to 300 W, respectively, the TMN nitride films evolved from crystalline, nanocrystalline to amorphous features. The multilayer films were further produced through tailoring of thin layers of above mentioned structural features to enhance the tribological behavior as protective coatings. Scratch and linear reciprocated pin-on-disc wear tests were practiced on singlelayer and multilayer TMN films to evaluate the adhesion strength and failure behavior . Severe cracking and chipping were found for the singlelayer TMN films with crystalline structure. Limited adhesive failure was observed for the multilayer coatings with alternate stacking of layers with different microstructures. Lower coefficient of friction for the crystalline/noncrystalline tailored multilayer TMN films during wear activities was also evident for their superior protective characteristics.

10:20am **B4-1-8 Investigation of Microstructure and Properties of Magnetron Sputtered Zr-Si-N Thin Films with Different Si Content**, ***Daniel Fernandez**,* Universidade Federal de Sergipe, Brazil*; F Freitas,* Universidade Federal de Sergipe, Brazil, Brasil*; L Félix, A Terto,* Universidade Federal de Sergipe, Brazil*; A Junior,* Universidade Federal do Rio Grande do Sul, Brazil*; F Mendes,* Instituto Nacional de Tecnologia, Brazil*; E Tentardini,* Universidade Federal de Sergipe, Brazil, Brasil

The incorporation of silicon into zirconium nitride (ZrN) thin films is a known alternative to effectively refine their grains and improve mechanical properties and oxidation resistance. However, it is not well clarified in literature information regarding the structure formation mechanism and the influence of Si content in the chemical and physical properties of Zr-Si-N thin films. Thus, the aim of this work is to investigate the influence of varying Si concentration in the microstructure, morphology, mechanical properties and oxidation resistance of ZrN films. Pure ZrN and Zr-Si-N thin films were deposited by reactive magnetron sputtering technique, with Si content set between 3 and 15%. Characterizations were carried out using GAXRD, TEM, XPS, and high temperature oxidation tests. It was identified amorphous and crystalline areas along the films microstructure, consisting in crystalline grains embedded in an amorphous phase, which were characterized by EDS as Zr and Si rich areas, respectively. GAXRD results indicate peak intensity reduction and broadening increase due silicon nitride segregation to grain boundaries, which is responsible for grain size reduction, reaching magnitudes lower than 10 nm, calculated by Scherrer. GAXRD peaks shift are observed for all samples and it can be explained due formation of a solid solution in which Si replaces Zr atoms in ZrN crystal lattice and due a strong interface between crystalline phase and amorphous one. XPS confirmed the presence of compounds like ZrN and Si_3N_4 and it is also possible to infer the formation of a solid solution of Si in ZrN lattice. Oxidation tests were performed at temperatures in the range of 773 K to 1373 K. ZrN film is almost fully oxidized at 773 K, while films with high silicon content maintain ZrN grains stable at 973 K. When oxidized, ZrN films form monoclinic ZrO_2 phase, but, in films with silicon addition, the stable phase is the tetragonal one. This happens due ZrN grain size reduction, because tetragonal phase has the lowest surface energy. Oxidation tests results confirm that there is a mechanism acting as diffusion barrier in films, preventing grains coalescence and oxygen diffusion into film structure. This mechanism is a direct consequence of silicon segregation process to grain boundaries, which ensures the formation of a nanostructure composed of ZrN grains embedded by an amorphous Si_3N_4 layer (nc-ZrN/a-Si_3N_4), allowing oxidation resistance improvement in at least 473 K.

10:40am **B4-1-9 Low Temperature Surface Modification on Selected Thin Films Using HIPIMS for Antibacterial and Bio Applications**, ***Wan-Yu Wu**,* Da-Yeh University, Taiwan **INVITED**

In recent years, high power impulse magnetron sputtering (HiPIMS) has drawn a lot of attentions due to its high ionization of the working gas and the target atoms, and its ability to improve the quality of the resulting films, for example, better adhesion, higher density, and reduced surface roughness. Also, HiPIMS process allows the use of temperature-sensitive materials as the substrates. This feature opens a new window of applications. In this study, Ti-Cu, Cu-Ag, and TiN thin films were deposited using HiPIMS under various the target currents. The characteristics of these thin films, including microstructure, morphology, composition, adhesion to the substrate, and chemical bonding state are reported and discussed. Furthermore, the antibacterial activity, the corrosion resistance in simulated bodily fluid, the wear resistance against to the Al_2O_3 ball, and the biocompatibility test to MG63/3T3 were also presented.

11:20am **B4-1-11 Using Nano-impact Method to Predict Erosion Performance of Advanced DLC Coating Systems**, ***Samuel McMaster**, T Liskiewicz, A Neville,* University of Leeds, UK*; B Beake,* Micro Materials Ltd, UK

Diamond-like carbon is a metastable form of amorphous carbon with varying ratios of sp^2/sp^3 bonding. These coatings possess attractive mechanical, optical, chemical and tribological properties [1]. DLC coatings are becoming increasingly popular in the automotive and aerospace industry due to their high hardness, resistance to wear and low friction coefficient [2]. They can suffer from poor adhesion at high loads and impact stresses [3].

Well characterised coatings will enable the relationship between mechanical properties and impact behaviour to be studied. Impact and erosion testing has been used as part of a comparative study equating the energies dispersed in the substrate surface and characterising the wear scars produced by each method. DLC impact fatigue resistance requires improvement for more demanding applications [4].

Mechanical properties have been measured by nanoindentation using a partial loading technique. Variations in hardness and elastic modulus have been mapped through the multilayer coating structure. Macro-scale coating adhesion has been tested though scratch testing.

The DLC coating systems have been varied in this study by changing the composition (a-C:H, Si-doped and W-doped), coating thickness (1 micron and 3 microns), substrate material (316L stainless steel and hardened M2 Tool Steel) and substrate roughness (0.01 microns and 0.08 microns). All DLC coatings in this study have a gradient interlayer present.

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11:40am **B4-1-12 A Novel Methodology for Damage Characterization in Thin Hard Coatings Submitted to Extreme Loadings**, ***Antonios Choleridis**,* Ecole Nationale Supérieure des Mines de St-Etienne, France*; C Héau, M Leroy,* Institut de Recherche en Ingénierie des Surfaces, Groupe HEF, France*; S Sao-Joao, G Kermouche,* Ecole Nationale Supérieure des Mines de St-Etienne, France*; C Donnet,* Université de Lyon, Université Jean Monnet, France*; H Klöcker,* Ecole Nationale Supérieure des Mines de St-Etienne, France

Cost efficient PECVD deposited DLC is especially used in the automotive industry. While DLC coated components exhibit very little wear having a reduced friction coefficient [1], under severe conditions blistering driven in service delamination can sometimes be observed.

Perfectly adherent DLC coatings with high compressive process induced residual stresses were deposited on a M2 steel substrate and a thin under layer. Residual stresses, quantified on FIB milled micro-beams and by FE analysis [2,3,4] vary between 1 GPa and 2 GPa for the thinnest and thickest DLC coating respectively.

The samples were tested in severe loading conditions in a novel friction test facility. This test consists of a rotating ring rubbing against the surface of the DLC coated sample in an oil bath at 100°C. At the same time, an oscillating in-plane movement of the specimen takes place. The damage induced by the extreme loading conditions has been characterized by post mortem SEM and FIB observations.

FIB cross sections on blisters reveal the substrate microstructure, the interface and the different layers of the coating. To analyze the damage mechanism a novel characterization methodology was applied.

Successive FIB cross sections allow analyzing blister nucleation. Blistering occurs close to the underlayer/steel interface inside steel. The steel thickness is maximal in the center of the blister and decreases moving to its borders. For these reasons the blister was withdrawn in order to analyze this supplementary layer by EDS. The quantity of iron (Fe) detected by EDX analyses through several zones of this film confirmed the previous SEM observations.

Cracks initiate inside the M2 steel substrate, several nanometers beneath the (M2)-(under-layer) interface. The cracks then propagate towards this interface and propagation ends with interfacial failure. Carbides lead to local crack kinking.

The new methodology for analyzing damage of thin hard coatings presented here gives the necessary inputs for modelling coating delamination at a scale defined by the substrate microstructure.

References

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Fundamentals and Technology of Multifunctional Materials and Devices

Room Sunrise - Session C2-1

Novel Oxide Films for Active Devices

Moderators: Marko Tadjer, Naval Research Laboratory, USA, Vanya Darakchieva, Linkoping University, Sweden

8:00am **C2-1-1 Characteristic of the bionic synapse on Lithium Aluminate Non-Volatile Resistive Random Access Memory**, ***Wan-Ching Su***, *T Chang, Y Hung, B Yan, S Huang, Y Tsao, T Tsai,* National Sun Yat-Sen University, Taiwan

This topic investigate the Characteristic of bionic synapse by non-voltage resistance random memory(RRAM). The material is aluminate lithium oxide as isolator. In operating process of RRAM the reset process reveals two reset stages. Moreover, The methods of measure it either DC voltage or Pulse have been applied to perform lithium aluminum oxide RRAM reveals the HRS resistance changing continuously. Applying the ionic diffusion and the titanium nitride attract is discussed ion model of lithium-ion, the phenomenon of the wide resistance value, and utilizing oxygen ions model. The redox reset resistance of lithium wire are explained for. Final, With Pulse voltage applied on lithium aluminum oxide RRAM can induce a bionic brain behavior: Spike-Timing-Dependent Plasticity.

8:20am **C2-1-2 Compared with the Different Thickness of Switch Layer on Resistive Random Access Memory**, ***Chih-Cheng Yang***, *T Chang, W Chen, C Lin, H Zheng, Y Chien,* National Sun Yat-Sen University, Taiwan

Resistive random acess memory(RRAM) is one of the next generated memory due to its low fabricated cost, structure simple, and high speed switch. In this work, the three HfO_2 thickness of Pt/HfO_2/TiN RRAM device was used to compared the IV curves. RRAM device was deposited by sputtering. After the device fabrication,the forming voltage and IV switch cycle was measured to compared with the different thickness. Moreover, IV curves was used to study the on/off ratio and the current fitting was used to identify the current conduction mechanism. Finally, the conduction model was proposal to explain the on off ratio and current conduction mechanism.

8:40am **C2-1-3 Investigating Abnormal Hump Under Positive Bias Temperature Stress for Hydrogenated a-InGaZnO Thin Film Transistors**, ***Yu-Chieh Chien***, *T Chang, T Tsai, H Chiang, Y Yang, Y Tsao, M Tai,* National Sun Yat-Sen University, Taiwan

Amorphous indium gallium zinc oxide (a-InGaZnO) is one of the most promising candidate for next generation electronics. A-InGaZnO is well known for its superior electrical characteristic, including high uniformity, high mobility (~10cm^2/Vs), low leakage current (~10^{-20}A). In addition, it can be fabricated by RF-sputtering at room temperature for application in transparent flexible displays. However, rapidly grown of display industry, including active-matrix liquid crystal display (AM-LCD) and active matrix organic light-emitted diode (AM-OLED), even 3D display technology, then enhance the requirement of carrier mobility. Thus, hydrogen were proposed to enhance device carrier mobility. However, reliability test after introducing hydrogen atoms need to be evaluated cautiously. In this investigation, a-InGaZnO TFTs after hydrogen plasma treatment (HPT) under positive bias temperature stress (PBTS) was compared to un-treated devices. An abnormal hump under PBTS condition was observed, in addition, the hump phenomenon only occurs in HPT devices. Hydrogen migrates to SiOx etching stop layer (ESL) induce positive fixed oxide charge was proposed and explained the degradation. Furthermore, different experiment conditions and COMSOL simulation were carried out to further verified the proposed model.

9:00am **C2-1-4 Optical and Electronic Properties of Monoclinic Ga_2O_3 Unravelled**, ***Mathias Schubert***, Linkoping University, Sweden, USA*; A Mock, R Korlacki, S Knight,* University of Nebraska-Lincoln, USA*; V Darakchieva,* Linköping University, Sweden*; B Monemar,* Linkoping University, Sweden*; Y Kumagai,* Tokyo University of Agriculture and Technology, Japan*; K Goto,* Tamura Corp., Japan*; M Higashiwaki,* National Institute of Information and Communications Technology, Japan

The stable monoclinic phase of Ga2O3 is currently at the forefront of research for high-power electronic and high-energy photonic applications due its large break down voltage and large band gap energy. Precise knowledge of its optical and electronic properties is crucial for further progress. Due to its monoclinic crystal symmetry, traditional techniques for measurement and calculation of solid state physics properties require careful reconsideration. In our presentation, we reveal how phonons [1], free carrier excitations [1], band-to-band transitions [2], optical constants [2], and exciton formation [2] differ fundamentally from previous front running semiconductors such as zincblende or wurtzite structure group-III group-V compounds. We demonstrate how traditional linear optical spectroscopy methods such as generalized ellipsometry and the optical Hall effect must be expanded to determine phonon, free carrier, and band-to-band transition characteristics from experiment, and we compare our findings with results from density functional theory calculations [2]. We discuss band ordering and polarization selection rules for band-to-band transitions, the peculiarities of valence and conduction band effective mass parameters, the breaking of phonon mode propagation degeneracies, the consequences for propagation of free charge carrier modes, and the need for the reformulation of the Lyddane-Sachs-Teller relationship [3]. We obtain a new description of dielectric function tensor properties from the Terahertz to the Deep Ultraviolet, and we revise previous incomplete phonon and band-to-band properties assignments [4,5]. [1] M. Schubert et al., Phys. Rev. B 93 (2016) 125209. [2] A. Mock et al., arXiv:1704.06711v1. [3] M. Schubert, Phys. Rev. Lett. 117 (2016) 215502. [4] C. Sturm et al., Phys. Rev. B 94 (2016) 035148. [5] C. Sturm et al., APL Materials 3 (2015) 106106.

9:20am **C2-1-5 Ga_2O_3 for Ultra-High Power Rectifiers and MOSFETs**, ***Stephen Pearton***, *F Ren, J Yang, P Carey,* University of Florida, USA*; M Tadjer, M Mastro,* Naval Research Laboratory, USA **INVITED**

Gallium Oxide (Ga_2O_3) is emerging as a viable candidate for certain classes of power electronics, solar blind UV photodetectors, solar cells and sensors with capabilities beyond existing technologies due to its large bandgap. The performance of technologically important high voltage rectifiers and enhancement-mode Metal-Oxide Field Effect Transistors benefit from the larger critical electric field of β-Ga_2O_3 relative to either SiC or GaN.Reverse breakdown voltages of over 1kV for β-Ga_2O_3 have been reported by several groups, either with or without edge termination.The on-of ratios ranged from $3x10^7$ to $2.5x10^6$ for this range of biases and showed only a small dependence on temperature in the range 25-100°C.The metal-oxide-semiconductor field-effect transistors (MOSFETs) fabricated on Ga_2O_3 to date have predominantly been depletion (d-mode) devices, with a few demonstrations of enhancement (e-mode) operation. The channels have been undoped, Si , Sn or Ge -doped and HfO_2, Al_2O_3 and SiO_2 have been the most widely used dielectrics.Si ion implantation has been employed to improve source/drain resistance in some cases.

10:00am **C2-1-7 Fabrication and Characterization of Pulsed-Laser Deposited $Ba_{0.8}Ca_{0.2}Ce_xTi_{1-x}O_3$ (BCCT) Thin Films**, ***Cristian Grijalva,*** The University of Texas at El Paso, USA; *J Jones,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *R Chintalapalle,* The University of Texas at El Paso, USA

Intrinsic and doped barium titanate ($BaTiO_3$) thin films have drawn considerable recent interest due to their second order nonlinear response, ferroelectric properties, and electro-optic properties. Co-doping approach, which proved to be quite successful with many of the multifunctional materials, has been attractive to tailor the structural, optical, electrical and mechanical properties of barium titanate ceramic thin films. Therefore, in the present work, the Ca,Ce co-doped barium titanate materials were considered to obtain tunable optical properties. $Ba_{0.8}Ca_{0.2}Ce_xTi_{1-x}O_3$ (BCCT) thin films with fixed Ca content and variable Ce content were fabricated using pulsed-laser deposition (PLD). While such BCCT thin films are anticipated to have applications in electro-optic and memory devices, a detailed characterization has been performed to understand the effect of Ce on the structural and optical properties of resulting BCCT films. BCCT films with a nominal thickness of 90 nm were deposited onto quartz and low-impedance Silicon wafers heated to 250 ºC. X-ray diffraction (XRD), spectroscopic ellipsometry (SE) and nano-mechanical were performed to understand the effect Ce on the structure and properties. The results indicate that the BCCT films were amorphous. All the BCCT films were optically transparent. The band gap decreases with increasing Ce content. The results and analyses will be presented and discussed in the context of utilizing these films in contemporary electronic and optical device application.

10:20am **C2-1-8 Thermo-Chemical Stability Evaluation of Titanium Doped β-Ga_2O_3 Thin Films**, *S Manandhar, A Battu,* ***Ramana Chintalapalle,*** University of Texas at El Paso, USA

Gallium oxide (Ga_2O_3), one among the wide band gap oxides, has drawn the attention of scientific and research community for its fascinating physical, chemical and electronic properties, which can be readily utilized in numerous technological applications. Ga_2O_3 with a band gap (E_g) of ~5 eV is an ideal candidate for utilization in the field of electronics, optoelectronics, spintronics, gas sensing, and ultraviolet photo detectors. Specifically, β-Ga_2O_3 is stable at very high temperatures and has shown to function as oxygen sensor at high temperatures (>700°C). We recently demonstrated improvement of response characteristics time and sensitivity towards oxygen sensing at high temperature using metal doped β-Ga_2O_3. However, a fundamental study of thermo-chemical stability of metal doped β-Ga_2O_3 is quite important to predict the thermodynamic stability and performance of such materials in extreme environments. In this work, we performed a detailed thermal study to understand the effect of extreme environment on titanium (Ti) doped β-Ga_2O_3 (GTO). The GTO films with variable Ti content were deposited by co-sputtering. The real environment condition for sensor (>700°C) application was simulated to understand the effect of temperature on the crystal structure, electronic properties and oxidation states of Ti doped β-Ga_2O_3.

New Horizons in Coatings and Thin Films
Room San Diego - Session F3

2D Materials: Synthesis, Characterization, and Applications

Moderators: Eli Sutter, University of Nebraska-Lincoln, USA, Liping Wang, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences

8:00am **F3-1 Crystallization Kinetics of Photonically Annealed Two Dimensional Materials and Heterostructures**, *R Vila,* Stanford University, USA; *R Rao, B Maruyama,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *E Bianco,* Air Force Research Laboratory, Materials and Manufacturing Directorate/Rice University, USA; *N Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; ***Chris Muratore,*** University of Dayton, USA

Synthesis capability for uniform growth of two-dimensional (2D) materials over large areas at lower temperatures without sacrificing their unique properties is a critical pre-requisite for seamless integration of monolithic van der Waals materials or their heterostructures into novel devices, especially on flexible substrate platforms. Developing effective strategies to synthesize 2D materials, such as MoS_2 and other transition metal dichalcogenides necessitates a fundamental understanding of the thermodynamics and kinetics controlling nucleation and growth processes. To elucidate crystallization mechanisms we utilize *in situ* Raman spectroscopy during photonic crystallization of amorphous 2D films to directly probe the diffusion-limited kinetics while eliminating contributions from factors adding extreme variability to growth mechanisms such as precursor delivery and gas-phase reactions. We employ a high-throughput autonomous experimentation technique to perform studies in rapid succession on the same substrate, while precisely monitoring temperature by analysis of Stokes/Anti-Stokes peak shifts on rigid (SiO_2/Si) or flexible (polydimethylsiloxane or PDMS) substrates. Preliminary results during isothermal heating reveal that nucleation of amorphous 2D MoS_2 occurs very rapidly and the crystallization rate follows an Arrhenius temperature relationship, yielding an energy barrier of 1.03 eV/atom that corresponds to sulfur diffusion. A correlation between crystallization rate and crystal quality was also observed, as the technique allows *in situ* measurement of atomic defect concentrations. materials. Comparison to theororetical results will allow use of the empirically determined activation barrier for diffusion-limited crystallization as a mechanistic fingerprint in TMD compounds with varying degrees of atomic mass-mismatch. Photonically annealed crystalline 2D materials derived from amorphous precursor films demonstrate device-quality performance, enabling correlation of device properties (i.e., lateral photodetectors and others) to the structure, composition and defect density resulting from different crystallization conditions.

8:20am **F3-2 The Application of Pulsed Laser Deposited a-BN for Temperature and Oxidation Resistance of 2D $MoTe_2$ Semiconducting Devices**, ***Benjamin Sirota,*** University of North Texas, USA, United States of America; *N Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *C Muratore,* University of Dayton, USA; *S Krylyuk, A Davydov,* National Institute of Standards and Technology, USA; *A Voevodin,* University of North Texas, USA

Pulsed laser deposition (PLD) of ultra-thin (2-10 nm) amorphous boron nitride (a-BN) films was previously shown to provide a wide band gap insulating material with excellent breakdown and dielectric characteristics [1,2]. The process enables large area coverage at near room temperatures which make it an attractive deposition technique for the use in with two-dimensional (2D) semiconducting materials; such as few monolayer thick transition metal chalcogenides (TMDs). 2D TMDs provide unique physical properties needed for electronic and opto-electronic devices, however they are also prone to degradation by oxidation, especially at elevated temperatures in atmospheric conditions. This study explores the benefit of a-BN for environmental stability of 2D TMDs, using an example of few monolayer thick exfoliated 2H-$MoTe_2$ capped with a PLD-grown a-BN top layer to create a 2D BN-$MoTe_2$ heterostructure. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements demonstrated a significant improvement in chemical stability and resistance to oxidation for BN-$MoTe_2$ hetrostructures as compared to uncoated $MoTe_2$ samples when heating in air up to 300 °C. Both XPS and Raman analysis showed a rapid oxidation and structural degradation for uncapped $MoTe_2$ while BN-$MoTe_2$ demonstrated significant durability after one hour of heating at 100 °C. This was correlated with heating in air experiments with BN-$MoTe_2$ 2D filed effect transistor (FET) devices. Uncapped $MoTe_2$ FET devices heated in air for 1 minute showed a polarity switch from n- to p-type at 150 °C, while BN-$MoTe_2$ devices switched only after 200 °C of heat treatment. Time dependent experiments at 100 °C in air showed that uncapped $MoTe_2$ FET devices exhibited the polarity switch after 15 minutes of heat treatment while the BN-capped device maintained its n-type conductivity for the 60 minutes of the heating exposure. This work demonstrates the effectiveness of an amorphous BN capping layer in preserving few-layer $MoTe_2$ material quality and controlling its oxidation rate at elevated temperatures in an atmospheric environment.

1. Glavin et al, Thin Solid Films, 572 (2014), 245-250.

2. Glavin et al, Adv. Funct. Mater. (2016) 26: 2640–2647.

8:40am **F3-3 A Predictive Thermokinetic Model of Friction in MoS_2**, ***John Curry,*** *A Hinkle,* Sandia National Laboratories, USA; *T Babuska, B Krick,* Lehigh University, USA; *M Dugger, N Argibay, M Chandross,* Sandia National Laboratories, USA

Building on more than a century of concerted effort to understand the friction behavior of 2D materials, we present a thermokinetic model for predicting the shear strength of MoS2 based on energetic barriers to sliding. This model accounts for a wide range of factors underlying the interaction between molecularly thin lamellae, including defects, temperature, crystallite size and commensurability. Findings are supported by results from thermally ramped sliding experiments and molecular dynamics simulations.

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9:00am **F3-4 Supercritical Fluid Assisted Synthesis of V_2O_5/VS_2 Nanocomposites for use in Supercapacitor**, ***Yen-Chun Liu***, *J Ting,* National Cheng Kung University, Taiwan

A novel one-pot Supercritical fluid (SCF) CO_2 synthesis method was used to fabricate V_2O_5/VS_2 nanocomposite. VS_2 was first synthesized using a microwave assisted hydrothermal technique. The obtained VS_2 powders were then mixed with an oxidizing agent and subject to the SCF treatment to form V_2O_5/VS_2 nanocomposites as follows. During the SCF process, the VS_2 was exfoliated to form nanosheets of VS_2 by the SCF CO_2. In the meantime, V_2O_5 nanoparticles (NPs) were formed due to the partial oxidation of the VS_2. The formed V_2O_5 NPs were intercalated into the VS_2 nanosheets also with the assistance of the SCF CO_2. The effects of the SCF condition and the strength of the oxidizing agent on the formation and characteristics of V_2O_5/VS_2 nanocomposites were investigated. Supercapacitor cells were assembled using the resulting V_2O_5/VS_2 nanocomposites as the electrodes. The cells were evaluated using cyclic voltammetry, and electrochemical impedance spectroscopy, and subjected to cycle life and charge-discharge cycling tests.

9:20am **F3-5 2D and Layered Metal Chalcogenide Semiconductors: Growth, Electronic Structure, Light-Matter Interactions**, ***Peter Sutter***, University of Nebraska-Lincoln, USA **INVITED**

Metal chalcogenides have received attention as layered crystals and as 2D materials beyond graphene. Semiconducting chalcogenides show promise for applications in energy conversion and next-generation low-dimensional (opto) electronics benefiting from carrier confinement and other unique characteristics, such as a thickness dependent or anisotropic electronic structure, non-charge based degrees of freedom, and strong light-matter interactions. Here, I discuss recent work using novel high spatial resolution probes to study the properties of 2D semiconductors and their variations on the nanometer scale.

Real-time microscopy provides insight into the microscopic mechanisms governing the bottom-up growth and transformation of 2D semiconductors. Local band structure measurements are used to establish the thickness dependent electronic properties, as well as other key aspects such as the interlayer coupling as a function of layer orientation. Finally, I present nanometer-scale measurements of light-matter interactions in 2D semiconductors, which offer a way to probe and manipulate optical excitations far below the diffraction limit near defects, edges, or engineered interfaces.

10:00am **F3-7 Fabrication and Photocatalytic Application of Functional group Modification of Carbon Nitride Derivatives nanosheets**, ***ChunHung Chen***, *K Chang,* National Cheng Kung University (NCKU), Taiwan

Carbon nitride has recently attracted much attention owing to its visible-light-driven hydrogen evolution capability which is first published in 2009.[1] Compared with 1D-structured melon, which has already been well-studied by other research groups, the melon oligomer and poly (triazine imide) (PTI/Li^+Cl^-) are two promising structures which show a better photocatalytic property. However, there still remains some room for improvements to be done such as increasing the amount of functional groups of carbon nitride, which are known to be active sites during a photocatalytic process. These active sites are regarded as the predominant factor in the carbon nitride series.[2] Herein, two strategies were applied to modify the PTI & melon oligomer for the purpose of enhancing its photocatalytic ability. The first process is by using isopropanol (IPA) and ethanol in distinct heat treatment to accomplish surface functionalization. Solid NMR, FTIR, and EA were used to prove that additional functional groups are successfully linked. Also, the UV-Vis results indicated that the absorption range had a red-shift to a higher wavelength which is due to the change in powder color. For the second process, liquid exfoliation method was used to obtain ultrathin nanosheets in order to enhance its photodegradation ability due to the further increase in surface area and active sites. By considering that the enthalpy of mixing should be minimized, water is considered as the optimal solvent and was applied due to having a similar surface energy to carbon nitride nanosheet.[3] The BET analysis showed that the surface area has significantly increased, which brought about more than five times enhancement in its photocatalytic property. Furthermore, from the photoelectrochemistry measurement, the modified carbon nitride shows the linear relationship as the sensor of Cu ion determination, indicating that our sample is a promising candidate for ion determination in water solution.

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[3] K. Schwinghammer, M.B. Mesch, V. Duppel, C. Ziegler, J. Senker, B. V. Lotsch, J. Am. Chem. Soc., 136 (2014) 1730-1733

10:20am **F3-8 Enhanced Photocatalytic Performance for g-C_3N_4 through the Addition of α-MoO_3 Nanobelts and Mesoporous TiO_2 Beads**, ***Yen Duong***, *J Ting,* National Cheng Kung University, Taiwan

Multi-component photocatalysts based on g-C_3N_4 was synthesized to enhanced the photocatalytic performance of g-C_3N_4. Exfoliated g-C_3N_4 was fabricated by heating melamine at 550^0C, followed by the use of hydrogen peroxide (H_2O_2) to exfoliate bulk g-C_3N_4. Mesoporous TiO_2 beads were prepared using a two-step process. α-MoO_3 nanobelts were made by hydrothermal method. Three groups of binary-component photocatalysts of TiO_2/g-C_3N_4, TiO_2/ α-MoO_3 and α-MoO_3 / g-C_3N_4 having various compositions were then made. Based on the performance of these binary-component photocatalysts, TiO_2/ α-MoO_3/g-C_3N_4 ternary composite photocatalysts were synthesized. The photocatalytic performance of all the single-binary and ternary component phtotocatalysts were evaluated by degrading methyl blue under both UV and visible light irradiations.

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10:40am **F3-9 Fabrication of Nanostructured MoS_2 Thin Films on Porous Silicon Substrate for Ammonia Gas Sensing Properties**, *S Sharma, A Kumar,* ***Davinder Kaur***, Indian Institute of Technology Roorkee, India

In the present work, we have fabricated the molybdenum disulphide (MoS_2) nanostructure thin films on the 2×2 cm^2 porous Silicon (100) substrates using DC magnetron sputtering technique. Porous silicon was fabricated by the metal-assisted chemical etching of the Si (100) substrate using HF as etchant solution. The structural and surface morphological properties of MoS_2 nanostructure thin films were systematically studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM) and Raman spectroscopy. The ammonia gas sensing properties of porous MoS_2 thin film sensor shows the remarkable response with fast response/recovery time towards the 100 ppm ammonia gas (NH_3) at the room temperature. These sensing performances suggest porous MoS_2 thin films a potential candidate for room temperature sensor devices. The sensing mechanism and response behaviour towards ammonia gas was also discussed in detail.

11:00am **F3-10 Wettability, Sructural and Optical Examination of Sputtered Zirconium Oxide Thin Films**, ***Uttkarsh Patel***, McMaster University, Canada*; P Dave,* Gujarat forensic science university, India*; K Chauhan,* Charotar University of Science and Technology (CHARUSAT), India*; S Rawal,* McMaster University, Canada

Zirconium oxide films were deposited by reactive magnetron sputtering at different sputtering pressure values of 0.4Pa, 0.7Pa, 1.0Pa and 1.5Pa. The effect of sputtering pressure on structural, hydrophobic and optical properties of deposited zirconium oxide thin films is reported in this research work. Due to this variation during thin film growth, it is observed that zirconium oxide thin films formed has monoclinic phase with (111) orientation. Its intensity increase with increase in sputtering pressure from 0.4Pa to 1.5Pa. The contact angle values of 96º for water and 44º for aniline were observed at 0.4Pa. The band gap of zirconium oxide films increases as sputtering pressure is increased from 0.4Pa to 1.5Pa.

11:20am **F3-11 Synthesis and Characterization of Molybdenum-based Thin Films for Flexible Electronics**, *T Jörg,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; D Music,* RWTH Aachen University, Germany*; R Franz,* Montanuniversität Leoben, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*; J Schneider,* RWTH Aachen University, Germany*;* ***Christian Mitterer***, Montanuniversität Leoben, Austria **INVITED**

Mechanical failure of thin metal films on compliant substrates presents a considerable challenge in the development of flexible electronics. In particular, this applies for sputter-deposited molybdenum thin films, which are frequently used as back electrode materials in flexible solar cells, as electrode materials in flexible piezoelectric micro- and nano-electromechanical systems, in the metallization of thin film transistors, e.g. as gate and source/drain electrodes, as adhesion promotion, diffusion barrier and ohmic contact layers due to their attractive combination of functional properties.

Within this work, different strategies for film synthesis and alloying are proposed to design Mo-based thin films on polymer substrates with enhanced fracture resistance. The fracture properties of pure Mo films can be tailored by their compressive residual stress state, enabling a considerable improvement in crack onset strain. Moreover, both fracture strength and crack onset strain of Mo thin films scale with their thickness. Since all Mo thin films exhibit a distinctly brittle fracture behavior, alloying with Re and Cu was explored as feasible concept to overcome their poor ductility. A substantial toughness improvement with rising Re content up to the solubility limit was obtained, which stems from the increased plasticity and bond strengthening in the Mo-Re solid solution. Furthermore, it was observed that Cu addition to Mo results in an increased ductility, which was rationalized by the low shear resistant bonding in the Mo-Cu solid solution. In general, both concepts proved to be promising in order to enable utilization of Mo based thin films in flexible electronics.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 1-3 - Session H1

Spatially-resolved Characterization of Thin Films and Engineered Surfaces

Moderators: Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Michael Tkadletz, Montanuniversität Leoben

9:00am **H1-4 Spatially Resolved Depth Profiling Of Residual Stress By Micro-Ring-Core Method**, ***Marco Sebastiani***, Roma TRE University, Italy

In this presentation, we will show some fundamental advances to the depth profiling capabilities for micro-scale ring-core focused ion beam (FIB) method. A new model, based on a single variable eigenstrain influence function approach, is developed and validated by comparison of FIB-DIC experimental results with synchrotron nano-diffraction experiments on the same reference sample (TiN PVD coating deposited by MS-PVD).

To this end, we revisit and revise the classical integral method proposed over quarter of a century ago. Instead of focusing on the residual stress that varies with every increment of hole-drilling, we concentrate on the reconstruction of eigenstrain, the invariant source of residual stress, and establish that the eigenstrain depth profile can be reconstructed by compact direct calculation, obviating the need for matrix formulation of the integral equation.

The method's sensitivity and robustness is further improved by the rational combination of multiple datasets obtained using different ring-core diameters. In this way, the approach has been shown to achieve depth resolution better than 50nm, opening up the prospect of reliable residual stress analysis at the nanometer scale.

9:20am **H1-5 Quantitative Depth Profiling from the First Nanometers Down to the Substrate within Minutes using RF GD-OES**, ***Philippe Hunault***, HORIBA Instruments, USA*; M Chausseau, K Savadkouei,* HORIBA Scientific, USA*; P Chapon, S Gaiaschi,* HORIBA Scientific, France

Glow Discharge Optical Emission Spectrometry (GD-OES) provides direct measurement of the chemical composition of materials as a function of depth and can be used to characterize various coatings, made of both thin and thick layers, conductive or non-conductive materials.

It consists in a pulsed radiofrequency glow discharge plasma source that is sputtering a large area of the material of interest and real time detection by a high resolution optical spectrometer of the sputtered species excited by the same plasma. All elements from H to U can be measured using this technique.

With its capability to perform depth profiling with a nanometric resolution and to go up to 150 µm deep into the sample within few minutes, GD-OES is an ideal tool to evaluate depth profiles on materials and to study interfaces between layers, diffusion processes or to optimize coatings processes. Many elements can be analyzed simultaneously, including Oxygen, Hydrogen, Deuterium, Carbon, Fluorine, Sulfur, Lithium… GD-OES is a versatile tool to study materials that complements other techniques such as XPS and SIMS.

Recent developments made possible using GD-OES for the direct determination of layer thickness and also for the analysis of odd shape samples.

Results obtained on various nm thin and thick coatings will be shown during this presentation: The use of RF GD-OES for the optimization of electroplating processes will be described with depth profiles of coatings on both inorganic and organic substrates and the direct determination of thickness using Differential Interferometry. How this technique can be used for Quality Control for the Aluminum packaging industry will also be shown with the help of real examples. Finally, we will discuss the latest results obtained for the characterization of the various coatings applied on drill bits which is a challenging sample by its shape and size.

9:40am **H1-6 Analysis of Thin Film Surface Stress Distribution using Raman Spectroscopy near Cohesive Cracks During Bending Tests**, ***Newton Fukumasu***, *G Francisco, R Souza,* University of São Paulo, Brazil

Stress distribution in a thin film is an important tool to control system performance in many applications. Usually, compressive stresses improve the wear behavior of the system, but the higher the compressive stresses, the higher the probability of coating adhesive failure. Stress calculation is based on the measurement of strain and present several pitfalls, frequently related to the elastic constants selected to correlate stains and stresses. This work aims contributing with the analysis of these constants in micro-Raman spectroscopy analyses. To this end, this work presents a technique to study the spatial distribution of the stresses at a coating surface near cracks generated by tensile stresses during bending tests. Literature reports that the stress state varies as a function of the distance from coating cohesive cracks, indicating that stresses are zero near the cracks. Local strains were measured based on the shift of the Raman spectrum. Measurements were conducted for a coated system composed of metal nitride films, deposited by sputtering, and ductile substrates. The stress evolution during the bending tests was reproduced numerically by means of simulations using the finite element method (FEM). Results were analyzed based on the correlation of the shift of the Raman spectrum and the stress evolution in bending tests, both during and after the test.

10:00am **H1-7 *In situ* Nanomechanical Characterization of Transition Metal Carbides**, *M Chen,* ETH Zurich, Laboratory for Nanometallurgy, Switzerland*; D Sangiovanni,* Linköping University, IFM, Germany, Sweden*; J Wheeler,* ETH Zurich, Laboratory for Nanometallurgy, Switzerland*;* ***Suneel Kodambaka***, *G Po,* University of California Los Angeles, USA **INVITED**

Refractory transition-metal carbides, owing to a mixture of ionic, covalent, and metallic bonding, exhibit high hardness, high stiffness, good resistance to wear, ablation, and corrosion, high-temperature mechanical strength along with good electrical conductivity. While these materials are exceptionally hard, their room-temperature structural applications have been limited by their brittleness. However, existing literature suggests that these carbides are not intrinsically brittle. Our recent nanomechanical tests carried out on sub-micrometer size carbide crystals have shown that these transition-metal carbides can undergo plastic deformation at room temperature.

In this talk, I will present results from our studies focused on understanding the mechanical deformation mechanisms operating in NaCl-structured TaC single-crystals. Using a combination of *in situ* scanning-electron-microscopy-based uniaxial micro-compression tests, *ab initio* molecular dynamics simulations conducted at temperatures up to 873 K, along with finite-element based modeling of discrete dislocation and crack dynamics, we determine the mechanisms leading to slip, dislocation nucleation and motion, and crack formation in TaC single-crystals. Our results provide new insights into the role of crystal orientation, size, and temperature on the correlation between plasticity and fracture in this class of materials.

Topical Symposia
Room Royal Palm 4-6 - Session TS1
Thermal and Kinetic Spray Deposition

Moderators: Andrew Vackel, Sandia National Laboratories, USA, Charles Kay, ASB Industries, Inc., USA

8:00am **TS1-1 Latest Developments for Turbomachinery Coatings*, Kirsten Bobzin**, L Zhao, F Linke, S Wiesner, B Yildirim, T Liang, M Welters,* Surface Engineering Institute - RWTH Aachen University, Germany **INVITED**

In accordance with the key objectives -higher efficiencies and lower emissions- components of modern turbomachinery systems, i.e. stationary and rotating blades, are subject to very high demands, which need to be fulfilled among others with innovative coating solutions. Protective coatings are, therefore, the state of art to ensure functionality of turbomachinery components with prolonged life times.

In this presentation, some of research work of Surface Engineering Institute of RWTH Aachen University on the above-mentioned coating solutions is introduced summarily. Firstly, an erosion resistant coating based on nanocomposite nitride (Ti,Al,Si)N applied by means of high speed physical vapor deposition (HS-PVD) for protection of gas turbine compressor blades and a thick erosion resistant Ni-based composite coating applied by deposition brazing for protection of steam turbine blades will be presented. Subsequently, EB-PVD thermal barrier coatings (TBC) based on different pyrochlore zirconates with multilayer coating architecture will be demonstrated. Furthermore, a highly porous, plasma sprayed TBC, based on Gd_2O_3- Yb_2O_3 co-doped ytrria-stabilized zirkonia (YSZ), will be introduced. Finally, two oxidation protective coatings for γ-TiAl substrates will be subjected. The first one is an amorphous (Al,Cr)ON coating deposited by means of HS-PVD. The second one is a plasma sprayed coating with a Ti-diffusion barrier interlayer. All of the coatings show promising results with respect to their intended functions.

8:40am **TS1-3 Repair of Nickel Base Superalloys by Cold Spray*, Robert Vaßen**, R Singh, T Kalfhaus, G Mauer, O Guillon,* Forschungszentrum Jülich GmbH, Germany*; J Gibmeier,* Karlsruhe Institute of Technology (KIT), Germany **INVITED**

In the cold spray process, deposition of particles takes place through intensive plastic deformation upon impact in a solid state at temperatures well below their melting point. The high particle impact velocities and corresponding peening effects can lead to high compressive residual stresses in cold spray coatings. This can be advantageous with regard to mechanical properties as fatigue life and hence, cold spray seems to be an ideal process for repair applications. In this study, Inconel 718 powder particles were cold-sprayed on Inconel 718 substrates by using nitrogen gas for an application as a repair tool for aero engine components. First, velocities of the cold sprayed particles have been determined as a function of process conditions and particle size. Critical velocities have been determined considering the deposition efficiencies.

Furthermore, the magnitude of the residual stress and its distribution through the thickness of the cold-sprayed coatings were measured by using the hole-drilling and the bending methods. Mainly compressive residual stresses were observed in cold-sprayed Inconel 718 coatings. Accumulation of residual stresses in the coatings is highly affected by peening during deposition and it decreases with increase in thickness. It has been observed that the bond--strengths of cold-sprayed Inconel 718 coatings are highly influenced by coating thickness and residual stress states of the coating/substrate system. A detailed discussion will be given.

In addition, also further results on cold spraying different Ni base superalloys on CMSX 4 type substrates will be presented and discussed. Especially the influence of substrate temperature will be highlighted.

9:20am **TS1-5 Multi-layer Metallization of Polymer Materials via Thermal Spray*, Andrew Vackel**, M Smith, A Miller,* Sandia National Laboratories, USA*; B Peter, B Post,* Oak Ridge National Laboratories, USA

With the emerging prevalence of 3D printed polymer materials for rapid prototyping, there is an increasing demand for a similar ease and quickness in producing metallic and multi-material components. One such approach is through the metallization of printed polymer parts using thermal spray, where thick deposits can be quickly and economically deposited. However, technical challenges include management of residual stress of the deposit, assessing the adhesion strength of sprayed metal onto polymers, and potential thermal degradation of polymer substrates from molten droplet impingement during spraying.

This presentation will discuss the methodologies used to accomplish successful metallization of polymer substrates (e.g., ABS, HDPE) including *in-situ* measurements of substrate deflection for calculation of residual stress, mechanisms and quantification of adhesion between polymers and sprayed metal, and optimization of spray processing and material layering.

9:40am **TS1-6 Dielectric Ceramic Thick Films produced via Aerosol Deposition*, EricA. Patterson**,* ASEE Postdoc, US Naval Research Lab, USA*; S Johnson, E Gorzkowski,* U.S. Naval Research Laboratory, USA

The aerosol deposition (AD) method is a thick-film deposition process that uses ~500 nm particle size oxide powders to produce 95% dense films, up to several hundred micrometers thick with nanometer sized grains. The deposition can be performed on a variety of substrates because bonding and densification between the film/substrate interface are thought to be facilitated by local temperature rise, high pressure, particle fracture, and chemical bonding during deposition, which leads to the nano-grained microstructures created at room temperature. In this work, we present film characterization results of depositing dielectric and ferroelectric materials using aerosol deposition. Film properties will be compared when adjusting process parameters such as varying flow gas rate, gas type, and substrate material. Further characterization will be performed by changing annealing conditions, and electrode application.

10:00am **TS1-7 Tribological Properties of Cold Sprayed Metal Matrix Composite Coatings*, Richard Chromik,*** McGill University, Canada **INVITED**

Metal matrix composites (MMCs) provide a significant advantage for their tribological properties compared to pure metals. There is a long history of metal-ceramic composites for enhancement of load carrying capacity and solid lubricating composites for friction reduction. Both type of composites will generate 'tribofilms' that help to reduce wear and control friction. One may also engineer MMCs with both hard phase and solid lubricants.

There are many methods of manufacture for MMCs in bulk form and a few options for manufacturing them as coatings. Cold spray is one such coating deposition technique that has received increased attention in recent years. Researchers have developed a wide range of MMC coatings by cold spray, typically basing materials selection on metal-ceramic or metal-solid lubricant MMCs made by traditional methods. Recent work from our group has included cold spray coatings of Al-Al_2O_3, Ti-TiC, Cu-MoS_2 and Ni-WC.

In this presentation, cold sprayed MMCs will be discussed in terms of their 'sprayability' and, for successful coating systems, their tribological properties. Coatings are tested in sliding wear and sometimes fretting wear test conditions. For both cases, post-characterization of cross-sectioned wear scars reveals microstructural evolution near surface leading to formation of tribofilms that provide wear resistance and friction control. Structure and properties of the tribofilms are determined with SEM, TEM, EDS, Raman spectroscopy and nanoindentation. Tribofilms are found to be mixtures of the two components in the MMC, but with finer microstructure and some level of oxidation that leads to higher hardness. The tribological performance of cold sprayed MMC coatings, similar to MMCs made by other methods of manufacture, depends significantly on the nature of the third bodies formed by the wear process. However, due to the cold-worked nature of cold sprayed metals and the lack of full metallurgical bonding in some coatings, some differences were observed and will be discussed.

10:40am **TS1-9 Assessment of Magnetic Orientation of Barium Hexaferrite Thick Films Deposited by Aerosol Deposition with *in situ* Magnetic Field*, ScooterD. Johnson**,* Naval Research Laboratory, USA*; D Park,* Korean Institute of Material Science, Korea*; A Hauser, S Ranjit, K Law,* University of Alabama, USA*; H Newman, S Shin, S Qadri, E Gorzkowski,* Naval Research Laboratory, USA

Devices utilizing magnetic materials such as frequency selective limiters, circulators, inductors, and filters are critical components in many of today's electronics [1]. The need for ferromagnetic materials in these devices poses many difficulties for minimizing device size, weight, and cost. One issue that hampers integration of ferromagnetic materials is the high-melting temperature of the ferrite compared with the low-melting temperature component structure [2]. Furthermore, the need for low-loss and narrow bandwidth operation adds another significant barrier to the advancement of integration of ferromagnetic materials into these device structures.

The high-frequency operation regime and strong uniaxial anisotropy of barium hexaferrite ($BaFe_{12}O_{19}$, BaM) makes this material particularly interesting to utilize as an oriented film for microwave components. In this study, we characterize BaM films deposited onto sapphire substrates by a room-temperature thick-film growth technique called aerosol deposition.

We perfomed alternating gradient magnetometry depth studies on a series of as-deposited films that show a variation in magnetization with depth. Cross-sectional SEM images indicate laterally uniform film density. Electron dispersive spectroscopy of the interfacial region suggest significant Al_2O_3 mixing into the film volume. Fe XPS spectra indicate a change in peak weighting as a function of thickness, possibly indicative of modified structure or oxygen incorporation due to Al incorporation.

To explore the possibility of magnetically orienting the films we deposited additional films in the presence of a 4 kOe static magnetic field. We report VSM, FMR, and XRD results of these films as-deposited and after post-deposition sintering at temperatures from 700C to 1000C.

The films deposited in the field show an increased saturation magnetization and remanence compared to the films deposited with no applied field. XRD results of all of the films in this study suggest good crystallinity. Rietveld refinement of the data also suggests that the films deposited in the field presence have a smaller unit cell volume compared to films deposited without the applied field. Post-growth sintering increases the crystallite size from about 10 nm to 25 nm. Annealing improves the overall properties of the films further increasing the magentic orientation and saturation.

[1] Adams, J., Davis, L., Dionne, G., Schloemann, E., and Stitzer, S., IEEE Transactions on Microwave Theory and Technology, **50** (2002), No. 3, pp.721.

[2] Johnson, S., Newman, H., Glaser, E., Cheng, S.-F., Tadjer, M., Kub, F., and Eddy, C., IEEE Trans. on Magnetics, **51**, (2015), No. 5, pp. 2200206.

11:00am **TS1-10 Development of Repair Methods for Nickel Based Super Alloys using Cold Gas Spray***, **Tobias Kalfhaus**, R Vaßen,* Forschungszentrum Jülich GmbH, Germany

The hot section parts in aviation engines and stationary gas turbines are exposed to extreme environments, where high temperatures and eroding atmospheres lead to oxidation, corrosion and fatigue damage of the inserted parts. As the manufacture of the nickel based superalloys for those high temperature applications is expensive, the repair of worn or damaged parts is from an economic viewpoint desirable, however, usually difficult due to the poor weldability of these alloys.

The coating technology Cold Gas Spray has been tested to repair such worn parts and reduce the maintenance cost. In this process heated and pressurized gas is expanded through a Laval-Nozzle. This leads to a high-speed gas jet and accelerates the powder to supersonic velocities. The operating temperature is relatively low compared to the melting point of the used alloys. The particles hit the substrate, deform and are bonded to the substrate by mechanical clamping and formation of intermixing zones. An oxide free and dense coating is formed. With an increasing coating thickness the stored elastic energy in the coating increases and can lead the delamination of the coating at a critical thickness.

In this study the alloys CMSX-4, Rene 80, Inconel 625, Inconel 713 and Inconel 738 are deposited on single crystalline substrates that are similar to CMSX-4 and polycrystalline Inconel 738 substrates. All used powders are spherical and have a diameter between 5-45 µm. To show different residual stresses that evolve during the coating process curvature measurements were performed on round Inconel 738 samples. Each powder shows different adhesion to the substrate. To characterize the differences adhesion tests were performed.

To reduce residual stresses and increase the critical thickness of the coating a heated stage is tested to investigate the influence of a heated substrate. Additional heat treatments were performed to investigate the change of porosity and microstructure within the coating and at the interface between the substrate and the coating. The evolving microstructures were examined using scanning electron microscopy (SEM) and Electron Backscatter diffraction (EBSD).

11:20am **TS1-11 Microstructure-scale Simulations of High-rate Loading of Porous, Thermally-sprayed Metal Coatings***, **Corbett Battaile**, N Moore, S Owen,* Sandia National Laboratories, USA

The properties of most engineering materials depend on the characteristics of internal microstructures and defects. In metals, these features can include grains in the polycrystalline aggregate, impurities, multiple phases, and in the case of thermally sprayed coatings, significant levels of porosity. The microscopic details of the interactions between these internal defects, and the propagation of applied loads through the body, act in concert to dictate macro-observable properties like strength, conductivity, spall, etc. In order to achieve a comprehensive understanding and control of a material's high-rate properties, the relevant structure-properties relationships must be understood. In this work, we used Sandia's Alegra finite element software [1] to simulate the high-rate loading of metal coatings manufactured by thermal plasma spraying. These simulations include a direct representation of the microstructural details of the material, such that internal features like second phases and pores are represented and meshed explicitly as individual entities in the computational domain. We will discuss the dependence of the high-rate mechanical properties of these materials on microstructural characteristics such as the shapes, sizes, and volume fractions of the second phases and pores. We will also examine the effects of pore collapse on high-rate response, and how the details of the microstructural representation affect the microscopic material response to the applied load. In particular, we will discuss the effects of using "stairstep" (on a cubic finite-element "grid") versus comformal (smooth) interfaces created via Sandia's SCULPT capability in CUBIT [3].

1. <http://www.cs.sandia.gov/ALEGRA/Alegra_Home.html>

2. <http://www.sandia.gov/mst/pdf/LENS.pdf>

3. <https://cubit.sandia.gov/>

11:40am **TS1-12 Simulation and Visualization of the Aerosol Deposition Process***, **EdwardP. Gorzkowski**, S Johnson, T Martin, R Saunders,* U.S. Naval Research Laboratory, USA*; A Borgdorff,* U.S. Naval Academy, USA*; D Schwer,* U.S. Naval Research Laboratory, USA*; E Patterson,* ASEE Postdoc, U.S. Naval Research Laboratory, USA

Aerosol deposition (AD) is a thick-film deposition process that can produce layers up to several hundred micrometers thick with densities greater than 95% of the bulk. Though this process has been used for two decades the precise mechanisms of bonding and densification is still debatable. Therefore, we have used a combination of computational fluid dynamics (CFD) and finite element (FE) modelling and high speed videography to help understand the flight of the particles as well as the interaction of the particle and the substrate. The CFD model results show the flight of particles from the nozzle to just before the substrate. At the point just before impact, the velocity and direction is collected and used to inform the FE model of the flight of the particle. Initially the FE model is run with the parameters obtained from the CFD model but the work is extended to include variations in particle size, velocity, and material to show their effects on the deposition process. The model is developed as full 3-D implementation with symmetric boundary conditions applied when/where appropriate. The particle and substrate materials are independent and each is varied between Al_2O_3, SiC, and float glass. Each material is simulated using a Johnson-Cook constitutive model, which includes plasticity, damage initiation and evolution, and failure. The mechanical properties of each material are taken from bulk properties. The particle velocity is varied from 100 m/s to 300 m/s with sizes between 0.5 µm and 1.5 µm. The bounds were informed by the results of the CFD analysis. High-speed videography will help validate this model and to better understand the process as a whole.

Coatings for Use at High Temperatures
Room California - Session A1-2

Coatings to Resist High Temperature Oxidation, Corrosion, and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Shigenari Hayashi, Hokkaido University, Sebastien Dryepondt, Oak Ridge National Laboratory, USA

1:30pm **A1-2-1 Effect of Pre- and Post-Coat Processing on the Fatigue Life of Coated Disk Alloys**, ***James Nesbitt***, *T Gabb, B Puleo,* NASA Glenn Research Center, USA; *R Miller,* Vantage Partners, USA **INVITED**

Increasing temperatures in aero gas turbines is resulting in oxidation and hot corrosion attack of turbine disks. Since disks are sensitive to low cycle fatigue (LCF), any environmental attack, and especially hot corrosion pitting, can seriously degrade the life of the disk. Application of metallic coatings is one means of protecting disk alloys from this environmental attack. However, since LCF is sensitive to surface conditions, pre- and post-coat processing can have a significant effect on the LCF life of coated bars.

Various pre-and post-coating conditions were examined with a Ni-45wt.% Cr coating applied by High-power impulse magnetron sputtering (HiPiMS) to a Ni-based disk alloy. Initial pre-coat surface conditions examined a grit blasted surface. Later pre-coat surface treatments involved wet blasting, two shot peening levels (8N-200% and 16N-200%) and a highly polished surface. Post-coat treatments involved two shot peening levels (4N-100% and 16N-200%) and a post-coat diffusion anneal in high purity Ar or a low PO_2 environment to encourage chromia scale formation. Half of the coated and uncoated bars were LCF tested at 760°C without further environmental exposure to evaluate the pre- and post-coat treatments. The second half of samples were either oxidized for 500 hours at 760°C in air, hot corroded for 50 hours at 760°C in air using a Na_2SO_4-$MgSO_4$ salt, or subjected to both exposures. Results of the LCF testing and post-test characterization of the various coatings will be presented and future research directions discussed.

2:10pm **A1-2-3 High-temperature Oxidation Resistance of Chromium-based Coatings Deposited by DLI-MOCVD for Enhanced Protection of the Inner Surface of Long Tubes**, ***Alexandre Michau***, CEA, France; *F Maury,* CIRIMAT, France; *F Schuster, J Brachet, E Rouesne, M Le Saux,* CEA, France; *R Boichot, M Pons,* SIMaP, France

For nuclear safety issues, there is an international effort to develop innovative "Enhanced Accident Tolerant Fuels" (EATF) materials. EATF cladding tubes are of particular interest because these components constitute the first barrier against radioactive fission species dispersal in case of accidental scenario such as LOCA (Loss of Coolant Accident). One of the EATF development objectives is thus to improve drastically the high-temperature steam oxidation resistance of the cladding tubes in LOCA situation (temperature up to 1200°C, water steam environment…). Let us recall that the actual nuclear fuel cladding tubes are made from Zr-based alloys (1cm in diameter, 0.6mm thick and more than 4m long).

Several alternatives for outer wall protection have been proposed worldwide but there is currently no solution for the inner wall protection. Upon LOCA transients, the fuel cladding may experience ballooning and burst due to the inner pressure and the high temperature achieved. Then, its internal surface can be exposed to steam environment at high temperature, leading to fast inner oxidation and other secondary degradation effects, which induce significant embrittlement and degradation of the claddings.

In order to resist to this harsh environment, Cr-based coatings deposited by low pressure DLI-MOCVD (Direct Liquid Injection of MetalOrganic precursors) have been investigated. These hard coatings could also be of use in high-temperature oxidative and corrosive environment such as in aeronautics and other industries to protect components with 3D complex geometries.

The process has been optimized to ensure a thickness uniformity along the tube through experimental studies coupled with numerical modeling of the reaction mechanism and the whole deposition reactor. Thanks to a suitable chemistry of the Cr precursor, bis(ethylbenzene)chromium, different coatings were deposited including: metal Cr, chromium carbides Cr_xC_y and mixed carbides $Cr_xSi_zC_y$.

The high-temperature behavior of these Cr-based coatings under oxidative atmospheres has been studied: HT XRD, TGA and various oxidation tests including pure steam environment followed by water quenching at room temperature to be representative of LOCA situations. Amorphous Cr_xC_y coatings showed the most promising properties. The results are discussed in terms of oxidation mechanisms and protection of the fuel claddings inner surface deduced from fine characterizations of the samples before and after the tests.

2:30pm **A1-2-4 A New Process to Produce Localized Chrome Coating and Platinum-Modified Chrome Coating for Protection against Type II Hot Corrosion**, ***Zhihong Tang***, *J McConnell, K Garing, S Sweeney,* Praxair Surface Technologies, Inc., USA

With increasing operating temperatures and more severe environments in today's gas turbine engines, there is a need for a localized chromium diffusion coating for protection against type II hot corrosion and stress corrosion cracking. Conventional pack and vapor phase chromizing process have their limitations of applying such a local chrome coating. Masking for these processes is costly and often unsatisfactory. Therefore, pack and vapor phase chromizing process typically coat the entire part surface and then require undesirable post-coating treatment to remove excess chrome coating from locations where it is unwanted.

This presentation will discuss a new slurry based process that produces a localized chromium diffusion coating on the selected regions of gas turbine components in a controlled and accurate manner. No post-chromizing treatments such as machining or chemical treatment are required to remove excess chrome coating in comparison to conventional process. The resultant coating chemistry and microstructure meet the OEMs' specifications. Other advantages of this new process include capability to coat large parts, and achieve uniform coating on parts having complex geometries such as shank and fir-tree root of turbine blades. This new slurry based process has been in production at Praxair Surface Technologies since 2015 yielding robust consistency in coating thickness and chemistry.

Based on this localized chrome coating technology, a platinum-modified chrome (PtCr) coating is under development. The addition of platinum can further enhance the resistance of chrome coating to type II hot corrosion attack. The PtCr coating process and its compatibility with other coating processes will be discussed.

2:50pm **A1-2-5 Characterization of Films Fabricated on AZ31 Magnesium Alloy by Heat Treatment and Immersion Methods**, ***Hyunju Jeong***, Pohang Iron and Steel Company (POSCO), Republic of Korea

There has been considerable interest in the use of magnesium and magnesium alloys because of their outstanding properties, although their low corrosion resistance inhibits widespread applications. Therefore, many studies have been carried out to investigate the corrosion behavior of magnesium and magnesium alloys. Various coating techniques have also been proposed to improve their surface properties and corrosion resistance.

In the present work,thin films fabricated by immersion in solution, deionized water and NaOH solution were studied on AZ31 magnesium alloy subjected to heat treatment**.** The films were grown by active reactions at the interface of the magnesium alloy and the solution due to the high temperature of the substrate. Surface morphologies showed that the surface of the magnesium substrates was covered by dense films formed in the initial stages of immersion. The results revealed that the surface structures were different from those of films grown by simply immersing in aqueous solution. Cross-sectional results showed that the films formed in NaOH solution with heat treatment were denser than those grown by DI water immersion. X-ray photoelectron spectroscopy results indicated that the films fabricated by immersion in solution with heat treatment were mostly composed of MgO and $Mg(OH)_2$ in both the outer and inner layers. Potentiodynamic polarization measurements revealed that the thin films could improve the surface properties, acting as passive layers.

3:10pm **A1-2-6 Degradation Processes of LSM Based Interconnector Coatings under the Conditions of Pressurized Steam Electrolysis**, ***MariadelMar Juez Lorenzo***, *V Kolarik, V Kuchenreuther-Hummel,* Fraunhofer ICT, Germany; *M Pötschke, D Schimanke,* Sunfire GmbH, Germany

To ensure energy for mobility in a post-fossil future, power-to-liquids converting electric power from renewable energy sources into liquid fuels is one of the approaches that have attracted attention. The steam electrolysis used to split water to hydrogen and oxygen is run under pressure up to 30 bar at temperatures around 850°C in order to achieve a high efficiency of the process. The impact of such severe conditions on the interconnector materials and coatings designed to retain the evaporating chromium is a crucial issue and needs detailed understanding to ensure a reliable operation.

Coatings of the type La-Sr-Mn oxide (LSM) were deposited on the interconnector material Crofer 22 APU by thermal spraying and by roll coating, the latter as a cost-efficient method. The samples were exposed in laboratory test autoclaves to 850°C and 30 bar in 100% water vapor up to 1000 h and in pure dry oxygen up to 3000 h, both representing the opposite extremes of the possible process atmospheres.

The LSM coating shows in water vapor a grain coarsening after 1000 h as well as a separation of grains with higher La content accumulated in the surface area and grains containing Mn in the interface area. Cr is detected very weakly in the areas with high La contents. In water vapor the oxide scales on the interconnector material with LSM coating are notably thinner than on the uncoated material. However, the LSM coating deposited by roll coating decomposes with the time to a coarse-grained lanthanum-rich phase in the surface area as well as in vicinity of the oxide scale and to a manganese-rich phase concentrated between them. The thermally sprayed LSM coating is more efficient in leading to thinner oxide scales, probably to its higher density. Additionally, it shows a less pronounced separation into the two phases.

After exposure to pure oxygen the LSM coating exhibits a homogeneous morphology with higher porosity in the case of the roll coating than for thermal spraying. Cr stemming from evaporation was found in the whole LSM coating when deposited by rolling and concentrated on the coating surface when thermally sprayed. The phases binding the Cr were identified by X-ray diffraction. After 1000 h the semi-conducting $LaCrO_4$ and $SrCrO_4$ are formed and after 3000 h $CrMn_2O_4$, which exhibits an electrical conductivity an order of magnitude higher than that of Cr_2O_3. The degradation processes influence the electrical conductivity of the chromium barrier coating.

3:30pm **A1-2-7 The Hot Corrosion Resistance of Hot-dip Aluminized Low Carbon Steel with Nickel Interlayer under Static Load**, ***Huan-Chang Liang***, *C Wang,* National Taiwan University of Science and Technology, Taiwan

The failure mechanism of hot-dip aluminized (HDA) low carbon steel with nickel interlayer under static loading was studied. The nickel interlayer was plated using electric method with a current density of 1.8 A/cm^2 for 10 minutes in Watts bath, followed by hot-dipped in molten pure aluminum (> 99.5 %) for 10 seconds at 700 °C. The specimens were smoothly deposited with 2 mg/cm^2 of $NaCl/Na_2SO_4$ salt mixture, with a portion of 50/50 wt. %. The tensile test with hot corrosion, induced by salt mixture, was carried out by applying a static load at 750 °C. The results show that the intermetallic layer of Ni/Al exhibits great adhesion and formability while the elongation of gauge length rising to 7 percent. Owing to the inter-diffusion between Ni/Al, the intermetallic layer gradually changes to laminar structure with higher nickel content which also contributes to enhance the performance. Meanwhile, hot corrosion induced by salt mixture reduces the amount of aluminum of the outer layer and lowers the thickness of Ni/Al intermetallic layer. As the perpendicular cracks formed, the salt mixture penetrate to the interface between substrate and coating layer causing the oxidation of the carbide and accelerating the phenomenon of break away. Overall, the HDA with nickel interlayer on low carbon steel could increase the lifetime about 5 times compared to bare material.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

1:30pm **B4-2-1 Target Race Track Chemistry is Different to What you Think: XPS Findings from Reactive dc and High Power Impulse Magnetron Sputtering Experiments**, ***Grzegorz Greczynski,*** Linköping University, IFM, Thin Film Physics Division, Sweden*; S Mráz,* RWTH Aachen University, Germany*; L Hultman,* Linköping University, IFM, Thin Film Physics Division, Sweden*; J Schneider,* RWTH Aachen University, Germany

It is demonstrated, that high power impulse magnetron sputtering (HIPIMS) of Ti target in Ar/N_2 atmosphere results in the formation of a nitride layer in the center portion of the race track, which is much thicker than during conventional dc process. Evidence comes from XPS *ex-situ* analyses of native Ti target surface chemistry [1][2] as well as from complementary sputter depth profiles, which reveal that, under identical process conditions and with N partial pressure optimized to yield stoichiometric TiN films, the compound layer is a factor of 2.5× thicker during HIPIMS. Even at values too low to yield stoichiometric TiN films on the substrate, the ~ 50 Å thick surface region of the HIPIMS operated target is severely nitrided (N/Ti ≳ 0.9), which is in stark contrast to dc magnetron sputtering where stoichiometric layers can be grown while avoiding target poisoning.[3] TRIDYN simulations of ion/target interactions reveal that such deep N implantation is only possible if N^+ dominates the ion flux to the target during HIPIMS. These results are crucial for an understanding of reactive HIPIMS sputtering processes and finding robust working points necessary to grow high quality functional coatings at acceptable deposition rates.

[1] G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, *J. Vac. Sci. Technol. A* 33 (2015) 05E101

[2] G. Greczynski, S. Mráz, L. Hultman, and J.M. Schneider, *Appl. Phys. Lett*. 111 (2017) 021604

[3] W. D. Sproul, D. J. Christie, and D. C. Carter, *Thin Solid Films* 491 (2005) 1

1:50pm **B4-2-2 Measurement of Residual Stress on TiN/Ti Bilayer Thin Films using Average X-ray Strain (AXS) Combined with Nanoindentation Methods**, ***JiaHong Huang***, *S Lei,* National Tsing Hua University, Taiwan*; H Chen,* National Chiao Tung University, Taiwan

Pure metal interlayers are commonly applied in the hard and protective coatings to relieve residual stress and enhance adhesion on substrate materials. Although extensive studies have been performed in the past two decades, the effect of stress relief by a pure metal interlayer has not been fully understood, mainly due to the difficulty in accurately measuring residual stress in the individual layer of a bilayer coating. Recently we proposed a method combining average X-ray strain (AXS) and the elastic constant determined by nanoindentation (E_{NI}) to accurately measure the residual stress of hard coatings with an uncertainty < 10% [1,2], which provided an effective tool to respectively measure the layer stress in a bilayer coating. Since TiN/Ti is one of the most popular bilayer combinations, TiN/Ti coating was chosen as the model system in this study. The objective of this study was to accurately determine the residual stress in the individual layer of the TiN/Ti bilayer specimens by the newly proposed method. TiN specimens with three different Ti interlayer thicknesses, 50, 100 and 150 nm, were deposited on Si substrate using unbalanced magnetron sputtering. The residual stresses in TiN top layer and Ti interlayer were separately determined by combining AXS and E_{NI}, where AXS was measured using both lab X-ray and synchrotron X-ray sources. The overall stress of the entire TiN/Ti specimen was measured by laser curvature technique. The results showed that the Ti interlayer with thickness larger than 100 nm could relieve residual stress of the bilayer specimen. However, when the interlayer thickness was insufficient (50 nm), the stress of the entire specimen may increase instead of decrease even the interlayer was added. It was found that the Ti interlayer with thickness of 50 nm was subjected to a compressive stress, while interlayers with thickness of 100 nm and above were under a tensile stress. A physical model was developed to describe the stress variation with the interlayer thickness, which could delineate the experimental findings where a switch of stress state from tension to compression occurred in the interlayer at a critical interlayer thickness. In addition, the switch of stress state in the interlayer may be also associated with the stress in the top layer. As the stress in the top layer increases, the interlayer thickness where the transition of stress state occurs will increase.

[1] A.-N. Wang,C.-P. Chuang,G.-P. Yu, J.-H. Huang, Surf. Coat. Technol., 262 (2015) 40.

[2] A.-N. Wang, J.-H. Huang, H.-W. Hsiao, G.-P. Yu, Haydn Chen, Surf. Coat. Technol., 280(2015) 43.

2:10pm **B4-2-3 Challenges and Recent Progress in the Development of Arc Evaporated $(Al_{1-x}Cr_x)_2O_3$ Coatings**, ***Christian Koller***, *A Kirnbauer, V Dalbauer, R Raab,* CDL-AOS at TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

Ceramic Al_2O_3-based coatings have been utilised for technical and functional purpose for decades. Their popularity with respect to protective applicability is based on the excellent combination of mechanical integrity, thermal stability, and chemical resistance. Physical vapor deposition (PVD) belongs to synthesis techniques of choice for industry, as process conditions allow for the utilisation of temperature sensitive substrate materials. Crystalline Al_2O_3 films can be grown at 600 °C and below, but the

phase composition is in many cases dominated by metastable Al_2O_3 polymorphs and not the more favourable thermodynamically-stable corundum (α) structure. Among different alloying elements investigated with respected to their ability to stabilise the α-phase, Cr appears to be the most promising candidate. Only recently studies on $(Al_{1-x}Cr_x)_2O_3$ films were extended to cathodic arc evaporation. In order to develop protective coatings with an optimised property spectrum it is imperative to have a comprehensive knowledge of interdependencies of the synthesis procedure. This in first place includes process parameters and structure-property relationships, but it also implies a profound understanding of arc-induced modifications at the cathode surface and the ability to link these to the coating performance. We therefore study on the structural evolution of $Al_{1-x}Cr_x$-based coatings grown in intermetallic state and their transition to stoichiometric oxides, both as a function of the Cr content and oxygen flow rate, and in further consequence examine cathodes and macroparticles with different compositions. Monolithically-grown and gradient-structured (for which the oxygen flow-rate was gradually increased during the synthesis), coatings were prepared by $Al_{0.75}Cr_{0.25}$, $Al_{0.70}Cr_{0.30}$, $Al_{0.50}Cr_{0.50}$, or $Al_{0.25}Cr_{0.75}$ cathodes and investigated with respect to their mechanical properties, thermal stability and oxidation behaviour. By the example of stoichiometric $Al_{0.70}Cr_{0.30}$-based oxides, the impact of alloying elements on either a promotion of the hexagonal corundum structure the stabilisation of transient phases is discussed and the significance of an optimised microstructure is demonstrated by multilayer architectures containing α-structured $(Cr,Al)_2O_3$ seed layers.

By taking different aspects of the cathodic arc evaporation process into account—i.e., cathode surfaces, droplets, oxide phase formation during synthesis—we could provide a further understanding towards the controlled synthesis of $Al_{1-x}Cr_x$-based coatings and thus introduce new concepts for their industrial application.

2:50pm **B4-2-5 Steel Doctor Blade Deposited by HIPIMS-CrN for Protection Purpose**, ***Jia-Hong Zhou***, *Y Liou, Y Chen, J He,* Feng Chia University, Taiwan

Doctor blade has long been used for printing, tape casting process, thin sheet formation, etc, where corrosion and wear environments are encountered. Relatively few study work is revealed for improving the performance of the blade edge to resist wear and corrosion attack. In addition to the wet processes having been considered for protection purposes, this study focuses on CrN coating by using high power impulse magnetron sputtering (HIPIMS), which provide dense and strong film adhesion. It is anticipated that with this layer, it would be possible to provide improved corrosion and wear resistance for steel doctor blade. Substrate fixturing technique is developed. The microstructure of the obtained HIPIMS-CrN is examined. Results of field test are compared with the laboratory test for the blading performances.

3:10pm **B4-2-6 In-Line HIPIMS-TiNxOy to Produce Colorful Decorative Coatings**, ***Yu-De Liou***, *Y Chen, J He,* Feng Chia University, Taiwan

Many study works based on batch-type PVDs (physical vapor deposition) have been commercialized, as an alternative to wet processes, due to their environment-friendly and color adjustable characteristics, as well as many other features. However, it will be more feasible to use in-line PVD system to produce decorative coatings by taking the advantages of cost-effectiveness, small-piece handling capability and high through-put production.

In the present study, the decorative coatings based on TiNxOy are produced on motorcycle chain plates by using in-line system, where high power impulse magnetron sputtering (HIPIMS) technique is powered. It is found that the obtained coatings are strongly adhered with their color adjustable over a large range (blue, orange, peach red, ocean blue, gem green, champagne gold, violet purple and rosy gold, etc). The color can be controlled by the repeated entering of the tray (substrate holder) into deposition zone as well as the flow ratio of oxygen to argon during deposition. As a whole, the in-line HIPIMS system is feasible for producing high-quality decorative coatings.

3:30pm **B4-2-7 Property of AIP Deposited Thick TiAlN Coating and Application to Actual Steam Turbine for Solid Particle Erosion Protection**, ***Kenji Yamamoto***, *J Munemasa,* Kobe Steel Ltd., Japan*; Y Liang,* National Cheng Kung University, Taiwan*; T Abe,* Toshiba Corporation, Japan*; S Takada, T Takazawa, Y Iwai,* University of Fukui, Japan

Erosion by high velocity solid particle (SPE) can produce a significant damage to high speed-moving aerodynamic objects such as blades for steam turbine or jet engine. SPE can cause a dimensional change and the result is compromising in aerodynamic integrity. Commonly these parts are made of ferrous alloy or light weight Ti alloy and erosion resistance of these metallic materials are not satisfactory. In case of steam turbine blade, mainly magnetite (Fe3O4) particles with relatively large diameter up to 150 um are generated due to the oxidation of inner side of boiler tube and transferred by high velocity steam to the turbine.

High temperature diffusion layer such as boronizing or thermal sprayed metal carbide is commonly used for preventing SPE. But recently, more SPE resistant PVD deposited hard nitride compounds such as TiN[1], TiSiN[2] or TiAlN[3] are in consideration. As the particle diameter becomes larger, it is increasingly difficult to obtain enough SPE resistance with thin coating and at least coating with more than 10um of thickness, preferably more, is necessary. PVD deposited nitride, however, is in large compressive stress and difficult to deposit thick coating particularly on complex shaped parts.

Kobe Steel developed a new magnetically steered cathodic arc source "SFC" which is characterized by a variable control of residual stress of coating. With this new arc source, low-stress and thick TiAlN coatings were deposited and structural and mechanical properties were investigated. TiAlN coatings with different Al compositions were deposited by SFC and erosion resistance was evaluated by MSE method [4] using 50 um alumina particle. It was found that best erosion resistance is obtained at Al composition between around 50 at%. The erosion rate of AIP-TiAlN is more than one order of magnitude smaller compared with conventional surface treatments such as boronizing or CrC thermal spray coating. Thick TiAlN coatings were also applied to fatigue and creep specimens made of 12 mass% Cr steel blade material and effect of coating on fatigue and creep resistance was investigated. The result showed that these properties remained unchanged by TiAlN coating. And finally, the thick TiAlN coating is applied to blades of an operating steam turbine in Japan and now they are in evaluation until the next overhaul.

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[3] Yamamoto et al. "High-velocity particle impact erosion resistance of PVD deposited hard nitride coatings" presented at ITC 2011, Hiroshima

[4] Y. Iwai et al. Lubrication Science Vol.21, No. 6(2009)213226

3:50pm **B4-2-8 Stress Evolution during Cr_2AlC Film Growth**, ***Andrius Subacius***, *A Matthews,* University of Manchester, UK*; M Hans, S Mráz, J Schneider,* RWTH Aachen University, Germany

Cr_2AlC is a compound which belongs to the family of materials known as MAX phase. The general formula that describes this kind of compound can be expressed as $M_{1+n}AX_n$, where M is a transition metal, A is an A group element, and X is either carbon or nitrogen. MAX phase compounds are regarded as promising for certain applications due to some distinctive characteristics, such as being machinable, having good electrical and thermal conductivity and being resistant to thermal shock.

Residual stress in any film can be a major problem affecting the film properties and limiting the thickness to which they can be grown, due to the risk of debonding. Therefore, it is important not only to evaluate the stress value after the film deposition but it is also beneficial to observe the stress evolution during the growth of the film. In this work, we observed the stress evolution of Cr_2AlC films during their growth. The films were deposited by DC magnetron sputtering from 2 or 4 compound targets at an average power density of 5 W/cm^2 each. Depositions were carried on in argon atmosphere at constant pressure of 3 mTorr (0.4 Pa). Substrate temperature was kept constant at 600 °C. Film thicknesses produced were between 2 mm and more than 8 mm. The in situ stress measurements were performed using a Multi-beam Optical Sensor (MOS) system by monitoring the curvature of the substrate and film with an array of parallel laser beams and a CCD detector. Stress values were calculated using Stoney's formula.

The residual stress of Cr_2AlC films was compressive ranging from about -1000 MPa to -200 MPa during the single film deposition process. In the early stages of the film growth the compressive stress is dominant reaching a peak value. As the film grows thicker the compressive stress decreases and becomes nearly constant.

4:10pm **B4-2-9 Composition and Temperature Influence on ZrAlN/TiN Multilayer Structure: In-situ X-ray Scattering during Growth, and Transmission Electron Microscopy Studies**, ***Naureen Ghafoor***, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *H Wang,* Linköping Univ., IFM, Thin Film Physics Div. and Max-Planck-Institut für Eisenforschung GmbH, Sweden; *J Muhammad, L Rogström, J Schroeder,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *D Ostach, N Schell,* Helmholtz-Zentrum Geesthacht, Germany; *J Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

A massive industrial sector uses hard ware resistance thin films for applications involving extreme temperatures and pressures, and to reform energy and cost-efficiency they constantly call for novel and/or improved materials and coating designs. Over the last 8 years [1-5], we have investigated self-organised ZrAlN nancomposites and related nanolaminated structures for such applications. We have shown that high immiscibility of ZrAlN alloys and sufficient mobility during growth lead to formation of nanostructures which possess high mechanical and thermal stability. The composite formation vary upon varying structural design and composition-temperature window and these parameter-space is a focus in this work.

Here, we present in-situ high-energy synchrotron wide angle X-ray scattering (WAXS) during growth of magnetron sputtered $Zr_{0.75}Al_{0.25}N$/TiN and $Zr_{0.5}Al_{0.5}N$/TiN multilayers complemented with structural characterization using cross-sectional transmission electron microscopy of as-deposited films[6]. The films are grown on MgO (001) substrates in Ar/N2 mixture at substrate temperatures between 350 °C- 950 °C. In situ characterization revealed epitaxial multilayer growth simultaneous to complete segregation of cubic-ZrN and wurtzite-AlN in $Zr_{0.5}Al_{0.5}N$/TiN deposited at 950 °C. When deposited at 350 °C, a preferential 002 texture evolve in these high Al containing films with two phase structure in nanocomposite layer with c- ZrAlN and h-AlN-rich phases. Low Al content in $Zr_{0.75}Al_{0.25}N$/TiN results in single phase c-ZrAlN layers with 111 texture when deposited between 350 °C- 675 °C, and dual phase c-ZrN and w-AlN evolve at 825 °C. The composition-temperature windows for dense smooth films and for the formation of advantageous TiZrN phase at the interfaces are determined. In general, 1D-WAXS obtained in post analysis are consistent with the result of lab-scale XRD and 2D-WAXS patterns resembles SAED patterns for all the $Zr_{1-x}Al_xN$/TiN multilayers studied in this work.

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4:30pm **B4-2-10 Self-toughening in the TiAlN System**, ***Matthias Bartosik***, TU Wien, Institute of Materials Science and Technology, Austria; *C Rumeau, R Hahn,* TU Wien, Austria; *Z Zhang,* Austrian Academy of Sciences, Austria; *P Mayrhofer,* TU Wien, Austria

Titanium aluminum nitride has evolved to one of the most well established hard coating systems over the last decades. Its industrial success is mainly based on the superior oxidation and wear resistance as compared to titanium nitride as well as its age hardening ability. Though Ti-Al-N is among the most widely studied thin film materials, up to now scarcely any attention has been paid to its fracture toughness. Here we report on the evolution of the fracture toughness of Ti-Al-N upon ex-situ vacuum annealing [1]. We found that Ti-Al-N ceramic coatings become harder and tougher simultaneously - two material properties which are often mutually exclusive. The exceptional properties are attributed to the formation of a self-organized nanostructure and precipitation of severely distorted B4 AlN with multiple stacking faults and indications of nano-twins that evolve upon annealing. The fracture toughness was evaluated by performing single cantilever bending tests on free-standing, 2 µm thick, sputtered Ti-Al-N coatings. Additionally, cube corner experiments were conducted on coated Al_2O_3 substrates.

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4:50pm **B4-2-11 Load Sensing Characterization of Silicon Oxide Coatings**, ***Tomasz Liskiewicz***, Leeds University, UK; *I Kolev,* Hauzer Techno Coating, Netherlands; *E McNulty, A Neville,* Leeds University, UK

Due to their high transparency, hardness, flexibility, barrier properties and hydrophilic properties [1,2], silicon oxide (SiO_x) coatings have been employed in a variety of industries including pharmaceutical, food packaging, corrosion protection as well as optical and electronic manufacturing [3,4].

In this work, SiO_x coatings were deposited on stainless steel substrates using the PECVD method with hexamethyldisiloxane (HMDSO) as a silicon precursor and oxygen (O_2) as the process gas. The HMDSO/O_2 ratio was varied between 1:1 and 1:36 in order to create coatings with different stoichiometry, and deposition time was varied to produce coatings with a total thickness ranging from 0.46 to 6.44µm. Coatings were characterised for their scratch resistance, nano-indentation hardness and elastic modulus, chemical composition (EDX) and crystallographic structure (X-Ray diffraction).

A dedicated test setup was developed in this study allowing measurement of coatings' insulating properties under mechanical stresses by simultaneous application of direct voltage through electrodes system, and mechanical compressive stress through varied normal load. The results obtained under constant normal load indicated that SiOx coatings are efficient insulators, characterised by electrical resistivity ranging from 1.62 to 9.72 GΩ-cm, sheet resistance from 15.10 to 38.12 TΩ/square and conductivity from 0.10 to 0.62 (GΩ-cm)-1. Moreover, coatings' insulating properties were characterised under ramped normal load, allowing to tune their load sensing capability by correlating applied mechanical stress with electrical response.

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5:10pm **B4-2-12 The Mechanical and Tribological Properties of TiZrNbN and TiZrNbN-Cu Films**, ***Ihsan Efeoglu***, Atatürk University, Turkey; *H Aghdam, A Keles,* Ataturk University, Turkey; *O Baran,* Erzincan University, Turkey; *Y Totik,* Atatürk University, Turkey

">Due to improve friction and wear properties of cutting tools, various films are deposited on high speed tool steel. Transition metal nitride films are common used films for cutting tools. But with the developing technology, transition metal nitride films are inadequate. Therefore, soft metal such as Cu is used to improve the mechanical and tribological properties of transition metal nitrides. So, in this study, TiZrNbN and TiZrNbN-Cu films were deposited under two different working pressure (0.26 Pa and 0.33 Pa) on M2 high speed steel substrate with closed field unbalanced magnetron sputtering (CFUBMS). The microstructure and thickness values were examined with SEM. The chemical composition was determined by EDAX. The crystal phase orientation, grain size and texture coefficient were evaluated by XRD. The mechanical properties and critical load values of the films were obtained by microhardness test and scratch tester, respectively. Tribological properties of films were analyzed with a pin-on-disc tribometer. The hardness values and grain sizes were calculated ranging from 9.5-30 GPa and 17-45 nm, respectively. The atomic contents of Cu were 0.99% and 7.5% at 0.26 and 0.33 Pa working pressures,respectively. The grain size increased with decreasing hardness value and increasing Cu content. The maximum critical load was obtained in the softest film as 75 N. TiZrNbN-Cu films have better mechanical and tribological properties than TiZrNbN films under the same working pressures.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Sunrise - Session C2-2

Novel Oxide Films for Active Devices

Moderators: Marko Tadjer, Naval Research Laboratory, USA, Vanya Darakchieva, Linkoping University, Sweden

1:30pm **C2-2-1 Investigation of Negative Bias Temperature Instability under Illumination on P-type Low Temperature Poly-crystalline Silicon Thin Film Transistors***, **Shin-Ping Huang**, T Chang, A Chu, W Su, W Chen,* National Sun Yat-Sen University, Taiwan*; Y Chen, Y Shih,* National Taitung University, Taiwan*; Y Zheng, Y Wang,* National Sun Yat-Sen University, Taiwan

This work investigates the effect of the negative bias temperature instability (NBTI) (temperature range from room temperature to 100°C) under illumination in p-channel low temperature poly-crystalline silicon thin film transistors (LTPS TFT), employing back-faced 20000 lux white light.

Experimental results show an apparent Vt shift after NBTI with illumination during the stress time since the trapped charge in insulator layer causes the degradation.

Moreover, off current in both of the linear and saturation region shows that the degradation is affected by strong and weak field effect under illumination.

1:50pm **C2-2-2 Mechanism of Reset Process with Varying Compliance Current in High-k Spacer Resistance Random Access Memory***, **Yi-Ting Tseng**, T Chang, W Huang, Y Guo, T Chang, W Chen,* National Sun Yat-Sen University, Taiwan

In this study, a problem of forming voltage increased during device cell scale-down in resistance random access memory (RRAM) has been solved by adding high dielectric constant (high-k) material as a side-wall (spacer) structure. In contrast, a normal side wall material is used low dielectric constant material. Electric characteristic of high-k spacer RRAM shows a great electric behavior and is the same with a normal RRAM. High resistance state (HRS) of reset process of values obviously increased during varying compliance current of set process form 1mA to 10mA in high-k spacer RRAM. However, HRS didn't clearly different change during controlled compliance current in normal RRAM. Varying compliance current of set process is as applying different energy to switch resistance. Then, AC pules was applied to switch resistance for verifying that relationship. AC pulse of rising time was controlled between 10μs to 90μs for applied reset process. As a result, value of HRS increases with increasing rising time. Mechanism of high-k spacer RRAM is dominated by Schottky emission. From intercept and slope of Schottky emission, HRS can be analyzed further for insulator of barrier and dielectric constant.

2:10pm **C2-2-3 Improve Reliability of Complementary Resistive Switching Induced by Carbon Dopant in Indium-Tin-Oxide as The Insulator in Resistive Random Access Memory***, **Chun-Chu Lin**, T Chang, W Chen, Y Tseng, S Huang, H Zheng,* National Sun Yat-Sen University, Taiwan

Among these possible candidates, resistance random access memory (RRAM) is recognized as the most capable of replacing flash memory due to its non-volatility, simple structure, and easy integration into CMOS fabrication. Previous experiments investigate the Complementary resistive switching (CRS) characteristic by co-sputtering indium–tin-oxide (ITO) with oxygen (O_2) gas as the insulator. However, Pt/ITO(O_2)/TiN RRAM device shows poor endurance of CRS I-V characteristic. In this work, double insulator layers are used by co-sputtering ITO with O_2 and carbon to improve endurance of CRS characteristic as the Self-Rectifying Cell (SRC) and also resistance switching (RS) properties of RRAM. The chemical bonds of this Pt/ITO(O_2)/ITO(C)/TiN device was also investigated with FTIR spectrum measurement.Moreover, endurance test was **also** carried out to confirm its RS stability and fast I-V measurement was applied to make sure its CRS I-V curve when giving the pulse. Finally, a conduction model was proposed to clarify the RS characteristics, and support the Pt/ITO(O_2)/ITO(C)/TiN device as appropriate for Self-Rectifying Cell (SRC).

2:30pm **C2-2-4 Study on the Characteristic of Cobalt Silicide Electrode Resistive Random Access Memory***, **Wen-Chung Chen**, T Chang, T Tsai, Y Zhang, S Huang, Y Lin, C Lin, H Zheng,* National Sun Yat-Sen University, Taiwan

Resistance random access memory (RRAM) is one of the promising next-generation nonvolatile memory devices due to its simple metal insulator-metal structure and its ability for high density integration. Furthermore, RRAM also has superior characteristics such as low operation voltage, fast operation speed, and nondestructive reading, and has attracted much interest by many academics and industries. On the other hand, colbalt silicide is popular to use on the semiconductor industry. It can use to reduce the contact resistance. In addition, the Self-alignment process can replace the lithography process by colbalt silicide. In this work, colbalt silicide was deposited as the top electrode, silicon oxide doped hafnium deposited as the translation layer, and the TiN was deposited as the bottom electrode. Though the device shows poor endurance, it has a large memory window by over reset. After reducing the thickness of colbalt silicide, the device shows a great improvement as compared to the device of thick colbalt silicide. Finally, we propose a model to explain the characteristic of cobalt silicide electrode on the resistive switching behaviors.

2:50pm **C2-2-5 Material and Device Engineering for Gallium Oxide Electronics***, **Siddharth Rajan**,* The Ohio State University, USA **INVITED**

The presentation will give an overview of our recent accomplishments and the future outlook for high-performance β-Ga_2O_3 based semiconductor materials and devices. The ultra-wide band gap semiconductor β-Ga_2O_3, is attractive for applications in next-generation high frequency and power switching devices due to availability of large area substrates, large breakdown field, and good electron transport properties. We will first discuss the main research opportunities and potential applications for these devices. This will be followed by an overview of our experimental results on molecular beam epitaxial (MBE) growth of β-Ga_2O_3, β-$(Al,Ga)_2O_3$, and Si doping. We will then discuss our work on growth and characterization of heterostructures based on β-$(Al,Ga)_2O_3$/ β-Ga_2O_3 and the demonstration of modulation-doping in β-$(Al,Ga)_2O_3$/Ga_2O_3 channels. We will then discuss recent our experimental device results on delta-doped and modulation-doped field effect transistors with high current density and transconductance, and discuss their DR, pulsed, and RF performance. We are grateful to Department of the Defense, Defense Threat Reduction Agency (Grant HDTRA11710034), ONR EXEDE MURI program, and the OSU Institute for Materials Research Seed Program for funding.

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3:30pm **C2-2-7 The Ultra-violet Light Effect on the Off-state Current of InGaZnO Thin Film Transistor with the Different Structure***, **Yu-Ching Tsao**, T Chang, Y Tsai, W Su, S Huang, Y Chien,* National Sun Yat-Sen University, Taiwan

In this work, we discuss the ultra-violet (UV) light effect in amorphous $InGaZnO_4$ (IGZO) thin film transistor with different drain metal capping area and different active layer thickness. An asymmetric off-state current of transistors in forward and reverse sweep due to different ultra-violet light exposure region and length. An obvious off-state current can be found as a result of a source barrier lowing causing by UV light exposure near the source side. Different off-state current can also be found in different thickness of IGZO active layers. A model is also introduced to interpret this phenomenon.

3:50pm **C2-2-8 Study on the Characteristics of Device in Copper Ion Movement during Operation Process in Conductive-Bridging Random Access Memory***, **Ming-Hui Wang**, T Chang, Y Tseng, H Zheng, C Wu, S Huang,* National Sun Yat-Sen University, Taiwan

In this experiment, Materials commonly used in semiconductor processes hafnium oxide as the insulating layer, The top electrode is copper, bottom electrode use titanium nitride, Conductive-Bridging Random Access Memory is metal-insulator-metal structure. The divice operational process happen abnormal phenomenon, In the resistance decrease process (SET) will first decrease after increase and then decrease until Low Resistance State similar to the negative differential resistance,and this feature is closely related to CBRAM conduction mechanism,because copper ion diffusion to the insulation lead to dielectric constant change,and then condition similar negative differential resistance phenomenon.

4:10pm **C2-2-9 The Degradation Mechanism of Tungsten Electrode on HfO_2-based Resistance Random Access Memory (RRAM)**, ***Hao-Xuan Zheng***, *T Chang, T Chu, M Wang, C Lin, C Yang,* National Sun Yat-Sen University, Taiwan

In this study, using tungsten as the role of the electrode in Resistive Random Access Memory (RRAM) has good characteristics. In addition, on/off ratio achieves two orders, and the 85°C Retention test also has a very good stability. However, after a number of the pulse cycle, there has a significant degradation in this kind of device, which is an uncommon phenomenon from the RRAM which electrode is made by inert elements such as platinum. RRAM can cause significant effects on endurance and retention due to the difference in the electrode material. By clarifying the switching mechanism and conduction current fitting, we can find that the on state conduction mechanism is transformed from Poole-Frenkel emission to Schottky emission. In addition, we use the Energy Dispersive X-Ray Spectroscopy (EDS) analysis and proposed a physical model to explain the main cause of degradation, due to oxygen ions diffusing to the electrode.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 1-3 - Session H2

Advanced Mechanical Testing of Surfaces, Thin Films and Coatings

Moderators: Benoit Merle, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Marco Sebastiani, University of Rome "Roma Tre"

1:30pm **H2-1 In Situ Observation of Strain Transfer and Crack Formation in Evaporated and Printed Thin Films and Devices on Compliant Substrates**, ***Patric Gruber***, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WBM), Germany

Compliant substrates enable the fabrication of flexible electronics for numerous applications like flexible displays, solar cells, batteries or wearable/biocompatible electronics. However, the reliability of such devices is limited by the stretchability of the inorganic components. So far, little experimental work has been carried out to investigate the mechanical properties of thin inorganic films on compliant substrates at high strains and cyclic loading. Here, we present experimental results for the flow stress, fracture strain and fatigue behavior of evaporated and printed Ag films as well as printed thin film transistors on compliant substrates. The film systems have been tested by a synchrotron-based tensile testing technique (up to 10% total strain) as well as cycling loading (50 Hz, strain amplitude up to 2.5%) and have been characterized by SEM and FIB microscopy. The synchrotron experiments yield the stress evolution and strain transfer within the film systems whereas the cyclic tests give the fatigue lifetime. On the other hand, *in situ* electro-mechanical testing, *in situ* tensile tests in the SEM and stationary FIB investigations reveal the evolution of electrical performance, crack morphology and crack density as well as fatigue damage in the individual films. First, results of electro-mechanical testing of printed and evaporated Ag films will be presented. Electrical conductivity and mechanical reliability are investigated with respect to the inherently nanoporous microstructure, and are compared to those of evaporated Ag films of the same thickness. It is shown that there is an optimized nanoporous microstructure for inkjet-printed Ag films, which provides a high conductivity and improved reliability. It is argued that the nanoporous microstructure ensures connectivity within the particle network and at the same time reduces plastic deformation and the formation of fatigue damage. Furthermore, results on printed In_2O_3 thin film transistors are presented. Here, the interplay of the polymer substrate and solid polymer electrolyte with the metallic and ceramic interlayers within the transistor structure will be discussed based on the strain evolution within the individual layers determined from the *in situ* synchrotron experiments.

1:50pm **H2-2 Comparison of Different Methods for the Investigation of Thin Film Adhesion**, ***Felix Schiebel***, Fraunhofer Institute for Mechanics of Materials IWM, Germany; *C Eberl,* University of Freiburg, Germany

The reliability of power electronic devices (e.g. in solar industries and electric automotive applications) depends strongly on their electrical and mechanical interconnections. Thin metallic films deposited on semiconductor substrates are used to improve the connection at its most critical interface. The performance of these thin films, with dimensions typically of a few hundred nanometers, therefore greatly influences the reliability of the entire device.

To evaluate the adhesion of such films, a typical stack of thin metallic films consisting of an adhesion layer, a solderable NiV layer, and an Au oxidation protection layer was deposited on an Si semiconductor substrate. Several experimental methods (e.g. cross sectional nanoindentation (CSN) and scratch test) have been implemented to evaluate the adhesion in both the as-deposited state and an annealed state. The results of those measurements will be used to discuss the influence of the annealing on the adhesion and also on the measurement technique.

Furthermore, a new experimental setup will be presented which allows monitoring the delamination during CSN experiments with two separate cameras. The captured image series provide new experimental data which can be used to further improve fracture toughness calculations and to gain a deeper insight in delamination processes, allowing more the design of more reliable devices in the future.

2:10pm **H2-3 Electro-Mechanical Characterization of Functional Thin Film Metallic Glasses**, *M Mühlbacher,* Montanuniversität Leoben, Austria; *O Glushko,* ***Christoph Gammer***, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *C Mitterer, J Eckert,* Montanuniversität Leoben, Austria

Thin film metallic glasses, which have a signature disordered structure with metallic bonding characteristics, are starting to emerge as functional materials. To investigate their electro-mechanical behavior, we prepare binary metallic PdSi thin films with varying thicknesses on the order of 5-300 nm by co-sputtering from elemental Pd and Si targets in an unbalanced DC magnetron sputtering device. In order to achieve amorphous film growth on Si(001) and flexible polyimide substrates, deposition proceeds without external substrate heating and film composition is chosen close to the deep eutectic composition in the Pd-Si phase diagram.

Selected samples deposited on flexible substrates are analyzed in a tensile testing set-up with *in-situ* resistance measurements. The strain at which cracks start to form in the brittle amorphous films can be determined exactly as the point where resistance starts to increase. Simultaneous confocal laser scanning microscopy of the strained samples provides more information on the failure mode. In thicker PdSi thin film samples, characteristic shear bands are evident with a 45° angle to the straining direction in addition to large cracks normal to, and film delamination in the form of buckles parallel to the tensile direction after straining to 10%. With decreasing PdSi film thickness down to 5 nm, a more ductile fracture behavior is observed. This is explained by a plasticity size effect, where deformation changes from a highly localized to a homogeneous mode due to geometric limitations. These findings are complemented by *in-situ* tensile tests of free-standing PdSi films in a transmission electron microscope. The gained understanding of the interplay of electro-mechanical properties in functional thin film metallic glasses will contribute to a successful application of these materials in future microelectronic devices.

2:30pm **H2-4 New Pull-off Tensile Tests for Adherence Assessment in Concrete-formwork Coated and Uncoated Contacts**, ***Nicolas Spitz***, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France; *N Coniglio, M El Mansori,* Arts et Métiers ParisTech d'Aix-en-Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France; *A Montagne,* Arts et Métiers ParisTech de Lille, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France; *S Mezghani,* Arts et Métiers ParisTech de Châlons-en-Champagne, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France

Nowadays buildings construction is performed by pouring concrete into molds called formworks that are usually prefabricated metallic modules. Defects such as stripping may possibly form during the removal of the formwork if the interfacial bonding between the concrete and the formwork is high. Making use of a new pull-off tensile test designed in our laboratory, a correlation has been established between the formwork superficial functional signatures and its adherence susceptibility to concrete. The originality of this near-to-surface test was to characterize the concrete-to-formwork adherence by measuring the required force to pull the concrete from the formwork surface. The design of the test coupon was validated by finite element analysis that proves the small deformation of the tested formwork specimen under the tensile loading and the homogeneity of the applied tensile stress at the interface. The interfacial bonding to concrete has been compared between bare and coated formwork. Both metallic and polymer coatings have been studied. The

analyses of the pull-off test results enabled us to understand the bonding mechanisms at the concrete-coating interfaces. The pull-off tensile test was proven capable of ranking formwork coatings according to their adherence to concrete.

2:50pm **H2-5 In-situ-squared: Combined Electro-mechanical Behavior of Thin Films with One Experiment***, **Megan Cordill,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria **INVITED**

Studying the combined electro-mechanical properties of thin metal films on polymer substrates under mechanical load is one way to advance flexible electronic technologies. Ductile films and lines allow current flow between semiconducting islands and other operating features, thus are an integral part of flexible electronics. Flexible electronics also contain brittle layers which can improve adhesion, protect again corrosion or have semiconducting properties. When films on polymer substrates are strained in tension the substrate can suppress some of the catastrophic failure that allows for their use in flexible electronics and sensors. However, the interplay between the different layers can be very different compared to similar films on rigid substrates. In order to improve mechanical and electrical properties of these complex material systems, more work at characterizing the processing-structure-property relationships as well as the thin film architectures should be performed. Studies of strained films on polymer substrates tend to emphasize only the electrical properties or fracture strains effects more than the role of film thickness or multilayer behavior. The thickness of a ductile film will influence the mechanical behavior but also the electrical behavior, while even brittle thin metal layers can greatly affect the failure of ductile films. To address the electro-mechanical and deformation behavior of metal films supported by polymer substrates, in-situ 4 point probe resistance measurements were performed with in-situ confocal scanning laser microscopy imaging of films surface during uni-axial tensile straining. The 4 point probe resistance measurements allow for the examination of the changes in resistance with strain of the more deformable layer, while the surface imaging permits the visualization of localized thinning and crack formation. Furthermore in-situ synchrotron tensile tests provide information about the stresses in individual films and show the yield stress where the deformation initiates and the relaxation of the film during imaging. The combination of electrical measurements, surface imaging, and stress measurements allow for a complete picture of electro-mechanical behavior needed for the improvement and future success of complex flexible electronic devices.

3:30pm **H2-7 Mechanical Behavior of Ductile/Brittle Multilayers Studied with In-situ Straining Methods***, **Patrice Kreiml,*** *M Rausch, V Terziyska,* Montanuniversität Leoben, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Mo thin films, which are frequently used as back-plane electrodes and as source/drain in thin film transistors, are inherently brittle compared to the electrical charge carrying ductile Cu or Al films. To improve the fracture behavior of stacks containing Mo layers for future flexible devices, and thus the reliability of the whole device, an optimum ductile/brittle layer thickness ratio is necessary. In this work the electro-mechanical behavior of multilayered Al/Mo thin films grown by dc magnetron sputter deposition on polyimide substrates is investigated. Various combinations of thicknesses for bi-layer and tri-layer architectures were evaluated (films of 50 to 450 nm thickness with different ductile/brittle layer thickness ratios). For a comparison of the behavior of the thin films, a combination of in-situ mechanical testing with electrical measurements, X-ray diffraction and 4-point probe resistance techniques were employed. In order to correlate the mechanical and electrical properties and to better understand the connection between crack onset, crack evolution and electrical resistance of the Al/Mo multilayers, in-situ confocal laser scanning microscope imaging was also performed. From X-ray diffraction data, individual film stresses during straining were determined, demonstrating that the ductile film thickness will dictate when through thickness cracks form in the multilayer. Once through thickness cracks form, the electrical conductivity deteriorates quickly and the multilayer stack can be considered failed. The combined in-situ testing also illustrates how brittle layers can cause typically ductile films to behave in a brittle manner due to the fact that cracks initially form in the brittle layers that act as stress concentrators in the ductile films. It will be shown that an optimized film architecture will improve the electro-mechanical behavior for flexible electronic applications.

3:50pm **H2-8 Fracture Behavior of Nanocrystalline BCC High-Entropy Alloys***, Y Xiao, H Ma, R Spolenak, **JeffreyM. Wheeler,*** ETH Zurich, Laboratory for Nanometallurgy, Switzerland

Refractory high-entropy alloys (HEAs) have attracted significant attention due to their superior mechanical properties at elevated temperature [1]. However, most of them are brittle and suffer from low ductility and toughness at room temperature, and their usage is limited due to the inadequate fracture-resistance property. Grain boundaries play an important role in the extraordinarily high temperature strength and stability [2] of bcc HEAs and can also be potential sites for fracture. Here, strongly textured, columnar and nanometer-size grains NbMoTaW HEA thin films with and without ion beam assisted deposition technique are produced. Mechanical properties, especially fracture toughness are determined by in situ micro-pillar and micro-cantilever tests. Further characterization is conducted by high-resolution SEM images and TEM analysis.

References

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[2] Y. Zou, et al., Nano Lett, 17 (2017) 1569-1574.

4:10pm **H2-9 Recent Advanves in Microcantilever Bending Experiments***, **Karsten Durst,*** Physical Metallurgy, TU Darmstadt, Germany*; M Göken,* University Erlangen-Nürnberg, Germany*; J Ast,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland **INVITED**

Microcantilever bending experiments are becoming more prominent in testing the local fracture toughness in a wide variety of materials. By focused ion beam milling or other techniques, a notched cantilever with micron sized dimensions is milled into a region of interest of a bulk material or thin coating. By loading the cantilever with a nanoindenter, a crack is nucleated at the notch tip and propagated through the sample and the fracture toughness can be evaluated at the local length scale. Applying conventional fracture mechanics approaches, the local critical stress intensity of the material is determined. With the presentation recent advances in the technique will be presented, focusing on elastic plastic fracture mechanics and crack tip plasticity.

4:50pm **H2-11 Temperature and Loading Rate Influence in Micro-Scale Fracture Experiments***, J Ast,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Schwiedrzik,* EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Wehrs,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Michler,* EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; **Xavier Maeder,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The process zone or plastic zone around a loaded crack tip can significantly influence the fracture behavior of a material. Especially in micro-scale specimens, the plastic zone size may make out a large share of the sample volume and lead to a different fracture behavior than the one usually observed for macroscopic samples of the same material. Furthermore, the theoretical description of the plastic zone according to Irwin is not valid for single crystals. Therefore, a characteristic elastic-plastic fracture behavior is observed depending on crystallographic sample orientation and slip system activation. It is the aim of the study to give insight into the fracture process and behavior in micro-scale specimens in the presence of crack tip plasticity.

Notched micro-cantilevers were prepared by focused ion beam (FIB) milling in a tungsten single crystal. This material has nearly perfect elastic isotropy, a limited amount of activated slip systems and detailed knowledge of the macroscopic fracture behavior is available [1]. The cantilevers have dimensions of 25 µm in length, 5-7 µm in thickness and crack length to thickness ratios a/w of ca. 0.4. Loading rate and temperature are known to influence the fracture behavior decisively in bcc metals. Therefore displacement-controlled fracture tests were performed inside a scanning electron microscope in the temperature range between -100°C and 500°C. Applying the recently presented J-Integral technique [2] to plot continuous crack resistance curves, the fracture toughness and brittle-to-ductile transition (BDT) temperatures, which depend on the applied loading rate, were determined. This allows a thorough investigation of the activation energy of the BDT at the micro-scale.

Crack tip plasticity before and during crack growth was investigated by high-resolution electron backscatter diffraction measurements (HR-EBSD) on FIB cross-sections of the micro-cantilevers after mechanical testing. Plastic zones, which are strongly depending on the activated slip systems, and plastic strain gradients in terms of geometrically necessary dislocations

were quantified and linked with the observed BDT behavior. Transmission electron microscopy was used to confirm the EBSD results and to provide dislocation analysis.

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5:10pm **H2-12 Investigating the Local Fatigue Properties of Materials in Small Dimensions by Dynamic Micropillar Compression***, **Benoit Merle**,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

A novel method was develop in order to investigate the local fatigue properties of ultrafine-grained copper on the micrometer-scale up to the high cycle fatigue (HCF) range, relying only on widely available nanoindentation hardware. This breakthrough was achieved by combining the widely used micropillar compression method with the fast actuation (40 Hz) provided by the continuous stiffness measurement (CSM) module, originally intended for pyramidal nanoindentation. Cyclic testing was performed at constant nominal stress amplitude for up to several million (3.10^6) cycles. The resulting strain amplitude was directly recorded and the plastic strain was evaluated from the phase angle measured by the lock-in amplifier during testing. Defining a threshold for strain amplitude decrease as failure criterion further enabled the determination of S-N curves. The fatigue behavior of the tested ECAP copper micropillars was found to be dominated by cyclic softening, which is in line with previous macroscopic observations on similar samples. The calculated plastic strain amplitude also matches the literature data closely. Generally, the new method has a great potential for studying the local cyclic effects taking place at interfaces in complex micro-architectured materials and coatings.

Special Interest Talk 2
Room San Diego - Session SIT2
Special Interest Talk 2

4:10pm **SIT2-9 Materials Design Guidelines for Improved Strength, Ductility, and Stability***, **Paul Heinz Mayrhofer**,* TU Wien, Institute of Materials Science and Technology, Austria

Whenever mechanical attack is dominating the loading profile of materials in industrial applications, nitrides are highly preferred, whereas oxide materials provide best protection against high temperature corrosions. Thus, when mechanical and thermal loading is combined, the nitrides used should also provide an excellent stability against temperature as well as corrosive attack (such as oxidation). How nitride materials can be developed – implementing computational and experimental materials science – to withstand high mechanical as well as thermal loading, is the focus of this talk.

We will use recent developments – where we applied alloying and architecture concepts (e.g., composition and/or phase modulated layers) to transition metal nitrides, for optimizing their properties – to derive important materials design guidelines for improved strength, ductility, but also stability. Especially the stability (here, we concentrate on phase stability with respect to chemistry and temperature, but also on the stability against oxidation) of nitrides is an extremely interesting task, as for example the face centered cubic (fcc) structure of TiN_x is rather insensitive to small (or even large) variations in chemistry and alloying elements (TiN even allows for the substitution of 66% Ti with Al to still crystallize in the fcc structure). Contrary, the preferred crystal structure of other transition metal nitrides (like MoN_x and TaN_x) is extremely sensitive to small chemical variations, even if only the vacancy content changes. Nevertheless, especially Ta is extremely versatile in increasing strength, but also ductility, as well as the thermal stability and oxidation resistance of Ti-Al-N coatings, which are still an extremely important material class.

With the help of various superlattice coatings, we show that also with such architectural concepts, strength and ductility (here, basically obtained by in-situ micromechanical cantilever bending tests) can be improved simultaneously. Additionally, we also give an example of transformation induced plasticity mechanisms, which can be implemented in nitride materials as well.

The individual concepts will allow designing materials to meet the ever-growing demand for further improved coatings, tailor made for specific applications.

Coatings for Use at High Temperatures
Room Grand Hall - Session AP
Symposium A Poster Session

AP-1 Feasibility of using Rare-earth (La and Ce) Sulfates as Functional Embedding Agents for Thermal Barrier Coatings, *D Song, T Song,* Hanyang University, Republic of Korea*; **HyeonMyeong Park**, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Indiana University Purdue University Indianapolis, USA

Feasibility of using rare-earth (La and Ce) sulfates as functional agent was demonstrated for thermal barrier coatings (TBCs). Both pellet and TBC specimens were prepared and intentionally cracked by indentation methods. Then an isothermal heat treatment for pellets and cyclic thermal fatigue (CTF) test for TBCs were performed. The phase transformation behaviors were investigated by X-ray diffraction and X-ray photoelectron spectroscopy. Rare-earth oxides and zirconates were formed during the heat treatment due to the high oxygen ion diffusivity of yttria-stabilized zirconia (YSZ) matrix. TBCs with rare-earth sulfates showed longer lifetime performance in the CTF test than typical YSZ TBC without functional agents. This is due to crack healing and inhibiting effects resulted from the reaction of the functional agents with YSZ matrix. This study and derived results demonstrate the applicability of rare-earth sulfates as functional embedding agent through further optimization of microstructure design and encapsulation process.

AP-2 Lifetime Performance of Yb-Gd-Y-based Thermal Barrier Coatings with Buffer Layer in Thermally Graded Mechanical Fatigue Environments, ***Bong-Gu Kim,*** School of Materials Science and Engineering, Changwon National University, Republic of Korea*; G Lyu, S Jung, H Park, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Changwon National University, Republic of Korea, USA

The effects of buffer layer on the crack generation and thermal fatigue behaviors of Yb-Gd-Y-stabilized zirconia (YGYZ) based thermal barrier coatings (TBCs) were investigated through thermally graded mechanical fatigue (TGMF) test. Double buffer layers were introduced to enhance the thermomechanical properties in the YGYZ based TBC systems, deposited with the regular and high purity 8YSZ buffer layers. TGMF tests were performed at 1100 °C with a tensile load of 60 MPa, till 50% spallation of the top coat or cracking at the interface between the top and bond coats. The multilayer TBCs showed longer lifetime performance compared to the single layer YGYZ based TBCs, showing delamination and/or cracking at the interface between the buffer layer and the top coat in the multilayer TBCs. The feedstock purity in the buffer layer was also effective in enhancing the lifetime performance of YGYZ based TBC system in the thermal and mechanical environments. Failure mechanisms in the layered TBCs were investigated and discussed based on the crack initiation and propagation behaviors observed through the TGMF tests.

AP-3 Thermal Durability of Thermal Barrier Coatings – Effect of Purity and Monoclinic Phase in Feedstock Powder, ***Yeon-Gil Jung,*** *H Park, S Jeon, G Lyu, S Jung,* Changwon National University, Republic of Korea*; K Park, I Kim, B Yang,* Doosan Heavy Industries and Construction, Republic of Korea*; J Zhang,* Indiana University, USA

The effects of the purity and monocline phase of feedstock powder on the thermal durability in thermal barrier coatings (TBCs) were investigated through the jet engine thermal shock (JETS) test. Three kinds of feedstock powders, such as regular purity (YSZ), high purity (HP), and non-monoclinic phase (nMP) in 8 wt% yttria-stabilized zirconia, were deposited on the Ni-Co based bond coat by an air plasma spray (APS) process. The thicknesses of the top and bond coats were designed and controlled as 400 and 200 µm, respectively. In each cycle of JETS test, the top surface of TBC was heated with flame of 1400 °C for 25 s, and then cooled for 25 s using nitrogen gas. Regardless of feedstock species, all samples showed sound condition in the JETS test up to 2000 cycles. As the number of cycles increased over 2000, the lifetime of the TBC with HP powder was longer than those with the YSZ and nMP powders. The TBC with YSZ powder showed the shortest thermal durability in the TBC with YSZ powder. The relationship between feedstock species and thermal durability is extensively discussed, based on microstructure evolution and phase stability during the JETS tests.

AP-6 Integral vs. Local Chemical Composition of (coating) Materials: Is your Solid Solution a Solid Solution?, ***Jochen M. Schneider,*** RWTH Aachen University, Germany

Atom probe tomography provides the opportunity to investigate the chemical composition of (coating) materials on the nm-scale. During the multimedia poster session differences (and similarities) between the integral coating composition determined by elastic recoil detection analysis and/or energy dispersive X-ray spectroscopy and the local composition determined by atom probe tomography will be presented. The effect of Si additions to Cr_2AlC which are known to affect the oxidation kinetics are presented as well as Mn additions to Cr_2AlC. Furthermore, differences (and similarities) in local and global chemical composition identified for the coating systems Mo_2BC as well as transition metal nitrides and oxynitrides are discussed.

AP-7 Coating Generation and Study for Materials Protection used in Extreme Atmosphere: Sustainability and Energy Efficiency, *A Illana,* Universidad Complutense de Madrid, Spain*; M Gutiérrez, I Baraibar,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; S Mato,* Universidad Complutense de Madrid, Spain*; R Muelas Gamo,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; M Benito, A Bahillo,* Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Spain*; **Francisco Javier Pérez-Trujillo,*** Universidad Complutense de Madrid, Spain*; A Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

The need to increase the efficiency in energy production in a sustainable way as well as reducing the environmental impact, has become evident. This leads to increasingly extreme conditions imposing more demanding performances on materials such as higher temperatures and pressures in more corrosive environments. Therefore, the main goal of "Coating Generation and Study for Materials Protection used in Extreme Atmosphere: Sustainability and Energy Efficiency" project is developing and optimizing protective coatings for structural materials of power plants generation to protect from aggressive environments present in power plants working under oxy-fuel atmospheres and employing biomass as fuel.

The technical goal aiming at studying the feasibility of using coatings as an alternative in a biomass oxy-combustion thermal plant working under supercritical conditions. Until now, it had been unexplored, so this project has assessed the corrosion behavior of bare and coated coupons of ferritic steels (T22 and P92) and a high-alloy multi-purpose austenitic stainless steel (Sanicro 28) which have been exposed to biomass oxy-combustion conditions on one side, and to supercritical steam on the other, both in laboratory and in pilot plants. The gravimetric evolution was analyzed at fixed intervals to study their oxidation kinetics. In addition, common characterization techniques have been used, such as x-ray diffraction (XRD), to explored the phases formed during the oxidation process, and scanning electron microscopy with energy dispersive detector (SEM-EDX), to evaluate the morphology and semi-quantitative composition.

On one hand, the samples were tested in pure steam at 650ºC and 0.1 and 30 MPa in order to evaluate the role of the pressure. After more than 1000 h, the coated materials exhibited an improved behavior compared with base materials. However, this parameter significantly affected the ferritic steels.

On the other hand, the oxy-combustion tests were firstly made in a laboratory with and without additions of K_2SO_4 and KCl and/or SO_2 in order to simulate the composition of thistle biomass, which has been used in experiments carried out after at the pilot plant. In all cases, ferritic steels have been severely affected, forming non protective oxides. Nevertheless, Sanicro 28 steel has been able to resist so it does not need to be covered. Regarding the coatings, they have successfully altered the catastrophic behavior of the ferritic steels. So it could contribute to reach the production of sustainable, clean and efficient electricity using existing infrastructures.

AP-8 The Influence of Reactive Elements on Thermogravimetric Behaviour of New Co-Ni-Al-W Superalloys Dedicated to Bond-coat Deposition, *G Moskal, A Tomaszewska,* ***Damian Migas,*** Silesian University of Technology, Poland

Characterization of as-cast microstructure and oxidation resistance of new type of cobalt based superalloys with γ/γ' microstructure were presented in this investigations. As a referential material the Co-20Ni-7Al-7W (at.%) was used as the modified version of basic (Co-20Ni-7Al-7W). All investigated alloys were modified by addition of yttrium, hafnium and zirconium on the level of 0.5, 0.2 and 0.05 at.% respectively due to

improvement of its oxidation resistance. All alloys were made in Institute of Materials Engineering of Silesian University of Technology in Poland.

The oxidation performance of all alloys were made during thermogravimetric investigations at temperature range from 25 to 1200°C. The main analyzed parameter was mass gain detected continuously during the test. After the test the overall and cross-sectional analysis of specimens was made and included analysis of oxide layer morphology on the surface of specimens with characterization of phase constituent of oxide layer. The detailed analysis of oxidized layer was made by scanning electron microscopy method when distribution of alloying elements was made with special attentions on yttrium localization after the test in oxide zone.

Obtained data showed that both addition of Y, Hf and Zr has a strong influence on oxidation performance of new Co based superalloys. Those influence is demonstrated mainly by different morphology of final oxide zone with strong segregations of yttrium containing oxidation products.

This work was supported by Institute of Materials Science of Silesian University of Technology, as a part of Statutory Research no BK-225/RM0/2017.

AP-9 Study the Surface-aluminizing Coating to Enhance High-temperature Oxidation Resistance of T91 Boiler-used Steel, ***Wu Kai***, *Y Chen, C Chung,* National Taiwan Ocean University, Taiwan

The oxidation behavior of surface aluminizing T91 boiler-used steel (T91A) was investigated over the temperature range of 600 ~ 900 ˚C in dry air. The surface-aluminizing parameters for T91A were to heat the T91 samples at 800 °C for 4 hr in 7% AlF_3 at a 200 cc/min flow rate of Ar. The results showed that the oxidation kinetics of T91A followed a single-stage parabolic-rate law at 600 ~ 750 ˚C, while a two-stage parabolic-rate law was observed at 800~900 ˚C. The steady-state oxidation rates at 850 ~ 900 °C were significantly slowly than those at lower temperatures. The oxidation rates of the aluminizing alloy were significantly lower than those of the T91 substrate by 6.2 orders of magnitude at 850 ˚C. Both α- and θ-Al_2O_3 formed on top of T91A surface after the oxidation. The amount of θ-Al_2O_3 gradually reduced and the amount of α-Al_2O_3 gradually increased with increasing temperature. It was found that the growth of α-Al_2O_3 is strongly dependant on the oxidation temperature and duration of time. The formation of α-Al_2O_3 is responsible for the lower oxidation rates of the T91A alloy at 850 ~ 900 ˚C.

AP-10 New Insights into the Oxidation Behaviour of AlCrSiN Coatings and an Approach to Avoid Trans-interface Diffusion at Elevated Temperatures, ***Nikolaus Jäger***, *S Klima, M Meindlhumer,* Montanuniversität Leoben, Austria; *H Hruby,* eifeler-Vacotec GmbH, Germany; *J Keckes, R Daniel,* Montanuniversität Leoben, Austria

Applications such as high-speed machining and dry cutting of metals demand the development of superior materials to withstand severe operating conditions. High loads and temperatures exceeding 1000°C in contact between the tool and the work piece require protection of the tool surface by advanced hard coatings. Under such conditions, thermal stability and oxidation resistance of the coated tool is of outmost importance. A solid understanding of the diffusional mechanisms resulting in the phase transformation of metastable phases and oxidation of the coating with subsequent deterioration of the mechanical properties is thus the basis for establishing strategies for improved high-temperature behaviour of the protective coatings. The coating performance may also be dramatically affected by structural changes driven by elements diffusing from the tool material into the coating.

In this work, AlCrSiN coatings with a Si content up to 10 at. % were deposited on cemented carbide and high-speed steel substrates by cathodic arc evaporation. To study the oxidation behaviour, the samples were annealed in ambient atmosphere at temperatures up to 1200 °C for 1 h. Powders made out of the coatings were investigated via differential scanning calorimetry and thermogravimetry. Additionally, an $AlCrSi_{10}N$ coating on cemented carbide annealed at 1400 °C for 1 h was characterized by cross-sectional, position-resolved synchrotron X-ray nanodiffraction analysis to gain information about structure, texture and residual stresses across the coating thickness including the oxide scale formed on its surface. To investigate the influence of diffusion of substrate elements into the coating, samples were annealed in vacuum in the same temperature range and analysed by means of scanning electron microscopy and energy dispersive X-ray spectroscopy. Additionally, one selected sample was characterized by cross-sectional, position resolved synchrotron X-ray nano-diffraction analysis to study the microstructural evolution, phase transformations and development of residual stresses near the substrate-coating interface affected by pronounced diffusion of substrate elements. Based on the results of this study, we will suggest strategies to suppress diffusion of Co from the cemented carbide and Fe from the steel substrates into the coating and enhance the oxidation resistance of AlCrN coatings to ensure high-temperature stability of the coating and thus enhanced operation performance of the coated tool.

AP-12 Gradient SiBCN Ceramic Coating for High-temperatue Anti-oxidation Protection of Carbon-carbon Composite, ***Zongbo Zhang***, Institute of Chemistry, Chinese Academy of Science, China

Carbon-carbon(C/C) composites , an important high-temperature structural material, face the severe problem of oxidation only above 500℃. Coating technology with ultra-high temperature ceramics (UHTCs) have been proved to be highly effective to improve the oxidation resistance of C/C composites[1]. Currently, the main coating techniques for C/C composites include pack cementation, plasma spraying, polymer derived ceramic coatings and so on. Among them, polymer derived ceramic coatings have gained more and more attention due to its easy for implementation, no need for special equipment and low sintering temperature. However, the technique of polymer derived ceramic coating usually needs multiple casting-sintering cycles to densify the prepared coating, which requires ultra long operation time thus affect its real application. In this paper, we present a novel strategy to fabricate gradient SiBCN composite coating with just one casting-sintering cycle by adopting polyborosilazane ceramic precursor[2] as the main raw material, well controlling the viscosity of the polyborosilazane-filler slurry and a low temperature pre-oxidation treatment.

The microstructure morphology, elements composition, thermal performance, and anti-oxidation property of the ceramic coating have been investigated. The coating surface macro appears uniform, no cracks, while microscopic loose and porous. The coated C/C composite exhibits excellent anti-oxidation property with weight loss of only 0.06% after oxidation at 1500 C for 30min. Due to the gradient structure, the coating shows no crack and no peeling off after 8 cycles of thermal shock from 1500°C to room temperature. The XRD analysis showed that the surface of the coating was oxidized to form a zirconium silicate material, thereby preventing oxygen from further penetrating and achieving the oxidation resistance. All above of the results indicate that SiBCN ceramic coating has high potentials for anti-oxidation protection of C/C composites.

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Hard Coatings and Vapor Deposition Technologies
Room Grand Hall - Session BP
Symposium B Poster Session

BP-1 Electrical and Reliability Characteristics of Dielectric Stack with Low Dielectric Constant SiCOH and Capping SiCNH Films, *C Lee,* National Chi-Nan University, Taiwan; *W Hung,* ***Yi-Lung Cheng***, National Chi Nan University, Taiwan

The electrical characteristics and reliability of a dielectric stack with a low-k SiOCH film and a capping SiCNH film were investigated in this study. Two different low-k SiOCH films without and with the porosity (called dense and porous low-k) were used to identify the role of the porosity. The deposition of the capping dielectric film on both the dense and porous low-k films increased the overall dielectric constant. A higher increase in the dielectric constant was detected for the porous low-k film due to more serious plasma damage during a capping film deposition. With a capping SiCNH film, O2 plasma damage and Cu diffusion were greatly retarded for both low-k SiOCH films. Lager improvements on TDDB and electromigration lifetimes were detected on the porous low-k film.

BP-3 Adhesion And Durability Of Multi-Interlayered Diamond-Like Carbon Film Deposited On An Aluminum Alloy, ***Hidenobu Maruno***, *A Nishimoto,* Kansai University, Japan

Aluminum alloys are light and have good workability; however, they have drawbacks such as low hardness and poor wear resistance. These drawbacks limit their wide application in the automotive field. The deposition of a diamond-like carbon (DLC) film, which has high hardness and good wear resistance, on the substrate surface can improve these

drawbacks. Because aluminum alloys and DLC films have poor affinity, the adhesion between them is poor. However, the usage of an interlayer can improve the adhesion between them. In this study, to investigate the effect of multi-interlayers on the adhesion and durability, a DLC film with an interlayer of Ti, Si-DLC, or Ti/Si-DLC was deposited on the EN AW-2024 Al alloy substrate via plasma enhanced chemical vapor deposition. Argon bombardment treatment was conducted to clean the substrate surface before deposition, the Ti interlayer was deposited via sputtering for 15 min, the Si-DLC interlayer was deposited using gas mixture of tetramethylsilane and methane for 15 min, and DLC was deposited using methane gas for 90 min. The nano-hardness of the Ti/Si-DLC multi-interlayered sample reached 21 GPa, which is nearly 4 GPa more when compared with single interlayered samples. A ball-on-disc test showed that the wear volumes of the ball and the multi-interlayered sample were smaller compared with the single interlayered samples. In addition, the durability distance of the Ti/Si-DLC multi-interlayered sample was 3300 m, increasing more than 1500 m than the single interlayered samples.

BP-4 The Effect of Cu on Fatigue Properties of TiZrNbN Coatings, *H Aghdam, A Keles,* Ataturk University, Turkey*; O Baran,* Erzincan University, Turkey*; Y Totik,* Atatürk University, Turkey*;* ***Ihsan Efeoglu,*** Ataturk University, Turkey

The fatigue properties are very important for cutting tools due to service life. Due to improve fatigue properties of cutting tools, transition metal nitrides with soft metal (Cu, Ni etc.) are coated on cutting tool materials. To investigate Cu effect on fatigue properties of transition metal nitride coatings, TiZrNbN and Cu doped TiZrNbN coatings were deposited on M2 high speed steel using reactive closed field unbalanced magnetron sputtering (CFUBMS) in bias voltage of -80V, coating pressure of 0.26 Pa and Cu target current of 0.6 A. Microstructure properties of the coatings were determined by XRD, SEM and EDAX. Mechanical properties of the coatings were examined with microhardness test. Fatigue properties of the films were examined using multipass scratch tester. According to the results, the mechanical properties of TiZrNbN doped Cu is better than TiZrNbN.

BP-5 Thermal Stability of Ni-B/ La_2O_3 Coatings by Electro-brush Plating Technique, ***Dan Zhang,*** *X Cui, G Jin, Z Cai, M Dong,* Harbin Engineering University, China

The metastable materials have gained a great deal of attraction due to their promising physicochemical properties, but the thermal stability limits their practical application. In this paper, Ni-B/La_2O_3 amorphous/nanocrystalline composite coatings were prepared on AISI 1045 steel substrate by electro-brush plating technique. The surface morphology, component and the phase structure of coatings were observed by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD), respectively. The coatings were further analysis by Transmission Electron Microscope (TEM). Then the thermal stabilities of coatings with different content of La_2O_3 were also analyzed under different annealing temperature. It was found that the coating had a unique microstructure consisting of amorphous and nanocrystalline structures. The addition of La_2O_3 does improve the thermal stability of metastable Ni-B coatings when the annealing temperature is over 355℃. In addition, the thermal stability of the amorphous/nanocrystalline coatings depends on the percentage of amorphous phase, grain sizes and textures.

Acknowledgements

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BP-6 Properties of CrN_x Thin Films Deposited in Plasma Activated Polymers by Reactive Magnetron Sputtering, *M Rodrigues, P Pedrosa,* Minho University, Portugal*; A Ferreira, L Godinho, M Amaral,* PRIREV, Portugal*; M Neto, F Oliveira, R Silva,* Universidade de Aveiro, Portugal*; J Borges,* ***Filipe Vaz,*** Minho University, Portugal

Polymers are replacing traditional metallic materials, particularly in the automobile, electronic and decorative industries. Their low density, flexibility, design versatility and low cost production, combined with the properties of a shining, highly reflective and conductive metallic coating, gives them a huge advantage over common metals. One of the most used metallization process in the last decades has been chrome plating using highly toxic hexavalent chromium. However, following all the enacted legislation during the last years against the use of hexavalent chromium solutions, new chrome plating alternatives have emerged and include chemical, physical, and mixed approaches. One of such techniques is magnetron sputtering, which can be used on a wide range of available polymers and has a reduced environmental impact, unlike chrome plating.

In this work, magnetron sputtered CrN_x thin films were deposited on several polymers, including ABS, PA and PP. Two sets of thin films were obtained by varying the N_2 flow inside the vacuum chamber (series 1) and the deposition time (series 2). The polymers where also subjected to plasma treatment in Ar prior to the CrN_x thin films' deposition in order to enhance the adhesion. The fundamental microstructural, chemical and physical properties, as well as the quality and adhesion of the CrN_x thin films, were accessed by SEM, XRD, 3D profilometry, colorimetry, electrical resistivity measurements and scratch test. Main results show that high-quality, dense CrN_x films with enhanced adhesion and low percentage of defects were obtained. Magnetron sputtering is thus a promising alternative to the hazardous chrome plating for an effective metallization of different polymers.

BP-9 Influence of Ti on the Phase Stability of Magnetron Sputtered Mo-Si-B Thin Films, ***Elias Aschauer,*** *H Riedl,* CDL-AOS at TU Wien, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Polcik,* Plansee Composite Materials GmbH, Germany*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

In terms of fuel and cost efficiency, the replacement of high-density Ni-based super alloys in aerospace industries came into the focus of research. A promising candidate are Mo-Si-B alloys, since they offer a high creep resistance, phase stability in a very broad range as well as excellent oxidation resistant. This broad field of mechanical and chemical properties is achieved by taking advantage of different phase combinations within the ternary phase diagram, leading to a multicomponent material. As it is well known in literature, molybdenum offers a poor oxidation resistance due to the formation of volatile oxides already above 400 °C – so called pesting phenomena. Alloying silicon and boron to refractory metals like molybdenum promotes the formation of glassy-like borosilicate oxide scales and inhibits the volatilisation of MoO_3. Nevertheless, retarded oxidation kinetics in a wide temperature field is strongly linked to the proper Si to B ratio. The molybdenum rich corner, known as Berczik triangle, offers a phase combination of Mo (A2), c-Mo_3Si (A15), and T_2–Mo_5SiB_2 ($D8_l$), next to the so-called Akinc triangle including c-Mo_3Si (A15), T_2–Mo_5SiB_2 ($D8_l$), as well as T_1-Mo_5Si_3 ($D8_m$). Especially, the T_1 and T_2 phases provide the ideal ratio of boron and silica to form either B-rich SiO_2 or even pure SiO_2 at low and high temperatures, respectively.

In order to access this highly interesting material characteristics, physical vapour deposition (PVD) can be used to make this promising material system accessible to many other applications and extend the field of operation. However, the most common deposition temperatures of about 500 °C do not lead to the desired phase combination, but rather to homogeneous, X-ray amorphous thin films. Alloying titanium to the ternary system is known to stabilise the T_2 phase, by substituting the Mo atoms within the tetragonal crystal structure up to concentrations of 40 % - also reducing the density significantly.

Therefore, the focus of the provided study is on the fundamental understanding of the phase evolution of magnetron sputtered Mo–Ti-Si–B thin films varying deposition parameters such as total pressure, bias voltage, and deposition temperature. Furthermore, the phase stability after thermal treatments in different atmospheres (vacuum, inert gas, and oxygen) is investigated up to temperatures of

1500 °C by using X-ray diffraction analysis as well as various (high-resolution) electron microscopy techniques and differential scanning calorimetry (DSC). The mechanical properties were investigated by nano-indentation of the as deposited and annealed state.

BP-10 Carbide Layer Coating on Titanium by Spark Plasma Sintering Technique, ***Akio Nishimoto,*** *C Nishi,* Kansai University, Japan

Titanium materials are widely used in aerospace, automotive and biomaterial engineering fields due to high specific strength, superior fatigue and corrosion resistance as well as excellent biocompatibility. However, titanium exhibits low hardness and poor wear resistance. Therefore, the development of a suitable surface modification technology is necessary to expand the use of titanium materials. In order to improve hardness and wear resistance of materials, there is the method to form the hard ceramics layer on the matrix surface. In this study, carburizing method was applied. The carburizing method can form the carbide layer which is superior in adhesion with the matrix compared with PVD or CVD method. However, in conventional carburizing methods, the deterioration of the mechanical properties of the matrix as a result of long-term and high-temperature processing is problematic. Therefore, spark plasma sintering

technique, which features short processing times, was applied to form a carbide layer in this study. The purpose of this research is to form a TiC layer on commercially pure Ti (CP-Ti) and evaluate its properties. CP-Ti was used as the substrate, and graphite powder was used as the carburizing source. XRD analyses indicated that a TiC layer was formed on the substrates. Corrosion tests indicated that the corrosion resistance of the carburized samples was remarkably improved compared to that of CP-Ti. Wear tests revealed that the carburized samples exhibited low friction coefficients and improved tribological properties.

BP-13 Growth Kinetics of Boride Coatings on AISI W2 Steel, ***MarcoAntonio Doñu Ruiz,*** Universidad Politécnica del Valle de Mexico, Mexico*; N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico*; V Serna Lara, V Cortés Suárez,* Universidad Politécnica del Valle de Mexico, Mexico

The present work evaluate the growth of the boride coatings formed in the surface AISI W2 steel by powder pack boriding. This process was carried out in the temperature range of 1173–1273 K with the exposure times ranging from 2 h to 8 h. The presence of borides Fe_2B formed on the surface of steel substrate was confirmed by optical microscopy and X-ray diffraction. The distribution of alloy elements from the surface to the interior was confirmed by energy dispersive X-ray spectroscopy.

The morphology presented the boride layer Fe_2B showed smooth and compact, with range thickness average from 9.96 ± 2.61 µm to 45.86 ± 4.13 µm. A mathematical model of the growth kinetics of the Fe_2B coatings on AISI W2 was proposed for the powder-pack boriding. The boron diffusion coefficient (D_{Fe2B}) was determinated by mass balance equation of the (Fe_2B/substrate) interface, the kinetic model was set for the Fe_2B coatings, assuming that the growth of boride layers follows a parabolic growth law. In addition, a contour diagram describing the evolution of Fe_2B coatings as a function of time and temperature parameters was proposed to be used in practical application. Finally, the boron activation energy for the AISI W2 steel is estimated as 183.44 kJ mol^{-1} and this value of energy was compared with the literature data.

BP-15 Study on Steels Boronizing Immersed in Diesel, ***Noe Lopez Perrusquia,*** *M Doñu Ruiz, G Perez Mendoza,* Universidad Politecnica Del Valle De Mexico, Mexico*; V Cortés Suárez,* Universidad Autónoma Metropolitana- Azcapotzalco, Mexico*; C Torres San Miguel,* Instituto Politécnico Nacional - ESIME, Mexico

This work shows the effect of diesel on a surface coating of boron in Microalloyed Steels. The steels are boronizing at 1273 K, with permanence of 6 h; the medium boriding by boron paste dehydrated; the medium boriding by boron paste dehydrated in solid box; the immersion of the steels Microalloyed boriding for 1 year in diesel at temperature ambient. The first phase consisted in the characterization and analysis of FeB/Fe_2B obtained by paste dehydrated of boron, using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and microhardness (Hv). The second phase is the immersion of the boriding specimens in diesel, after the permanence time, were evaluated by the tensile test and analyzed the mechanical properties. This work presents the formation of boron coating, with the purpose of showing an alternative for the manufacturing industries; which generate containers for storage of liquids, biofuels and fuels

BP-17 Deposition of Nanodiamond Coatings on Steel Implant Materials with CrN/Al Interlayer, *Y Li, F Ye, C Zhang, M Taheri, J Corona,* ***Qiaoqin Yang,*** University of Saskatchewan, Canada

Integration of smooth nanocrystalline diamond coatings on steel substrates for biomedical implant applications has great application potentials due to their extraordinary wear/corrosion resistance and biocompatibility. However, CVD deposition of adherent and continuous diamond coating on steel substrates has met technical barrier of easy delamination. We will report on our recent progress on enhancing the adhesion of diamond coatings on steel substrates by using CrN/Al interlayer. The morphology, microstructure, composition and adhesion of the formed surface products are comprehensively characterized by SEM, TEM, XRD, Raman and synchrotron XAS as well as indention test. The fundamental mechanism of enhanced interfacial adhesion is discussed.

BP-18 MoN/TaN Superlattices: from a Computer Design to a Realization, *N Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; R Hahn,* CDL-AOS at TU Wien, Austria*; J Zalesak,* Montanuniversität Leoben, Austria*; M Friak,* IPM, Academy of Science, Czech Republic*; M Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria*; M Sob,* Masaryk University, Czech Republic*; J Keckes,* Montanuniversität Leoben, Austria*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*;* ***David Holec,*** Montanuniversität Leoben, Austria

Nitrides are fascinating class of materials constantly revealing new and unexpected features, often related to metastable phases accessible via, e.g., non-equilibrium physical vapour depositions. Cubic MoN and TaN have been recently shown to strongly favour vacancies.

First principles calculations of undefected MoN/TaN superlattices suggest an interface-induced structural transformation from cubic to tetragonal phases (ζ-TaN, ζ-MoN). An analysis of their elastic constants reveals that the TaN volume fraction must be larger that that of MoN in order to be mechanically stable. This stability range can be further influenced by considering the point defects, namely vacancies. It is shown that the stability of superlattices critically depends not only on the amount of vacancies, but also on their distribution as well as on the superlattice bi-layer period. Impact of the interface and its orientation on the tensile strength is also briefly presented.

To compare the calculated results with experiments, magnetron-sputter deposited superlattices with various bi-layer periods are studied using conventional XRD, conventional and high-resolution TEM, and mechanical testing. The structural analysis confirms single-phase cubic superlattices with a strong (100), (110) or (111) interface orientation, as dictated by the MgO substrate orientation. Quantitative EELS measurements are used to prove the non-stoichiometry of individual constituents, MoN and TaN, as a function of the bi-layer period.

BP-20 Effect of Mo Concentration on Structure and Properties of Zr-Mo-N Thin Films Deposited by Reactive Magnetron Sputtering, *A Junior,* ***Daniel Fernandez,*** *L Félix,* Universidade Federal de Sergipe, Brazil*; R Hubler,* Pontifícia Universidade Católica do Rio Grande do Sul, Brazil*; F Mendes,* Instituto Nacional de Tecnologia, Brazil*; G Brito,* Universidade Federal de Sergipe, Brazil*; E Tentardini,* Universidade Federal de Sergipe, Brazil, Brasil

Zirconium nitride (ZrN) thin films are mentioned in many studies because of their excellent characteristics that allow their application in cutting and molding tools. However, the columnar growth, micro cracks and porosity of that material compromise its mechanical properties and limit its oxidation resistance. One of the alternatives to solve that problem is the addition of a third element to its matrix. Some studies show that molybdenum addition result in expressive improvements in mechanical properties and wear resistance, as in TiMoN and CrMoN, however there are few works about the effect of Mo in ZrN coatings properties. The objective of this work is to study the influence of molybdenum on the structure, morphology, mechanical properties and oxidation resistance of zirconium and molybdenum thin films (ZrMoN). Thus, thin films of the system ZrMoN were deposited using reactive magnetron sputtering (RMS) technique, varying the molybdenum content in 23, 31 and 37 at.%. Thin films were characterized by GAXRD, SEM, XPS and high temperature oxidation tests at three different temperatures, 773K. 873K and 973K. GAXRD analysis showed a molybdenum accommodation in the lattice forming substitutional type solid crystalline solution and a small displacement of the ZrN peaks to the right as theMo content rises. Sample with 23 at% of Mo into structure reach 33 GPa, the highest value for all coatings studied. All samples failed in oxidation tests, with reduction of hardness values; appearance of bubbles and loss of adhesion.

BP-21 Anti-staining Coatings on PET Fabrics by Using a Spraying/ Plasma-Polymerization Duplex Technique, ***Cheng-Wei Lin,*** Feng Chia University; Central Taiwan University of Science and Technology, Taiwan*; J He,* Feng Chia University, Taiwan

To fulfill better wearing quality, PET fabrics are considered for further treatment to resist environmental dust and oil stains. This study aims to prepare a hydrophobic surface on PET fabrics to minimize the risk of dust adhesions or oil stains by using a duplex technique combining spraying and low-surface-energy plasma polymerization. The anti-staining coated fabrics are tested their durability by using the AATCC 130 of washing test for barbecue sauce and ketchup.

Experimental results reveal that the duplex treated fabrics can achieve water contact angle (WCA) over 118°. Anti-staining tests performed at 1, 4, and 10 weeks after surface treatment show that the the tested fabrics can tolerate 10 times of the washing test without altering surface appearance.

Results of SEM and EDS analysis show that fluorocarbons still exhibit on the surfaces of PET fabrics after anti-staining tests. Above all, a spraying/plasma polymerization duplex coating on the surfaces of PET fabrics exhibits favorable hydrophobicity and anti-staining durability.

BP-22 Fracture Resistance of Nanocomposite/Metal Nitride Multilayers: Role of Interfaces, ***Naureen Ghafoor***, *P Persson,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; I Petrov,* Linköping University, IFM, Thin Film Physics Division, Sweden, USA*; J Barriero, F Mücklch,* Saarland University and Materials Engineering Center Saarland, Germany*; J Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; W Clegg,* Cambridge University, UK

The focus is deformation mechanisms of transition metal nitride nano-composites coatings. The deformation in these materials is strongly dependent on interface structure and become more complex in nano-composites involving high density of interfaces. We present mechanical response of TiN/ZrAlN multilayers and monolithic ZrAlN nano-composite coatings investigated through nano indentation and micropillar compression tests. The study highlights effect of interface structure on pre yield and post yield behavior of nano scale multilayer deformation in compression.

To understand stress-strain response in a uniaxial micropillar compression tests the pillars of height of 1 mm and diameter of 300 nm were compressed using in situ SEM nanoindenter equipped with a flat punch (diameter 5mm)[Ref 2]. The pillars were milled using focused ion beam. The interface structure of the multilayers is tuned by varying growth parameters during magnetron sputter deposition on MgO (001) substrates. The growth temperatures above 700 °C facilitated in situ segregation of ZrN-and AlN- rich domains within ZrAlN layer during growth [Ref 1]. The growth conditions and multilayer design are varied to tailor crystal structure of AlN rich domains from cubic to wurtzite and consequently to obtain coherent, semicoherent, and incoherent interfaces. Dependence of plastic deformation and work hardening on the multilayer period as well as on the coherency of involved interfaces is investigated. Micropillar compression tests revealed higher yield stresses and larger post yield displacements in 2 and 5 nm thin ZrAlN layers consisting of cubic phases of ZrN and AlN- rich domains forming coherent interfaces. For 15 and 30 nm thick ZrAlN layers, involving incoherent interfaces, the dominant crack propagation occur through layer interfaces. The dominant deformation mechanisms in connection with interface coherency and multilayer periodicity will be presented.

BP-23 Vacancies in Al-O-N Crystallites, ***Maria Fischer***, *D Scopece, C Pignedoli, D Passerone, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Aluminum oxynitride (Al-O-N) in its transparent ceramic form provides attractive properties for hard coatings. Thin films of this material with different O and N contents were deposited by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS) and investigated with respect to the induced changes upon varying O/N ratios.

It was discovered that O addition leads to a gradual transformation of polycrystalline wurtzite AlN via Al-O-N nanocomposite towards amorphous Al_2O_3. The boundary between polycrystalline AlN and Al-O-N nanocomposite is set by the solubility limit of O in AlN and was found to be at 8 at% O. Below this critical value, O substitutes N in in the wurtzite lattice. This leads to a continuous unit cell shrinkage in c direction measurable by XRD. Above 8 at%, O starts to surround crystallites in the form of an amorphous Al_2O_3 matrix.

The shrinkage of the c lattice parameter upon O incorporation can hypothetically be attributed to the generation of Al vacancies. Since O has one valence electron more than the N it replaces, the ideal wurtzite 1:1 stoichiometry of electron donor and acceptor as found in AlN can no more be matched. In order to maintain the wurtzite crystal structure, the proportional amount of Al has to reduce to fit the stoichiometry $AlO_{1.5x}N_{1-x}$. The hypothesis that this is achieved through vacancies in the Al lattice positions was tested by ab initio DFT calculations. Lattice parameter changes upon O introduction and consequent Al vacancy defect generation were calculated and found to be in good agreement with the experimentally observed values. The obtained results were compared to data for the related ternary Al-Si-N system.

BP-26 Effects of Bias Voltage on Microstructure and Properties of Al-doped Hydrogenated Amorphous Carbon Films Prepared by a Hybrid Deposition Technique, ***Songsheng Lin***, *W Xu, H Li, M Dai, Q Shi, C Wei, H Wang, K Zhou,* Guangdong Research Institution of New Materials, China

Al-doped hydrogenated amorphous carbon films were deposited on Si wafers and stainless substrates by a hybrid deposition technique composed of middle-frequency magnetron sputtering and anode layer ion source. Effects of substrate bias voltage on the deposition rate, surface topography, microstructure, residual stresses and mechanical properties were characterized using scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and nano-indentation. It was shown that the aluminum atoms were embedded in carbon matrix without bonding with C atoms. The surface of the films evolved from a rough surface with quasi-columnar characteristic to a smoother surface with the applied bias voltage increased from 0 to -400V. The residual stresses of the films deposited at 0V and -50Vwere tensile stress, while it transformed to compressive stress with bias voltage increased to -100V or higher. The hardness of the film stayed in the highest level of nearly 17GPa, while the bias voltage ranging from -150 to -300V. The ball-on-disk tribo-meter was further used to study the tribological behavior, the results demonstrated that the film deposited at -150V exhibited excellent lubrication performance with a fiction coefficient of about 0.047 and good wear resistance.

BP-27 Comparison of Chromium Carbide Thin Films Grown by Different Power Supply Systems, *Z Li, C Wang,* National Taiwan University of Science and Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan*;* ***Jyh-Wei Lee****,* Ming Chi University of Technology, Taiwan

The potential use of chromium carbide thin films has been a great interest to academia and industry due to their outstanding properties such as chemical stability, low coefficient of friction, adequate hardness and high wear resistance. In this study, the chromium carbide thin films were fabricated by a magnetron sputtering using different power supply systems, including direct-current (DC), high power impulse magnetron sputtering (HiPIMS), and superimposed middle-frequency (MF)-HiPIMS. The Cr target poisoning status was controlled by a plasma emission monitoring system by adjusting the gas flow ratio of Ar and acetylene (C_2H_2). The morphology and microstructure of thin films were evaluated by scanning electron microscope. The crystallinity of films was studied using X-ray diffractometer. The electron probe micro analyzer, X-ray photoelectron spectroscope, and Raman spectroscope were used to determine the chemical compositions and binding structures of thin films. The mechanical, adhesion and tribological properties were explored by using scratch tester, tribometer, and nanoindentation. The influence of different power supply systems on the microstructure, chemical composition, and mechanical properties of chromium carbide films were investigated in this work.

BP-28 Self-organized Formation of Different Nanostructure in Carbon-metal Films Prepared by Reactive Magnetron Sputtering, ***Hongxuan Li***, *W Wang, L Ji,* Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

Metal-containing carbon-based films (Me-C films) have been attracted much attention because metal-dopping can effectively improve and regulate film's properties (such as reducing the internal stresses, enhancing the adhesion to the substrate and improving environmental sensitivity of tribology). It has been wildly reported that various metals have been introduced into carbon-based films by different groups. However, it will bring wide differences in precisely controlling microstructure and interaction mechanism etc. aspects to metallic dopping carbon-based films due to diverse metallic elemental, prepared methods and conditions.

This report highlights a peculiar phenomenon that spontaneous formation of various nanostructure in the carbon-based films during co-deposition of different metallic element process. Consideration of different interaction between metal and carbon, we choice copper, titanium, and nickel as three typically dopping metals. The influence of various metallic elements on self-organizing special nanostructure in carbon-metal films is systematically studied. For copper, it is noncarbide and immiscible with carbon, self-organized nano-multilayered structure can be formed in the copper-carbon film when the copper concentration maintaining at 20%-40% at.%; Titanium are strong carbide former, the nanocomposite structure of titanium carbide nanocrystalline dissolved in the amorphous carbon matrix is observed in the titanium-carbon film; Nickel possess the ability to catalysis the growth of carbon nanowires, and self-organized carbon nano-wires structure in nickel-carbon film has been successfully prepared, the

field-emission tests of this self-assembled carbon nanowires structured film shows excellent behaviors.

BP-29 Anticorrosive Properties of (Zr-Si-Ti-N)Ni Thin Films Deposited by Co-Sputtering, ***EstrellaNatali Borja Goyeneche***, *J Olaya,* Universidad Nacional De Colombia, Colombia

In the present work, the influence of nickel content on the structural and electrochemical properties of the TiZrSiN films was investigated. The nanostructured ZrSiTiN thin films with nickel additions were deposited onto stainless steel AISI 316L and TiAlV alloy substrates using the reactive magnetron co-sputtering technique. The structure was analyzed by X-ray diffraction and the chemical composition was identified by energy dispersive X-ray spectroscopy (EDS). The corrosion resistance was studied by potentiodynamic polarization test and electrochemical impedance spectroscopy using a 3.5 wt% NaCl corrosive solution. Nickel leads to improve the anticorrosive properties of thin composite films because to the incorporation of a physical barriers against the propagation of the corrosive electrolyte. The corrosive mechanism is discussed in this paper.

BP-30 Corrosion Resistance of Stainless Steel Coatings With and Without Silver Deposited by Sputtering, ***ClaudiaLiliana España***, *J Olaya,* Universidad Nacional De Colombia, Colombia*; A Candido Recco,* Universidade do Estado de Santa Catarina, Brazil

The anticorrosive properties of stainless steel coatings deposited with different amounts of silver by unbalanced magnetron sputtering were studied. The structure of the coatings were characterized by means of X-ray diffraction, the morphology and chemical composition were evaluated by means of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) respectively. The corrosion resistance was determined through out of potentiodynamic polarization tests and electrochemical impedance spectroscopy using a Ringer's solution as a simulated biological fluid. It was determined that the coatings deposited in inert atmosphere presented BCC structure, while the coatings deposited in the reactive atmosphere shows the BCC and FCC phases. A compact morphology was observed in coatings with a higher silver content. The corrosion resistance was increased in the coated substrate compared to the uncoated substrate. Corrosion mechanism of coating deposited is disscused in this paper.

BP-31 Evolution of Structure and Mechanical Properties of Nanocrystalline Multi-layered Arc-evaporated AlCrN-AlTiN Coatings upon Thermal Loading Revealed by X-ray Nanodiffraction and Tribological Testing, ***Stefan Klima***, *N Jäger, M Meindlhumer,* Montanuniversität Leoben, Austria*; H Hruby,* eifeler-Vacotec GmbH, Germany*; J Keckes, R Daniel,* Montanuniversität Leoben, Austria

Nanocrystalline coatings are typically characterized by inherent variations in the structure (texture and size of grains), residual stress and mechanical properties over the thickness, which is associated with the competitive nature of their growth. On the other hand, the microstructure and thus the coating properties may be intentionally controlled by a specific multilayer architecture, in which crystallographic structure, size of grains as well as the stress state may be influenced by layer thickness and templating effects. In order to understand the complex structure-stress-property variations in hierarchical nanostructured coatings, a multi-layered multi-phase arc-evaporated AlMeN-based coating system (where Me=Cr and Ti) was developed and studied by cross-sectional position-resolved synchrotron X-ray nanodiffraction and tribological testing in the as-deposited state and after thermal treatment. Since both AlMeN systems are metastable transition metal nitrides having either cubic or hexagonal crystallographic structure depending on the Al-content, their phase composition was controlled either by the cathode composition or deposition conditions. Furthermore, potential (de)stabilization of the crystallographic structure of the metastable constituents was studied in detail for the multi-layered system, where AlCrN and AlTiN sublayers prepared at bias voltages ranging between -30 and -600 V alternated with layer thicknesses varying from 10 to 300 nm. The X-ray nanodiffraction analysis revealed that the cubic structure of the AlMeN layers may be stabilized even at high temperatures while combed with cubic sublayers in a multilayer structure, although they otherwise exhibit a dual phase structure as monolithic coatings. The role of the coating architecture on the structural stability and the stress state will be demonstrated for a number of multilayer design variations.Furthermore, coatings with a specific architecture were selected based on the results of the cross-sectional combinatorial approach and tested by pin-on-disk experiments at RT and 600 °C. The results document strong relationships between the architecture, phase composition, stress state, thermal stability and wear resistance of the coatings, which allow to establish specific design rules for thermally and mechanically stable multi-layered AlN-based coatings.

BP-32 Corrosive Resistance of Nanostructured ZrSiN-Ag Films Deposited by Reactive Sputtering, *H Vanegas Parra,* ***JhonJairo Olaya***, *J Alfonso,* Universidad Nacional De Colombia, Colombia*; S Calderon,* International Iberian Nanotechnology Laboratory, Portugal*; S Carvalho,* University of Minho, Portugal

Due to their physical and chemical properties the multifunctional materials have been study extensively in the last years. In this work we present the growth of nanostructured ZrSiN-Ag films deposited on common silicon and stainless steel substrates via magnetron co-sputtering with aim of analyze the influence of silver amount on the crystalline structure and corrosive resistance. The coatings structure have been characterized through X-ray diffraction (XRD) and the morphology has been evaluated via scanning electronic microscopy (SEM); anticorrosive properties were carried out through potenciodinamic polarization test. The preliminary results, shows that the films are polycrystalline and the corrosion resistance improve as a function of the Si and Ag amount in the films deposited. The corrosion mechanism in the films will be discussed in this work.

BP-33 Mechanical Properties of ZrSiN-Ag Thin Films Deposited by Reactive Magnetron Sputtering, ***HenrySamir Vanegas Parra***, *J Alfonso, J Olaya,* Universidad Nacional De Colombia, Colombia*; S Calderon,* International Iberian Nanotechnology Laboratory, Portugal*; S Carvalho,* University of Minho, Portugal

ZrSiN-Ag thin films were deposited by reactive magnetron sputtering in order to study the effect of addiction of silver on the structure, chemical composition and mechanical properties in ZrSiN thin films. The structure of thin films was characterized by X-ray diffraction (XRD), the morphology by scanning electron microscopy (SEM) and the chemical composition by energy-dispersive x-ray spectroscopy (EDS). A nanoindenter was used to study the mechanical properties such as hardness and elastic module in function the silver content in the films deposited. The XRD results showed that nanostructured ZrSiN-Ag thin films were obtained. The ZrN film exhibited a face-centered cubic (f.c.c) phase with columnar structure while that the Zr-Si-N films showed a mixture of f.c.c and near-amorphous phases without columnar structure, similar to the ZrSiN-Ag films. The hardness obtained for ZrN film was of 58,80 GPa, which decreases as silver contents increase.

BP-34 Hardness and Adhesion of AlSiN Thin Films Deposited by the Simultaneous Laser Ablation of Two Targets, ***Enrique Camps***, *L Rivera, I Campos-Silva,* Instituto Nacional de Investigaciones Nucleares, Mexico*; S Muhl,* Universidad Nacional Autonoma de Mexico, Mexico

Aluminum silicon nitride (AlSiN) thin films with different Si content were deposited using the simultaneous laser ablation of aluminum and silicon targets in a nitrogen atmosphere and a substrate temperature of 200 °C. Films were deposited at two values of working pressure, 0.6 and 1 Pa. The silicon content in the films ranged between 3 and 20 at. %, and was varied by changing the density of the plasma produced during the ablation of the silicon target, i.e. the highest the plasma density gave the highest the silicon concentration in the films. The plasma parameters (mean kinetic ion energy and plasma density) were measured using a planar Langmuir probe. Samples deposited with low silicon contents (up to about 6 at. %), contained nanocrystals embedded in an amorphous matrix. Those crystals were identified as hexagonal aluminum nitride (w-AlN). For higher concentrations of silicon the amorphous phase was predominant and the nanocrystals were no longer observed. The hardness of the films had a maximum value of 30 Gpa, and an elastic recovery of about 50 % when the silicon content was close to 4 at. %. For higher silicon concentrations the hardness was lower at 19 GPa. Scratch tests were carried out on samples with different silicon contents. For the samples with low silicon contents (the highest hardness) delamination was observed at loads of 90 N, in the transition to the solid solution regime (Si content of 8 at. %) delamination was observed to begin at 10 N, and for the highest concentrations of silicon no delamination of the films was observed even for loads of 90 N.

BP-35 Plasma Enhanced Chemical Vapor Deposition of Carbon Film into a Small Hole 100 µm in Diameter with MVP and Source Gas Blowing, *R Ota,* Nagoya University, Japan*;* ***Hiroyuki Kousaka***, Gifu University, Japan*; L Raja,* University of Texas at Austin, USA*; N Umehara, M Murashima, T Tokoroyama,* Nagoya University, Japan

Diamond-like carbon (DLC) is widely applied to mechanical parts because of its low friction performance, high wear and corrosion resistance. When it is applied to the internal surface of a hole, plasma enhanced chemical vapor

deposition (PECVD) is typically used because of its excellent coating coverage to 3-dimensional internal surfaces. However, it is not feasible to generate plasma in an 100's-µm-diameter hole due to the formation of ion sheath whose width is comparable to the inner diameter. In this case, the precursor molecules of DLC such as CH_3 radical are transported by diffusion into the inside of a hole from plasma generated at the outside. However, the radical density decreases exponentially in axial direction by sticking loss to the internal surface of a hole. Consequently, the depth of the internal surface covered by DLC (referred to as coating depth) has no choice but to become almost the same as its diameter [1]. Since the aspect ratio of a hole in mechanical parts is typically more than 10 (e.g. fuel injector), it is strongly required to increase coating depth. Thus, in this research, we propose the novel coating method by PECVD coupled with source gas blowing to increase coating depth for an 100-µm-diameter hole. Particularly, We investigate the effect of blowing source gas and flow rate on the coating depth of DLC.

In order to deposit DLC to the inner surface of a small hole 0.1 mm in diameter and 5 mm in depth, PECVD employing MVP is conducted with blowing source gas from nozzle to the hole inlet. After DLC coating, film thickness is measured by 0.1 mm in axial direction of the hole and the maximum depth where a film thickness is detectable is defined as coating depth. We found that blowing source gases increases coating depth. Furthermore, the linear increase of coating depth from 0 to 1 mm was observed with the increase of the flow rate of blown gas from 0 to 780 sccm. We are going to further investigate the effect of source gas flux on coating depth by numerical simulation of plasma with the commercial software VizGlow at the conference.

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BP-37 Effect of Silicon Content on Structure and Properties of AlCrSiN Coatings Prepared by Arc Ion Plating for Milling Tools, ***Wangryeol Kim***, *S Heo,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; Y Kim, J Kim,* KORLOY, Republic of Korea*; I Park,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Quaternary AlCrSiN coatings with silicon content ranging from 0 to 21 at.% were deposited on WC-Co alloy substrates by an arc ion plating technique using Cr-Al and Cr-Si composite targets in an N2/(Ar+N2) gas m ixture for hard material processing milling tools. The microstructure, mechanical, wear, tribological properties of the coatings were investigated by XRD, XPS, FESEM, HRTEM, surface 3D profiler, nano-indentation, scratch tester, and ball-on-disc tribo-meter. As the silicon content increased, the microstructure of the coatings changed from columnar grains to interconnected fine grains, and finally to nanocomposite structure, in which (Al,Cr)N nanocrystallites were surrounded by an amorphous silicon nitride matrix. The incorporation of silicon results in the (Al,Cr)N crystallite size refinement and the decrease of the average surface roughness. The nanohardness of the AlCrSiN coatings showed higher hardness values than that of AlCrN coating. The strengthening mechanisms include solid solution hardening and grain boundaries strengthening through the formation of a thin amorphous layer. Moreover, it was found that the improved nanohardness and the H/E ratio contributed to excellent wear resistance of the coatings. The friction coefficient and wear rate of the AlCrSiN coatings first decreased and then increased with increasing silicon content. The friction coefficient and wear rate were also mainly related to the lubricant wear debris in this work.

BP-38 Coatings and Performance Evaluation of Ti–Al–Si–N–O Coated Cutting Tools, ***Sungbo Heo***, *H Kim, U Jung,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; Y Kim, J Kim,* KORLOY, Republic of Korea*; I Park,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Functional graded Ti–Al–Si–N–O nanocomposite coatings were deposited onto WC-Co substrates by a filtered arc ion plating system using $TiAl_3$ and Ti_4Si composite targets under N2 atmosphere. XRD and XPS analyses revealed that the synthesized Ti–Al–Si–N–O coatings were nanocomposite consisting of nanosized (Ti,Al,Si)N crystallites embedded in an amorphous Si_3N_4/SiO_2 matrix. The hardness of the Ti–Al–Si–N–O coatings exhibited the maximum hardness values of ~43GPa at a Si content of ~5.63 at.% due to the microstructural change to a nanocomposite as well as the solid-solution hardening. Ti–Al–Si–N–O coating with Si content of around 5.63 at.% also showed perfect adhesive strength value of 105.3N. These excellent mechanical properties of Ti–Al–Si–N–O coatings could help to improve the performance of machining tools and cutting tools with application of the coatings. Ti-Al-Si-N-O coatings were applied to insert tools. Their performances were evaluated about cutting-time and cutting-length to Inconel 718 super alloys. Performance of the coated tools were evaluated and compared with different Ti-Al-Si-N-O coatings onto cemented carbide substrates. Especially, the Ti-Al-Si(5.63at%)-N coated tool showed better performance and best tool life in this work.

BP-39 Transparent and Low Resistance Hard Amorphous Carbon Thin Films by HiPIMS for Electronic Applications, ***Kerstin Thorwarth***, *R Ganesan, A Chacko,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Grein, R Bandorf,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; D McKenzie, M Bilek,* The University of Sydney, Australia*; H Hug,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

High power impulse magnetron sputtering (HiPIMS) was used to deposit optically transparent amorphous carbon thin films with low electrical resistance. The films were deposited on Si substrate. The film of 75 nm thickness exhibit the sheet resistance of 2.5 kW/□ and high visible transmittance of 76 % at 450 nm. The room temperature mobility of the deposited amorphous carbon films lies in the range of 14 - 18 cm2v-1s-1, which is higher than the previously reported values. The X-ray Photoluminescent studies and the optical bandgap by Tauc's method suggest that the bandgap of films lies between 1.75 to 2.35 eV, and depends on the values of negative bias voltage applied to the substrate. The films are totally hydrogen free (H content < 0.7 %) and exhibit densities varied from 2 to 2.6 eV. The measured hardness values are greater than 33 GPa for the films with thickness = 800 ± 40 nm, but deposited at similar deposition conditions. Such properties of the amorphous carbon films have a great potential in the application of transparent conducting electrodes.

BP-40 Reactive Magnetron Sputter Deposition of Bismuth Tungstate Coatings for Water Treatment Applications under Natural Sunlight, *M Ratova,* ***Peter Kelly,*** Manchester Metropolitan University, UK*; R Marcelino, C Amorim, P de Souza,* Federal University of Minas Gerais, Brazil

Photocatalysis is a promising method for decontamination of air, water and soil. In particular, photocatalytic purification of wastewater is becoming an increasingly popular process, with the wide range of titanium dioxide-based materials successfully applied as photocatalysts for water treatment application. However, the use of titanium dioxide for efficient water treatment application is restricted with two major limiting factors, namely a relatively high band gap value and low photonic efficiency. The high band gap value results in titania photocatalysts being activated only with ultraviolet (UV) irradiation (<5% of the solar spectrum), therefore, for practical use, additional irradiation sources are required. Consequently, it is rather difficult to achieve high reaction rates, as required when dealing with heavily-polluted industrial wastewater or high throughput systems. As photocatalytic wastewater treatment is aimed at being an economical and practical technique, it is desirable to avoid the extra costs of using artificial light sources in the photocatalytic treatment setup. Use of natural sunlight represents a cheap and sustainable irradiation source, however, as in the case of titania-based photocatalysts, its efficiency can be rather low. Therefore, there is an obvious need for the development of photocatalytic materials based on the use of low band gap semiconductors, combining visible light activity with high photonic efficiency and high surface area.

In the present study narrow band gap semiconductor bismuth tungstate has been deposited onto 2 mm glass beads via reactive magnetron sputtering from a dual source system. The beads were used to increase the surface area, as opposed to flat substrates, and manipulated using an oscillating bowl placed under the magnetrons in order to provide uniform coverage. The atomic ratio of Bi/W was varied through the variation of the power applied to the magnetrons. The deposited coatings were analyzed by SEM, EDX, XRD, XPS and AFM. The photocatalytic properties of the coatings were assessed via their ability to degrade an methylene blue under artificial (fluorescent light) and natural (sunlight) irradiation. The photocatalytic performance of the bismuth tungstate-coated beads was compared to that of titanium dioxide coatings deposited onto identical beads. The results showed that the photocatalytic performance of bismuth tungstate-coated beads was superior to that exhibited by TiO_2-coated beads. Reactive magnetron co-sputtering has been shown to be a promising technique for deposition of narrow band gap bismuth tungstate onto irregularly-shaped substrates for potential use in water treatment applications.

Fundamentals and Technology of Multifunctional Materials and Devices
Room Grand Hall - Session CP

Symposium C Poster Session

CP-2 Effect of Nitrogen Content on Structure and Properties of MoN_x Coatings, ***Jian Wang,*** University of New South Wales, Australia

Molybdenum nitride (MoN_x) coatings were deposited onto AISI M2 tool steel substrates (hardened to HRC 60) by closed field unbalanced magnetron sputtering ion plating (CFUMSIP) and controlled by means of a closed-loop optical emission monitor (OEM), which was used to control the nitrogen content. The structure of the coatings was investigated by X-ray photoelectron spectrometry (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The analysis showed that increased nitrogen content led to a transformation from bcc Mo phase to fcc Mo_2N phase and then to fcc MoN phase as the OEM level was decreased. The mechanical and tribological properties were evaluated by nano-indentation, wear and scratch testing. During the wear test, the Mo_2N exhibited the lowest coefficient of friction. Further, during the scratch test, the Mo coating failed at the lowest load. This presentation will relate the processing conditions to the structure and hence mechanical behavior of these coatings.

CP-3 Stress Metrology for G6 and Larger Flat Panel Displays, ***Wojtek Walecki,*** Frontier Semiconductor, USA*; W Hung,* Frontier Semiconductor, USA, United States of America*; D Kim,* Sejong University, Korea

We report novel photo-elastic method for measurement of the stress in polyimide (PI) based flat panel displays (FPD) and flexible displays (FD) structures. Method is based on measurement of the change of the state of polarization of the light undergoing reflection (or transmission) in the structures containing PI layer(s). Commonly used FPD and FD contain layers of 5 um or thicker PI layers. PI has stress optic coefficient of about 3.4E-10 Pa^-1 [1], which is almost 100 times larger than glass [2]. This allows easily measurement of stress with sensitivity of the order of 5 MPa and less. We present apparatus for local stress measurements having lateral resolution of 3 cm, and stress resolution of 5 MPa. Presented tool gives promise to become capable of measuring glass panels of the size 1.5 m x 1.85 m does not contained any moving parts. Our tool can be combined with more traditional stress induced deflection based stress measurement [3]. We discuss also methods of numerical analysis of optical data, including stress separation algorithm optimized for this problem, and practical problems related to analysis of the data.

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CP-4 Hydrogen Barrier Properties of Diamond-like Carbon Coatings, ***Motonori Tamura,*** University of Electro-Communications, Japan

The hydrogen barrier properties of the coatings of diamond-like carbon (DLC) were evaluated. Using plasma chemical vapor deposition and sputtering, DLC coatings were deposited on Type 316L stainless steels. The hydrogen permeation rate was reduced to 1/1000 or lower by the DLC coatings. The DLC coatings with high hydrogen content had high hydrogen barrier function. For hydrogen diffusion in coatings, the movement of atoms through hydrogen trap sites such as pores in coatings, and crystal defects such as dislocations, is important. The DLC coatings are amorphous, and there are both sp^3 and sp^2 bonds, and excess hydrogen could be found in the interstitial space and the hydrogen trap sites. In the DLC coatings with high hydrogen content, these hydrogen trap sites are likely already filled with hydrogen atoms, and the movement of new hydrogen atoms could be limited.

CP-5 Effect of N_2 Flow Rate on the Properties of TiN film on Si Substrate for Thermal Detector Application, ***Yi-Ching Huang,*** *K Lin, Y Lai,* National Nano Device Laboratories, National Applied Research Laboratories, Taiwan

Titanium nitride (TiN) is a suitable material for the mirror film of thermal detector due to its high IR reflectivity property. TiN thin films have been deposited on p-type Si (100) substrate with different nitrogen flow rate by magnetron sputtering system. Increasing the N_2 flow rate played a significant factor in controlling the properties of TiN films. In the study, the surface performance, phase, element ratio, and the optical and electrical properties of the TiN films will be characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectrometer (XPS), Fourier Transform Infrared Spectroscopy (FTIR), and current-voltage (I-V) measurement. The results indicated that the TiN film with 40 sccm N_2 flow rate had high reflection (88%) in the IR range and exhibited the lower sheet resistance and high I_{on}/I_{off} ratio.

CP-6 Gradated Multilayer Thin Film of $BaTiO_3$/PVDF with High Energy Storage Density, ***XiaoHui Wang,*** Tsinghua University, China

Organic-inorganic 0-3 nanocomposites, which combine the potentially high dielectric strength of the organic matrix and the high dielectric permittivity of the inorganic filler, are extensively studied as energy-storage dielectrics in high-performance capacitors. To obtain high dielectric constants, a large volume fraction of the inorganic component is necessary, but this will frequently deteriorate the dielectric (breakdown) strength and thus limit the energy density value of the overall nanocomposite. In this study, a gradated multilayer $BaTiO_3$/poly(vinylidenefluoride) thin film structure is presented as a means to achieve both a higher breakdown strength and a superior energy-storage capability. Key to the process is the sequential deposition of uniform dispersions of the single component source, which generate a blended PVDF-BTO-PVDF structure prior to full evaporation of solvent, and thermal treatment of the dielectric. The result is a 2-2 like sandwich structure with partial 0-3 character, seamless interfaces between layers and a concentration gradient of the BTO. The central layer designed to provide the high electric displacement, is composed of high volume fraction 6-10 nm BTO nanocrystals produced by a TEG-sol method. The outer layers of the structure are predominantly PVDF, with a significantly lower volume fraction of BTO, taking advantage of the higher dielectric strength for pure PVDF at the electrode-nanocomposite interface. The film is mechanically flexible, and can be removed from the substrate, with total thicknesses in the range 1.2 – 1.5μm. Parallel plate capacitance devices exhibithighly improved dielectric performances, compared to reported values for BTO-PVDF 0-3 nanocomposites, with low-frequency permittivity values of 20-25, a maximal discharged energy density of 19.4J/cm^3 and dielectric breakdown strengths of up to 495 kV/mm.

CP-7 Synthesis of Bi_2O_3:TiO_2 Nano Structured Thin Films for Photocatalytic Applications, *M Calheiros, F Correia, J Marques,* ***Carlos Tavares,*** University of Minho, Portugal

The increasing scarcity of potable water has served as motivation for the development of decontamination processes. Photocatalytic degradation is one of the most viable processes compared with conventional ones. This process uses the UV radiation effect to produce hydroxyl radicals, with the assistance of a photocatalyst. The most commonly used catalyst is TiO2 semiconductor, characterized by its low toxicity and high chemical stability. This work aims to synthesize Bi2O3 thin films with fibrous morphology for subsequent functionalization with a top TiO2 thin film. A Hastelloy B3 thin film was used as an interface layer between the glass substrate and the Bi seed layer in order to promote some interfacial roughness and improve film adhesion. The growth of Bi2O3 thin films was performed by magnetron sputtering and adapted to abide the vapor-liquid-solid (VLS) mechanism, mainly concerning its 3D growth morphology and its high roughness templates. Subsequently, the TiO2 photocatalytic thin films were deposited onto the Bi2O3 thin films. SEM observations revealed a pine-tree morphology for the Bi2O3 nano structures, with an enhanced surface area. The photocatalytic efficiency assessment was performed by conducting an assay using methylene blue dye as the pollutant and a solar radiation simulator. The tests show that the thin films of Bi2O3:TiO2 are more efficient at degrading the pollutant when compared with the TiO2 thin films.

CP-8 Improvement of Mechanical Properties in 3D Printed Ceramic Core, ***Hye-Yeong Park,*** *B Kim, G Cho, E Kim, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Indiana University Purdue University Indianapolis, USA

Ceramic core employed in a precision casting process is typically not recyclable, which reduces productivity and increases production cost. Therefore, a new fabrication process for ceramic core combined with 3D printing process and organic-inorganic binder conversion process was proposed in our previous study. However, the core made of coarse mullite bead (average particle size: 250um) did not develop sufficient green and firing strengths due to the porosity and pore size. Therefore, to improve the mechanical properties, especially the strength, the packing density of ceramic core was increased, through mixing fine mullite powder (average particle size: 16um) and zircon flour (average particle size: 43um) with

coarse mullite bead. Green bodies with the two types of poly vinyl alcohol (PVA), which have the same molecular structure with a large difference in their boiling points were 3D printed. Then the samples were heat-treated at 250°C to evaporate the PVA with a lower boiling point. The heat-treated core samples were dipped into the inorganic precursor, and dried and heat-treated at 1000°C for the organic-inorganic conversion process. Through the combination of starting powders, the compact density of the sample was increased and the pore size was reduced, resulting in an increase in the inorganic binder coating efficiency and an improvement in the glassification conversion efficiency. The study demonstrates the feasibility of fabrication of ceramic core with excellent strength through 3D printing process.

CP-9 Enhanced Efficiency of Perovskite Solar Cells with Ferroelectricity, *T Nguyen, S Shin, S Kim, H Choi,* ***ChungWung Bark,*** Gachon University, Republic of Korea

Perovskite solar cells (PSCs), which emerged as tremendously attractive devices in thin-film photovoltaic technology to utilize renewable energy sources, have been improved with the unprecedented breakthrough in recent years. Ferroelectric materials with a vast array of intriguing electrical properties have been applied in photo-related devices; however, there was rarely that these materials appeared in solar cell device configuration. In this work, mesostructured TiO2 combined lanthanum bismuth titanate (BLT) nanoparticles in a combination with perovskite CH3NH3PbI3 light absorber is capable of maximizing the absorbed visible light. Interestingly, the robust spontaneous electrical polarization of these ferroelectrics under applying positive bias voltage promotes the desirable separation of photoexcited carriers and drives the charge transportation that contributes to high-efficiency PSCs. Application of uniform nano-sized BLT powders through high-energy ball milling process and perovskite layer fabricated by two-step solution deposition technique will pave the way for fabricating hybrid organic-inorganic perovskite solar cell with high solar energy conversion in the coming years.

CP-10 Improvement in Hygroscopicity of Inorganic Binder through Dual Coating Process, ***Hyun-Hee Choi,*** *H Lee, G Cho, E Kim, Y Jung,* Changwon National University, Republic of Korea*; J Zhang,* Indiana University-Purdue University Indianapolis, USA

In a conventional sand casting process, the mold is manufactured by mixing ceramic materials and organic binders, which is widely used in foundry industry due to the simple manufacturing process and low production cost. However, it is difficult to form complicated products since the organic binders are decomposed and the defects in the mold are generated during casting at high temperatures. In order to solve these problems, organic-inorganic binder conversion process has been proposed. One issue in the process is that, when stored at room temperature for a long time before heat treatment, the mold strength is reduced and/or the mold is fractured, which is caused by the hygroscopicity of the water-soluble inorganic binder. Therefore, in this study, a dual coating process was proposed and applied to reduce the hygroscopicity of the inorganic binder in preparing the casting mold. The prepared sample was dipped into a solution of inorganic binder precursor (TEOS: SiO_2 precursor and NaOMe: Na_2O precursor), and then dipped into a solution of water-insoluble organic binder after a drying process. Finally the sample was heat-treated at 1000 ˚C to generate a glass phase by organic-inorganic conversion process. The contact angle of the sample with the water-insoluble organic binder was increased, while it was impossible to measure the contact angle in the conventional sample. It was confirmed that the green and firing strengths were maintained by the water-insoluble organic binder coating layer. The effects of the holding time and humidity at room temperature on the strength and microstructure of the mold were investigated, in terms of organic binder species employed in the dual coating process.

CP-11 Synthetic Parameter Influence on Morphological and Electrochemical Properties of Porous NiO Thin Films Prepared by Chemical Bath Deposition, ***Jung-Hoon Yu,*** *H Yang, R Jeong, J Lee, D Kim, K Hwang, H Seo, S Nam, J Boo,* Sungkyunkwan University, Republic of Korea

Chemical bath deposition (CBD) is an advantageous thin film deposition technique for depositing compound semiconductors at low temperature. In this paper, nickel oxide (NiO) thin films were prepared by CBD method under aqueous solution containing nickel sulfate, potassium persulfate, and ammonia water at room temperature. Prepared NiO thin film has porous structure with two dimensionally networked nanoflake arrays. In this process, concentration of ammonia water and nickel sulfate significantly affect on morphological features. Increase of ammonia concentration cause the growth kinetics until 30 ml of ammonia. Over 30 ml, however, it tended to not only decrease the thickness of films but also change the growth direction of flakes. In addition, lower concentration of nickel sulfate form a thicker NiO thin film but high concentration forms a lower thickness. This phenomenon is derived from Oswald ripening between crystal growth and aggregation at the CBD process. Each prepared NiO thin films were characterized by electrochemical measurement to apply on elctrochromic window. Optimized NiO thin film shows good elctrochromic performance with fast switching speed (11.0 s and 7.5 s), high optical modulation ($T_{bleaching}$: 80% and $T_{coloring}$: 17 %) and high cycling durability (over 5000 cycle).

CP-12 Characteristics of Perovskite Solar Cells Fabricated by using Lead Free Perovskite, *S Shin, C Bark,* ***HyungWook Choi,*** Gachon University, Republic of Korea

Lead halide perovskite is an excellent candidate for use as a light harvester in solar cells. The perovskite structure $(CH_3NH_3)PbX_3$ (X = halogen) consists of organic components at cuboctahedral sites and inorganic components at octahedral sites, and perovskites exhibit the chemical properties of the organic component. Solid-state hybrid organic–inorganic solar cells often employ a layered structure of nanoparticulate titania, an organometal halide perovskite, and a spiro-MeOTAD hole transport material (HTM). One concern, however, is the potential toxicity of lead, an important component of conventional perovskite solar cells. Currently, the most likely substitute is a tin, and it is a Group 14 metal, similar to lead. In this paper, we develop a new type of perovskite photoresist for non - toxic perovskite solar cell applications. This is also a non-toxic material for solar cells compared to conventional materials used for perovskite solar cells. The perovskite precursor solution was prepared by dissolving CH_3NH_3I and SnI_2 in N-dimethylformamide (DMF). The application of the perovskite layer produced by the sequential deposition technique through the perovskite produced by using the tin is likely to replace the Pb-based perovskite, which is a safety and commercialization of the perovskite solar cell Improve technological progress.

CP-14 The Influence of Disordered Grain Boundaries on Carrier Transport in Degenerated Polycrystalline AZO Thin Films Deposited by Magnetron Sputtering, ***Hiroki Tokunaga,*** *T Miyata, T Minami,* Kanazawa Institute of Technology, Japan

The influence of disordered grain boundary on carrier transport is investigated for degenerated polycrystalline Al-doped ZnO (AZO) thin films prepared using two magnetron sputtering deposition (MSD) apparatuses . The AZO thin films with an Al content of 3 at.% and a thickness of 500 nm were prepared on glass substrates at a substrate temperature of room temperature (RT) in a pure Ar gas atmosphere at a pressure of 0.6 Pa using a dc and an r.f. (13.56 MHz) power supply applied either separately or in combination; dc-MSD and rf-MSD or rf+dc-MSD. When the electrical properties were evaluated by the van der Pauw method, the obtained mobility (μ^{Hall}) and carrier concentration (n^{Hall}) in polycrystalline AZO thin films prepared by MSD methods exhibited the location dependences (distributions) on the substrate surface, when moved from the location corresponding to the center on the target surface to one corresponding to the erosion area on the target. The location dependences of μ^{Hall} and n^{Hall} were also controlled by rf+dc-MSDs carried out with varying superimposed r.f. power. However, we found that the μ^{Hall}-n^{Hall} relationship resulting from those location dependences always exhibited a positive slope. In addition, we found that the main scattering mechanism, which limits the mobility of AZO thin films is attributed to grain boundary scattering caused by the reflection of electron s from the potential barrier at the grain boundary between crystallites. The obtained μ^{Hall}-n^{Hall} relationships with a positive slope in degenerated AZO thin films prepared by various MSDs always exhibited fair agreement with those calculated using Mayadas and Shatzkes (MS) theory. However, the significance and reliability of reflectivity used as a fitting parameter in the semi-classical MS theory seem questionable. Munoz's group recently reported that the increase in the resistivity of a metallic specimen must be estimated under the effect of electron scattering from disordered grain boundaries based upon Kubo formalism. Disordered grain boundaries were represented by a one-dimensional periodic array of Dirac delta functions separated by a distance producing a Krönig-Penney (KP) potential. They used Green's function built from the wave functions, which are solutions of the KP potential. In quantum theory, the positively sloped μ^{Hall}-n^{Hall} relationship in degenerated semiconductors such as AZO thin films is attributed to Anderson localization, induced by electron grain boundary scattering from disordered successive grains.

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CP-15 Physical and Electrochromic Behavior of the $ZnWO_4$ Active Layer synthesized by Co-sputtering Technique for the Energy Harvesting Devices, *G Malik, S Mourya, J Jaiswal,* ***Ramesh Chandra,*** Indian Institute Of Technology Roorkee, India

This article presents a detailed investigation on a zinc tungstate (ZnWO4) active layer, prepared by reactive DC magnetron co-sputtering using standard Zn and W targets, on a transparent conducting glass ITO (indium doped tin oxide) substrate at various temperatures. The ITO substrate is used as a working electrode and $ZnWO_4$ active layer serve the purpose of a mixed conductor, which is a source of ions and electrons for the electrochromic devices. The physical properties of the fabricated active layer are investigated by x-ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), and UV-Vis-NIR spectrophotometry. The quality and the elemental distribution of the active layer are confirmed using X-ray photoelectron spectroscopy (XPS).To determine the optical behavior, Variable angle spectroscopic ellipsometry (VASE) is deployed to calculate the optical constants (*n* and *k*). Finally, the electrochemical performance of the active layer was analyzed by cycle voltammetry technique (CV). XRD diffractogram professed that the films are polycrystalline in nature with a monoclinic structure having P2/c space group. SEM micrographs and the cyclic voltammogram of the active layer revealed the surface modification and temperature dependent electrochromic response. This work is an attempt towards the "green nanotechnology" with energy harvesting for human comfort and financial benefits.

CP-16 The Influence on Electrical Characteristics of Amorphous Indium Tungsten Oxide Thin Film Transistors with Multi-Stacked Active Layer Structure, ***Kai-Jhih Gan,*** *P Liu, D Ruan, Y Chiu, M Yu, T Chien, Y Chen, P Kuo, S Sze,* National Chiao Tung University, Taiwan

A novel amorphous indium-tungsten-oxide thin film transistor with a multi-stacked active layer is well discussed in this work. A multi-layer channel is proposed to effectively enhance the carrier mobility and device stability, simultaneously. A top capping oxygen-rich a-IWO thin film is used for suppressing the plasma damage to channel layer during backchannel passivation layer deposition process or the oxygen desorption from channel layer by the backchannel passivation material. In addition, a bottom buffer oxygen-rich a-IWO thin film is deposited to avoid the oxygen vacancy formation during the following thermal process. On the other hand, a 1-nm thick WO_3 layer is inserted between the high-k gate insulator and the multi-stacked active layer, which plays important roles as interfacial layer for improving the interface quality and reducing the surface roughness. Besides, a HfO_2 dielectrics film is chosen as gate insulator for realizing low-voltage operation. In this research, the sample with multi-stacked active layer exhibits a high On/Off current ratio of $\sim 1\times10^7$ for low gate leakage current, attributing to the bottom oxygen-rich thin film. Then, a high field-effect mobility of $\sim$ 21 cm^2/V.s is achieved by a low surface roughness. Due to the good interface quality, the subthreshold swing is about 0.1 V/decade. This multi-stacked active layer structure exhibits its potential application for the future high-resolution and large-size display manufacture.

CP-17 Assessment of Structural and Magnetic Properties of Cobalt-Iron-Nickel Thick Films on Copper Formed by Electroforming, ***ScooterD. Johnson,*** *C Joye, H Newman, N Nepal, A Kozen, S Shin,* Naval Research Laboratory, USA

Co-Fe-Ni alloys form a family of soft magnetic material with a large magnetic saturation (~20 kG) and very low coercive field (< 10 Oe) that can play an important role in developing micro electromechanical systems and other novel device structures. For example, integration of magnetic structures into vacuum electronic traveling wave amplifier circuits may dramatically reduce the bulk magnetic material needed in these devices, thereby producing favorable scaling opportunities in larger systems . Vacuum electronic devices have been made using ultraviolet photolithography and electroforming (UV-LIGA) to form bulk copper structures. Magnetic components to aid in directing the electron beam passing through the electromagnetic circuit are traditionally machined, brazed together and drilled out to accept the copper circuit structure. To explore the integration of magnetic materials into these circuits by additive manufacturing, we explore tuning the elemental and structural composition of the electroformed Co-Ni-Fe magnetic films. The resulting films were assessed using x-ray photoemission, x-ray diffraction, scanning electron microscopy, vibrating sample magnetometry, and ferromagnetic resonance techniques.

Samples were formed using a sulfate electrolyte bath consisting primarily of cobalt sulfate, nickel sulfate and iron sulfate with several additives to act as a buffer, improve adhesion, and reduce stress. The pH was varied from 2.8 to 3.2, and the galvanic methods were varied. The plating was carried out in a nitrogen glovebox to exclude oxygen in the atmosphere. The effects of hydrogen annealing are also studied, since vacuum electronic devices are often hydrogen brazed at temperatures up to 1050 deg C.

Film thickness was estimated to be about 100 um. VSM results on initial samples suggest that the films have a good magnetic saturation value of about 19 kG with a small coercive field of about 50 Oe. The anisotropy field was estimated using a Stoner-Wohlfarth fit and suggests a high degree of magnetic anisotropy perpendicular to the film surface. XPS results indicate that the sample compositions vary in Ni and Fe content. Additional Co and Ni increases the magnetic saturation value while the coercive field remains unchanged.

CP-18 Sputter-deposited Nanostructured Metal-Oxide Films for Hydrogen Gas Sensing, *S Haviar,* ***Jiří Čapek,*** *N Kumal, Š Batková, M Fialová, R Čerstvý,* University of West Bohemia, Czech Republic*; T Duchoň, F Dvořák,* Charles University, Czech Republic

We present the study of nanostructured metal-oxide films prepared using a gas aggregation cluster source. The main advantage of the use of the cluster source is the possibility to prepare films with a high reactive area without the need for the use of wet techniques (often used for preparing nanostructured sensors). The films with the desired stoichiometry can be prepared directly without the need for subsequent thermal and/or chemical treatment.

Mixtures of tungsten oxide (WO_3) and cupric oxide (CuO) were deposited by cluster source and/or by conventional reactive dc sputter deposition. Sputtering conditions were tuned to vary the chemical composition and structure of the prepared films. The prepared films were characterized by means of X-ray diffraction, scanning electron microscopy, atomic force microscopy and Raman spectroscopy. The elemental composition was determined by energy and wave dispersive spectroscopy. The oxidation state of metals was studied by X-Ray Photoemission Spectrometry. Subsequently, the films were examined for their sensorial response when assembled into a hydrogen gas sensor. Noble-metal catalysts (Pd, Pt) deposited by dc magnetron sputtering were used to support the response and to lower the working temperature.

The layers were tested for response to a time-varied hydrogen concentration in synthetic air at various temperatures. The response sensitivity and the response time were evaluated. It is shown that optimization of the structure and composition results in enhanced sensorial properties.

CP-19 A Library of Broadband Reference Dielectric Functions, Valence Band Spectra and Raman Spectra of Epitaxial Conductive Nitride Films Grown on MgO, *S Kassavetis, T Zorba, J Arvanitidis, D Christofilos,* Aristotle University of Thessaloniki, Greece*; G Abadias,* Université de Poitiers, France*; D Gall,* Rensselaer Polytechnic Institute, USA*;* ***Panos Patsalas,*** Aristotle University of Thessaloniki, Greece

Conductive nitrides, such as TiN, ZrN, and TaN have emerged as significant alternative materials for photonics and plasmonics, due to the combination of their electronic conductivity with their thermal and mechanical stability and refractory character. One of the major drawbacks for the implementation of these materials in plasmonics and photonics is their excessive electronic losses, which are usually originating from the small grain size of the grown films due to their high melting point. Therefore, their refractory character is both a blessing (in terms of stability) and a curse (in terms of grain size). This drawback might be overcome by growing nanostructures of the finest crystalline quality that can be achieved by epitaxial growth. Epitaxial or pseudo-epitaxial growth of most conductive transition metal nitrides can be achieved on MgO along all the principal orientations, or on c-cut sapphire, respectively. Therefore, for the design of photonic and plasmonic devices, it is of utmost importance to know the optical response and the electron density of states of epitaxial transition metal nitrides on MgO. In this work, we provide a library of: i) the dielectric function spectra of epitaxial transition metal nitrides (TiN, ZrN, NbN, TaN, MoN, WN) in the broad range 0.193-125 μm (6.5-0.00992 eV), which were extracted by combining spectroscopic ellipsometry and FTIR reflectance/transmittance measurements, ii) the Raman spectra and the stability of these films upon exposure to intense laser beams, and iii) the experimental electron density of states of the valence band based on X-ray photoelectron spectra. In particular, the dielectric function spectra and Raman spectra of this library may also be used as references for in-situ and

real-time monitoring of film growth by ellipsometry or Raman spectroscopy.

CP-21 Electrical Properties of Molybdenum Doped β-Ga2O3 Thin Films, *J Galindo,* ***Anil Krishna Battu****, R Chintalapalle,* University of Texas at El Paso, USA

Gallium oxide (Ga_2O_3), which is a stable oxide of Ga, has been attracting the scientific and research community in view of its interesting physical, chemical and electrical properties. β-Ga_2O_3 thin films find numerous applications in high temperature sensors, photovoltaics, optoelectronics, and anti-reflection coatings. The structural and electrical properties β-Ga_2O_3 thin films are quite important for their integration into optoelectronics, photovoltaics and sensors. Recently, we proposed an approach to obtain tunable structural and electronic properties of β-Ga_2O_3 thin films using refractory metal incorporation. In this work, we performed a comprehensive study of the electrical properties of molybdenum (Mo) doped β-Ga_2O_3 (GMO) thin films. The results indicate that the resistivity, sheet resistance, conductivity, charge carrier concentration, and mobility are dependent on the microstructure, chemistry and Mo-content. Most importantly, the variable Mo content from 0 to 12 at% found to influence the electrical properties and allow us to obtain GMO films with a wide range of electrical properties. The results and implications for utilizing GMO films in electronic and optoelectronic devices will be discussed.

CP-22 Electron Beam Deposition and Characterization of Transparent WO_3/Al/WO_3 Multilayer Thin Films, *A Leyva, K Makeswaran,* ***Ramana Chintalapalle****,* University of Texas at El Paso, USA **INVITED**

The ever-increasing demand for sustainable energy calls upon practices for efficient energy utilization, management, and harvesting. Smart windows, which can control the throughput of visible light and solar radiation in buildings can contribute to the energy efficiency and cost savings. In this work, an attempt is made to fabricate the multilayered D/M/D architecture using WO_3 (D) and Al (M). The effect of Al thickness [Al(*t*)] on the performance of WO_3/Al/WO_3 multilayered films fabricated by electron-beam deposition onto silicon and glass substrates has been evaluated. Efforts were made to understand the effect of Al(*t*) on the structure, morphology, mechanical durability and optical behavior of the D/M/D multilayered films. The optical, electrical and mechanical responses suggest possible integration of these WO_3/Al/WO_3 films for smart window applications with enhanced performance.

CP-24 Numerical Ellipsometry: Extension of Concepts of n-k Plane Solutions from Isotropic to Anisotropic Films, ***Frank Urban****, D Barton,* Florida International University, USA

Ellipsometry is an optical technique for determining properties of laminar reflecting (or transmitting) structures from the measurement of light polarization state change resulting from the light-sample interaction. In all but the simplest of cases, the measurements must be followed by data processing in which the measured data is compared to an appropriate mathematical model of the sample derived from Maxwell's equations and measurement conditions. Thus a key common problem is determining how many and which measurements to make. A single ellipsometer measurement consists of a single complex data point and therefore usually more than one measurement is required. Previously we have addressed these problems using Complex Analysis in the n-k plane for homogeneous isotropic films. One of the key findings was that certain angles and wavelengths are useful and others are not. The purpose of the work here is to extend that analysis to anisotropic films. These films have a greater number of unknowns and consequently require more measurements. The central question remains, how many measurements are needed and which specific measurements will provide sufficiently independent equations considering the unknowns. It can be that additional measurements vary to such a small degree that they are not useful considering measurement error tolerance. The work to be presented will show how to identify useful measurements based upon the anticipated sample configuration. The approach avoids making unnecessary measurements which can actually reduce rather than increase the solution accuracy.

CP-25 Piezophotocatalytic and Piezoelectric Performance of Titanium Zinc Nitride Nanorod, ***Hsin-Yi Lee****, K Chang,* National Cheng Kung University (NCKU), Taiwan

Flexible strain sensors have many applications such as structural health monitoring, mechanical testing, and pulse power suppliers. Piezotronic strain sensors, which consist of a metal–semiconductor– metal interface, are well-suited for these applications due to their high sensitivity and fast response times. Zinc oxide (ZnO) nanowires (NWs) are a popular material for use in piezotronic strain sensors.[3] However, Zinc oxide has relatively high work function, so we can enhance its field electron emission with titanium nitride (TiN) coating, which has good electrical conductivity and relatively low work function.[1][4][5] Therefore, TiN thin film makes it potential in ideal field emitters. In our research, we want to develop the new material which has piezo-related properties and low work function simultaneously.

In this work, piezophotocatalytic and piezoelectric performance of Titanium Zinc Nitride Nanorod thin films deposited by RF magnetron sputtering were described. TiN and ZnN have centrosymmetric structure. However, thin film capacitors fabricated by sputtering Zn doped TiN nanorods from Zinc and Titanium targets in N2 ambient has non-centrosymmetric structure, because electric polarization and relative permittivity measurements yield distinct ferroelectric properties.

Based on various measurements including piezopotential, piezotronic, piezophototronic, and piezophotocatalytic analyses obtained by characterization tools, (i.e. X-ray diffraction, X-ray photoelectron spectroscopy, Raman scattering, Scanning electron microscope, Transmission electron microscopy, Secondary-ion mass spectrometry, UV-Vis, and I-V methods) we found that the base pressure of vacuum chamber, the chamber pressure and temperature, the sputtering power, and gas flow significantly influenced this material's crystallinity, morphology (i.e. surface roughness), structure properties (i.e. crystallite size), electrical properties (i.e. refractive index), optical, and mechanical properties. In addition, we use combinatorial methodology to fabricate the material [6], which has significant piezoelectric properties in the specific concentration of Zinc, for use as a piezoelectric sensor.

Keywords: Titanium Zinc Nitride, Zinc doped, nanocolumn, morphology control, composition spread, combinatorial magnetron sputtering, piezotronic / piezophototronic effects, photocatalysis / piezophotocatalysis.

CP-26 Well-alignment $ZnSnO_3$ by Epitaxially Oriented PVDF and Synergistic Piezo-related Performance of the $ZnSnO_3$/PVDF Nanocomposites, ***Chen-Hui Chou****, K Chang,* National Cheng Kung University (NCKU), Taiwan

According to previous researches, two-step hydrothermal method was used to deposit $ZnSnO_3$ on the different kinds of substrate and control their alignment with different conditions such as substrate, temperature, surfactant, and others. [1,2] In this research, a novel way was proposed to fabricate $ZnSnO_3$/polymer nanocomposites by simple hydrothermal and polymer epitaxy method. This research emphasized on improving the alignment of $ZnSnO_3$ nanorods[3,4] by polymer epitaxy[5] such as PVDF and its synergistic piezo-related performance of the $ZnSnO_3$/PVDF nanocomposites.[6] PVDF was used to control the alignment of the fabricated $ZnSnO_3$ nanorods and enhance its piezo-related performance including piezopotential, piezotronic, piezophototronic, and piezophotocatalytic analyses.

XRD and SEM were used to characterize the $ZnSnO_3$/PVDF nanocomposites. The results from the XRD confirmed the presence of $ZnSnO_3$. SEM analysis showed the morphologies and alignments of the $ZnSnO_3$ nanorods and PVDF. These nanocomposites exhibited average piezopotentials. Piezotronic analysis was also conducted on $ZnSnO_3$/PVDF nanocomposites, exhibiting high current density when the $ZnSnO_3$ are well-aligned. When under UV light illumination, the output current density obtained were several times higher for $ZnSnO_3$/PVDF. These confirmed the alignment control and synergistic piezophototronic property of the material.

In a piezophotocatalytic experiment, the decomposition of methylene blue (MB) was also investigated. The $ZnSnO_3$/PVDF nanocomposites exhibited better degradation property than pure $ZnSnO_3$. All the promising enhancement was attributed to the well-aligned $ZnSnO_3$, whichreduced the recombination of photogenerated electron−hole pairs and enhanced the mobility of these pairs resulting from the energy band distortion caused by applied stresses. Finally, we can use this nanocomposites or this epitaxially fabricating method to other materials on various electronic applications, such as multifunctional electronic-skin.[7]

Keywords: $ZnSnO_3$/PVDF nanocomposites, epitaxy, $ZnSnO_3$ nanorods, piezophotocatalysis, electronic-skin

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CP-27 Challenges and Limitations for the Optical Characterization of Sub-micron Temperature Fields in Plasmonic Metamaterials, ***Juan Antonio Zapien,*** City University of Hong Kong, Hong Kong

Surface plasmons at metal-dielectric interfaces can efficiently confine and amplify electromagnetic (EM) energy in deep sub-wavelength volumes. Concomitant with the large EM field enhancement, Joule heating occurs which severely limits performance for applications such as miniaturized optical circuits. However, the same effect provides a great opportunity to remotely control temperature distributions in the micro- to nano- scale. These highly localized thermal fields have applications to research in catalysis, heat-assisted magnetic recording, phononic circuitry, and photothermal medical therapy among others. A fundamental step to advance the emerging applications of thermoplasmonics is the capability to provide fast, quantitative, contactless experimental determination of the resulting temperature distributions.[i]

Spectroscopic ellipsometry (SE) is a phase sensitivity and self-referenced technique expected to have tremendous impact for contactless, marker-free, optical characterization at the nano-scale. [ii] However, numerical, fully-vectorial SE data analysis is required for non-layered samples with characteristic lateral dimensions (L) between l/10 and 10(l). To date, two systematic approaches seem favorable and will be reviewed; namely, the rigorous coupled-wave analysis (RCWA) method which was highly successful to study optical critical dimension (OCD) of 1D gratings by the semiconductor industry,[iii] and, more recently, the Finite-Difference Time-Domain that is being systematically investigated by our group. [iv]

In tis presentation we will provide an assessment of the expected capabilities of SE to provide quantitative optical characterization in plasmonic metamaterials including changes in refractive index and thermal expansion effects based on the known instrumentation and computational limitations currently available.

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CP-28 The Modification of Refractive Index by using Solid State Diffusion, ***Hung-Pin Chen,*** *W Cho,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan*; C Lee,* National Central University, Taiwan*; Y Lin,* National Tsing Hua University, Taiwan*; W Chen,* Instrument Technology Research Center, Taiwan

The optical coatings with excellence performance would be achieved more easily when the materials chosen have relatively adjustable refractive index. In this study, $Al_2O_3/ZnO/Al_2O_3$ structures were fabricated using electron beam evaporation and 800°C post-annealing treatments were carried out. According to the inter-diffusion, the ZnO layer became a high refractive index material with porous structure and the $ZnAl_2O_4$ spinel was formed as low refractive index material and the refractive index contrast of the multilayer was increased. In the $Al_2O_3/ZnO/Al_2O_3$ structure, the porous ZnO layer with an average porosity of 19.78% was successfully prepared and the refractive index was from 2 reduced to 1.357 by 800°C post-annealing process due to solid state diffusion mechanism.

CP-29 Effect of Silicon Content on the Structural, Optical and Electrical Characteristics of SiOx Films Prepared by Sputtering, ***Karim Monfil Leyva,*** *A Salazar Valdez,* Benemérita Universidad Autónoma de Puebla, Mexico*; A Morales Sánchez,* Centro de Investigación en Materiales Avanzados SC, Mexico*; J Luna López, M Domínguez Jiménez, A Muñoz Zurita,* Benemérita Universidad Autónoma de Puebla, Mexico

Currently, electronics and semiconductor studies have focused a great effort to overcome the intrinsic disadvantages of bulk-Si to develop optoelectronic devices. The non-stoichiometric Silicon dioxide (SiO_X) has been proposed as a cheap and effective alternative to develop ultraviolet absorbers or silicon-based light emitters. SiO_X can be deposited by several physical vapor deposition techniques but Sputtering technique particularly allows a great control on film thickness. SiO_x films can be obtained by simultaneous co-sputtering of Si and fused quartz (SiO_2) targets. The Si content in the SiO_X layers can be modified by a variation on RF-power applied to Si (Psi) target and keeping constant the RF-power applied to SiO_2 target.

In this work, we studied the effect of the increase of silicon content on the optical, structural and electrical properties of thin SiO_x films obtained by Sputtering. The Psi was changed between 10 and 50 W. All the films were annealed at 1100 ºC in N_2 for 3 hours. Ellipsometry and step measurements were applied to calculate thickness and the refractive index. Fourier transform infrared (FTIR) measurements were obtained from all the SiO_x films to confirm a change on stoichiometry. Absorbance spectra of SiO_x films showed rocking and bending vibration modes similar to stoichiometric silicon dioxide but an asymmetric stretching mode revealed the non-stoichiometric nature of our SiO_x films. X-ray photoelectron spectroscopy (XPS) measurements in depth profile revealed that Si content was increased from 3.5 to 10.7% in the SiO_x films. AFM images were obtained to calculate and relate the surface roughness according to Si content. SiO_X films showed a wide photoluminescence (PL) at room temperature (RT) between 575 nm to 875 nm. The PL intensity and peak position also showed a dependence on Silicon content and the possible presence of defects.

An Indium-Zinc Oxide (IZO) gate, optically semitransparent in the visible range, was deposited onto the SiO_X films surface. Also, Aluminum backside contact was added by Sputtering. Current–voltage (I–V) measurements of IZO/SiO_x/Si devices were obtained. A high conduction regime was measured even for low gate voltages. Electroluminescent (EL) emission was observed with the naked eye as discrete shining points on the surface of the devices. The intensity of the shining points showed a dependence on the Si content of SiO_X films. The EL emission was related to the recombination of charge moving through conductive paths within the SiO_X film.

CP-30 Optical Properties of the TiO_2 Films Grown by Atomic Layer Deposition using Tetrakis(Dimethylamino)Titanium and H_2O, ***Wen-Hao Cho,*** *P Huang, C Chen, Y Yu, C Yang, C Kei,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

Titanium dioxide (TiO_2) is a promising material due to its attractive physical and chemical properties. Atomic layer deposition (ALD) is one of the deposition methods for TiO_2 and could provide films with excellent conformality. The $TiCi_4$ precursor has been widely used with H_2O to deposit TiO_2 films in ALD process. However, the reaction by-product HCl are corrosive. In this study, TiO_2 films were grown on silicon substrates and glass by ALD using H_2O and tetrakis(dimethylamino)titanium (TDMAT) instead of $TiCl_4$ to avoid the damage from reaction by-product. The thickness of TiO_2 films at different substrate temperature were measured by ellipsometer and the highest growth rates per cycle (GPC) was 0.6649 Å at 100°C. The X-ray diffraction showed that the TiO_2 films were anatase phase. The transmittance (T) and reflectance (R) were measured and the absorption was obtained from 1-T-R. From absorption spectrum, we found that the TiO_2 films had slight absorption in visible light range. This should be caused by the residual carbon and nitrogen in the films. Furthermore, the TiO_2 film had lowest absorption at 100°C. The composition analyses were also carried out.

CP-31 Fractal Analysis of Titanium Nitride Films with Different Morphologies and Evaluation for the Direct Methanol Fuel Cell Applications, ***Kai-Ling Chuang,*** *M Tsai, Y Tsai, F Lu,* National Chung Hsing University, Taiwan

TiN is an important coating material with many technological applications because of its high hardness and chemical stability, as well as low resistivity. With various surface morphologies, conductive TiN films are expected to take part in many more applications. In our previous work,

granular and pyramidal morphologies TiN films could be tailored by merely adjusting the gas flow ratio, leading to changes in the texture coefficients. The objective of this work is to further analyze morphologies of the TiN films by estimating fractal dimensions of the films. The TiN films with different morphologies were then employed for the supporting electrodes on direct methanol fuel cells. Pyramidal and granular TiN films were produced with N_2, air, and simulated-air as the reactive gas during magnetron sputtering. With the TiN films turning from granular to pyramidal morphology, the value of fractal dimension decreased from 1.95 to around 1.63 for those three reactive gases. The development of the morphologies was associated with the texture of the films that changed from rather random orientation to a mainly (111) preferred orientation. From the test of methanol oxidation, the TiN electrodes with different morphologies showed promising current densities responses, compared to traditional metal and carbon supports.

CP-32 Growth Kinetics Behavior and Morphology of Multicomponent Coating on Zirconium Hydride during Oxidizing Atmosphere, *G Yan,* ***Jiandong Zhang****, L Wang, S Bai,* GRINM company, China

Zirconium hydride, as essential structural materials within the nuclear reactors, has the problem of hydrogen loss, which reduces the neutron moderating efficiency and service life. To prevent or slow down the hydrogen loss in moderator from zirconium hydride, multicomponent coatings (MC) for preventing hydrogen escaping were formed on zirconium hydride by in-situ oxidation method in oxidizing atmosphere decomposed by carbamide. Growth kinetics and morphology of in-situ oxidation MC on zirconium hydride were studied using x-ray diffraction (XRD), scanning electron microscope (SEM), auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy(XPS), focusing on kinetics of growth kinetics and morphology of the coating. As a result, it shows growth kinetics followed a parabolic law with respect to in-situ MC duration. XRD shows the phase structure of coating consists mainly of ZrN and ZrO_2, including tetragonal zirconia (*t*-ZrO_2) and monoclinic zirconia (*m*-ZrO_2). SEM depicts coatings were accumulated and combined densely with substrate. AES indicates that the coating is mainly composed of carbon, nitrogen, oxygen and zirconium, which show that the atomic concentration of carbon and nitrogen decreased continuously, while, oxygen and zirconium increased with sputter time increasing. XPS investigates the chemical binding states in the coatings were Zr-O、Zr-C、Zr-N-O、Zr-N bonds. Under the test of simulated working condition, the MC reduce the hydrogen loss effectively, compared with other single oxide/nitride coatings.

Coatings for Biomedical and Healthcare Applications
Room Grand Hall - Session DP
Symposium D Poster Session

DP-2 Ti-Nb COATINGS Deposited on AISI 316L Stainless Steel by Magnetron Sputtering for Biomedical Applications, *E Gonzalez, D Tallarico,* Federal University of Sao Carlos, Brazil*; A Gobbi,* Brazilian Center for Research in Energy and Materials, Brazil*; C Afonso,* ***Pedro Nascente****,* Federal University of Sao Carlos, Brazil

AISI 316L stainless steel (SS) and Cr-Co alloys are commonly used for manufacturing biomedical implants due to their reasonably adequate bulk properties. Titanium and its alloys are more biocompatible, but also significantly more expensive, than SS and Co-Cr alloys. Ti-based alloys have and additional advantage compared to SS and Co-Cr alloys: their elastic modulus values are more compatible with those of the human bones (10-40 GPa). The elastic modulus values for AISI 316L, Cr-Co alloys, and pure titanium are 190 GPa, 210-253 GPa, and 105 GPa, respectively The β-Ti (body cubic centered structure) alloys can have an elastic modulus even lower than 55 GPa. Niobium has been used as a nontoxic β-stabilizing agent, and its addition to Ti causes a decrease in the elastic modulus. An interesting option would be to coat an implant with a Ti-Nb thin film having adequate composition and thickness so that the coating would enhance the material biocompatibility. Care should be taken about the corrosion products of the biocompatible β-Ti-Nb coatings, since the implant devices are subjected to harsh environments into the human body and can deteriorate, affecting their service live and releasing potentially harmful particles generated by the corrosion processes which may affect the cell metabolism. Thus, the comprehension of the corrosion and osteointegration processes that occur on the metallic biomaterial surfaces is very important. In this work, β-Ti-Nb coatings were deposited on AISI 316L SS substrate by magnetron sputtering, and then were characterized by atomic force microscopy (AFM), scanning electron microscopy SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) . Four compositions were produced: 15, 20, 30, and 40 at.% Nb. The addition of Nb in the coatings affected their growth modes. The elastic modulus and the hardness values were in the ranges of 91.8-95.4 GPa and 5.4-7.4 GPa, respectively. The surface oxide layers were constituted of mainly titanium oxides and, to a lesser extent, niobium oxides. These partially oxidized surface layers are highly desirable for implant materials since they provide higher corrosion protection.

DP-4 Investigation of High Performance Hydroxylapatite Coated PEEK Composite Materials for Biomedical Applications, *J Su,* Chang Gung Memorial Hospital, Taiwan*; C Chen,* ***Gwomei Wu****,* Chang Gung University, Taiwan

Abstract In orthopedic surgery related to trauma or disease, it often requires the use of artificial bone plate to hold the fractured bones to effectively heal the fracture of a long bone. During surgery and postoperative healing period, the antibiotic management is critical to patients with infection control. A wound healing is also promoted by osteointegration and bone regeneration. A proper system needs to be effective to treat the wound, to reduce pain, and to restore function of a healthy life. High performance polyetheretherketone (PEEK) biomedical composites have been investigated for bone plate applications. By appropriate design, the biomedical composite materials can match the different parts of human body bones, quite helpful for long-term functional rehabilitation after surgery. They also remain x-ray transparency, making it easier for clinicians to assess the healing process. We have been developing PEEK composites with biodegradable polylactic-co-glycolic acid (PLGA) double layer structure bone plates and hydroxylapatite (HA) to promote bone regeneration and to derive antibiotic applications. In this report, the analysis of the material characteristics, in-vitro tests, and comparison with literature data will be presented and further discussed. A good understanding in the structure-property relationship would provide better guidelines for implant designs.

DP-5 Structural and Morphological Properties of PEO Films Grown on Ti-10Nb and Ti-20Nb and their Cellular Viability, ***Carlos Lepienski****,* Universidade Tecnológica Federal do Paraná, Brazil*; A Luz,* UFPR, Brazil*; N Kuromoto,* Universidade Federal do Paraná, Brazil*; G Lima,* Athlone Institute of Technology, Ireland*; B Pereira,* Universidade Federal do Paraná, Brazil*; M Sá, D Lima,* Universidade Federal de Campina Grande, Brazil

Recent investigations have been focused on β type titanium alloys as they present biocompatibility, non-toxicity, improved mechanical properties and also exhibit corrosion resistance. These novel alloys are bioinert, consequently surface modifications are required to improve its bioactivity. Plasma Electrolytic Oxidation (PEO) can be employed to produce a porous film which contains oxides of elements that compound the titanium alloys, that is known to exhibit good bioactivity and biocompatibility. With the continuous interest in titanium alloys, the purpose of this study was to modify two different titanium-niobium surfaces via PEO and understand the structure of these films while also analyzing the improvement in bioactivity via cellular viability. Ti-10Nb and Ti-20Nb alloys were treated by PEO under 250 V in 1mol.l^{-1} H_3PO_4 electrolyte during 60 s. For the samples characterization we perform metallographic analysis, X-ray diffraction, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Nanoindentation technique, and cellular viability tests with MC3T3 cells with further analysis on SEM to understand the cellular behavior with the titanium implants. Metallographic analysis and X-ray patterns showed that Ti-10Nb and Ti-20Nb are composed by (α+ β) which were due to the process performed above the β transus temperature to a (α+ β) region, and the slow rate of cooling during the manufacturing process. Nanoindentation testes revealed that Ti-20Nb alloys exhibited the highest value to hardness,(3.0 ± 0.2) GPa, and the lowest elastic modulus, 98 ± 2 GPa. Using the 3D view of SEM technique, Ti-Nb coatings presented important values of roughness with round porous and random diameters. In addition, these images presented values of tickness from ~1.7 μm for Ti-10Nb and 1.0 μm for Ti-20Nb. Due to the electrolyte used, the presence of phosphorous compound which was incorporated into the coating during the PEO process was detected by the EDS spectra. X-ray patterns exhibited a highly crystalline film on Ti-10 Nb alloy which was also observed in great intensity with Raman spectroscopy with anatase phase. Conversely, Ti-20Nb presented a highly amorphous film with a decrease amount of bands of anatase phase observed by Raman spectroscopy. Cellular viability with MC3T3 cells showed no signs of cytotoxicity of these alloys with values higher than the control sample (>70%) but no significant differences were observed between these alloys; although TiNb10% presented mean higher

values. These cells attached, differentiated and proliferated well in these alloys due to the porosity, roughness and the elements presented in the film.

DP-6 Tribocorrosion Behavior of SiC Films with and without TiO_2 Nanoparticles on AISI 316L for Prosthesis Application, *A Vieira, T Santos,* Univap, Brazil*; P Radi,* ITA, Brazil*; S Silva,* IEAv, Brazil*; A da Silva,* Univap, Brazil*; G de Vasconcelos,* IEAv, Brazil*;* ***Marco A. Ramirez R.****,* Universidade do Vale do Paraíba (UNIVAP), Brazil*; L Vieira,* Univap, Brazil

Stainless steel (AISI) materials have an important role in the manufacture of many devices subjected to the corrosive environment including implants. It occurs due to their higher mechanical strength, hardness, and resistance to wear. Regards to the AISI 316L, it is one of the most used implanted material due to its mechanical properties and low cost. However, many papers have been reporting its tribocorrosion and the needing of replacement before ten years. The deposition of Silicon Carbide (SiC) coatings is a cheap strategy to improve its lifetime in corrosive environments due to its properties such as high hardness, biocompatibility, and resistance to corrosion. Additionally, TiO_2 nanoparticles can be incorporated into the SiC films to improve its corrosion resistance.

This paper show was investigated the effect TiO_2 nanoparticles of SiC film on chemical structure, the film morphology, and tribocorrosion behavior in Ringer's solution. The AISI 316L substrates were covered with SiC films with and without TiO_2 nanoparticles using Laser Cladding technique. The laser cladding provides a fast and cheap way to modify the material surface. The mechanical and structural properties of the SiC films were evaluated according to the power and speed parameters of the laser. The tribocorrosion were performed using open circuit potential (OCP) performed in three steps: Static, reciprocating, and static modes with an exposed area of 1.5 cm^2 with 5N force and 5 mm/s sliding speed using an alumina ball as the counter body. The corrosion rate was lower for both films when compared with bare AISI 316L. The best tribocorrosion resistance result was achieved for SiC film+TiO_2 mixture.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Grand Hall - Session EP
Symposium E Poster Session

EP-2 Effect of Power on Soft Magnetic and Tribological Properties of Fe-Co based Coating by Laser Cladding, ***Xiaoshan Yang****, X Cui, G Jin, J Liu,* Harbin Engineering University, China

Fe-Co based coatings which have a broad application in improving the surface properties have excellent wear resistance and soft magnetic properties. In this study, (FeCoNi) Si B Cu Mo coatings with high saturation magnetization and good tribological properties were prepared using lasers cladding.The different process parameters effect on the microstructure, mechanical properties of the cladding layer wereinvestigated. It was found that laser power P, scanning speed V and laser remelting technology which had a significant effect on the magnetic properties and tribological properties. The optimum process parameters were determined and the coatings showed bcc dominated microstructures. The average microhardness and friction coefficient of the coatingsreached 1032 $HV_{0.5}$ and 0.291 respectively. With the decrease of grain size, wear resistance and microhardness of coatings improved significantly. In addition, the coatings exhibited higher saturation magnetization (212emu/g), comparable magnetic properties to those of their conventionally processed counterparts.

Acknowledgements

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EP-3 Tribological Behavior of the FeB Phase in Boron Coating Formed on an AISI L6 Steel using Ball On Disc with Dry Conditions, ***Daniel Sanchez Huerta****,* CBI, Universidad Autónoma Metropolitana unidad Azcapotzalco, Mexico*; I Hilerio Cruz,* Universidad Autonoma Metropolitana unidad Azcapotzalco, Mexico*; N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico*; E García Bustos,* Catedras CONACYT, Mexico, México*; M Doñu Ruiz,* Universidad Politecnica del Valle de Mexico, Mexico*; M Flores Martinez,* Universidad de Guadalajara, CUCEI, Mexico

The coefficient of friction (CoF) and wear behavior in a boron coating was studied at different temperatures of 1173, 1223 and 1273 K, with residence times of 0.5, 2 and 3 h for each temperature. The boron coating was obtained by powdered box technique on AISI L6 steel (DIN 1.2714). The roughness of each treatment was studied by roughness profile (2D) measurements, obtained an increase in R_a between 0.352 (1173 K with 0.5 h) to 0.965 µm (1273 K with 3 h) for the FeB phase. The reciprocating tribometer tests were studied at normal loads of 7 and 10 N with humidity and temperature controlled in dry conditions. For the FeB phase, we obtained CoF values from 0.49 to 0.64 at 36 m of displacement. The topography of the wear traces, were analyzed by optical profilometer (3D). The wear in the FeB phase obtained in the sliding tests, suggested a resistance wear of the treatment at high thicknesses; in the Fe_2B phase the wear was not obtained, because the thickness wear is around from 0.44 to 0.98 µm. The wear behavior are two bodies with an adhesive behavior in the FeB phase.

EP-4 Tribocorrosion Behavior of Boronized AISI 4140 Steel, ***Steffen Aichholz****, R Torres, M Meruvia, P Soares,* PUCPR, Brazil

In this study, AISI 4140 steel was boronized using solid state thermochemical boriding technique, producing a monophasic iron boride (Fe_2B) layer with a mean thickness of 49,5 µm. The microstructural and chemical characteristics were evaluated by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD). To investigate the tribocorrosion behavior samples were immersed in 3,5% NaCl solution subjected to a pin-on-disk wear test and connected to a potentiostat monitoring the open circuit potential (OCP).

The results obtained show that boronized samples have an improved tribological behavior compared to unboronized samples and the evaluation of the OCP curve indicates the formation of a passivation layer during de wear test. These results can be explained by the high hardness and chemical inertness of iron boride layer.

EP-5 Influence of Sputter Power Ratio on Microstructure, Mechanical and Tribological Properties of Ti-B-C Coatings Deposited onto AISI M2 Steel, ***Elbert Contreras****, M Gómez,* Universidad de Antioquia, Colombia

Despite being a ceramic material widely known for its high hardness, chemical resistance and high thermal stability; TiB_2 coatings using in industrial conditions has been really limited due to the high residual stresses associated with the reduction of adhesion. Recently, several investigations have shown that the incorporation of carbon within TiB_2 coatings reduces the residual stresses, increasing the adhesion and becoming Ti-B-C coatings in excellent candidates for applications at high temperatures. In this research, Ti-B-C coatings were deposited onto M2 steel substrates by DC UBMS. Prior to the coatings deposition a plasma cleaning process was carried out both substrates and targets with a 40 sccm flow of Ar and a pressure of 3 Pa for 0.5 h. For the deposition, two targets of TiB_2 (99.9%) and graphite (99.9%) opposite each other was used. The power density of TiB_2 was fixed to 2.4 W/cm^2 and four different power ratio W_{TiB2}/W_C was made in order to varied the carbon content in the Ti-B-C coatings. Microstructural analysis by X-ray diffraction (XRD) showed h-TiB_2 crystal structure with preferential orientation (001), increasing the carbon content, the intensity of (001) peak decrease becoming the crystalline coatings in amorphous coatings. Using AFM technique, an increase in roughness and grain size was observed with higher carbon content, except for coatings with ~20%. SEM images revealed columnar, dense and homogenous structure for all coatings. A progressive decreasing in hardness and Young modulus was observed with the increasing in carbon content, hardness up to 27 GPa was reached with lower carbon content and a decreasing under 5 GPa with the higher carbon content. The Young modulus exhibited the same featured. Tribological properties of the coatings were investigated using Pin-on-disk, all coatings showed COF higher tan AISI H13 substrate, only the coatings with 36% of carbon showed COF over 0.30. respecting to the wear rate it was keep almost constant for all Ti-B-C coatings.

EP-6 Structural and Mechanical Properties of W-doped HfO_2 Thin Films, *A Uribe, M Garcia, R Chintalapalle,* ***Cristian Orozco****,* University of Texas at El Paso, USA

Hafnium oxide (HfO_2) is a high temperature ceramic with interesting mechanical properties. HfO2 is distinguished by its wide band gap (~5.7 eV), high dielectric constant (20-25), and high chemical stability. In an effort to tune and enhance the structural and mechanical properties, this work was focused on doping tungsten (W) into HfO_2 thin films. While the doping effects of other metals have been studied, there is a lack of knowledge on the effects of W doping into HfO_2. On the other hand, refractory metal incorporated dielectrics are expected to meet the functional requirements of high-temperature device applications. W-doped HfO_2 thin films were deposited on silicon and quartz substrates via radio

frequency magnetron sputtering. The W content was varied by changing the sputtering power from 0-100 W. The films were characterized by performing x-ray diffraction (XRD), nanoindentation, scanning electron microscopy (SEM), and contact angle measurements. Nanoindentation studies revealed increases in hardness and elasticity with increasing W content. XRD displayed the predominant (-111) peak of monoclinic HfO_2 and revealed amorphization induced by increasing W concentration. SEM data also showed gradual amorphization in the samples with increasing W-content. Finally, contact angle measurements showed all the samples were hydrophilic. Based on the experimental data, a structural-mechanical-property relationship is established.

EP-7 Tribological Studies on Self-Lubricating (Cr,Al)N/MoS_x Coatings at Elevated Temperature, *K Bobzin, T Brögelmann,* ***Nathan Kruppe****, D Hoffmann,* Surface Engineering Institute - RWTH Aachen University, Germany*; F Klocke, P Mattfeld, D Trauth, R Hild,* Laboratory for Machine Tools and Production - RWTH Aachen University, Germany

Due to the high material utilization and the associated resource and energy efficiency, production processes from the field of cold forging of steel are of great importance. At present, environmentally harmful lubricants have to be used to ensure process stability as well as low wear and friction. Due to environmental, economic and legislative aspects, there is an increased research potential to reduce or to completely substitute lubricants. To achieve the goal of lubricant free dry cold forging of steel, physical vapor deposition (PVD) coatings with self-lubricating properties are applied on forming tools. Promising for this application are PVD coatings on the basis of a (Cr,Al)N hard phase with embedded MoS_x which simultaneously meet the requirements of high wear resistance and friction reduction. Furthermore, a sufficient compound adhesion is needed to withstand high contact stresses up to σ = 3,000 MPa during cold forging of steel. In addition to the mechanical stresses, a thermal load up to T = 250 °C occurs during cold forging. In the presented work, three self-lubricating coatings (Cr,Al)N/MoS_x deposited with varying bias voltage were investigated. The hybrid PVD technology, consisting of direct current and high power pulse magnetron sputtering dcMS/HPPMS, was used for the coating deposition in an industrial coating unit. Two different steels AISI D2 (X155CrMoV12, 1.2379) and AISI M2 (HS6–5–3C, 1.3343) were used as substrate materials. The influences of the substrate material and heat treatments at T = 250 °C on mechanical, compound adhesion and tribological properties were investigated. The samples were analyzed with respect to the universal hardness HU and modulus of indentation E_{IT} using nanoindentation. To determine the interfacial adhesion of the compound coating/substrate, Rockwell indentation and scratch tests were carried out dependent on the heat-treatment. For the analysis of the tribological behavior, AISI 5115 (16MnCr5, DIN 1.7131) and AISI 4140 (42CrMo4, DIN 1.7225) were used as counterpart materials, since these are widely used as forming material. As closed tribometer, a Pin-on-Disc (PoD) was used at varying temperatures. In this case, the coated substrate is continuously loaded with the worn pin on the same track. As open tribometer, a newly developed Pin-on-Cylinder (PoC) was used. The particular feature of the PoC is that the pins (AISI D2) are coated and pressed by means of a defined feed along a rotating cylinder (AISI 5115 and AISI 4140). Thus, the coated pin is permanently in contact with an unworn surface of the cylinder. The contact region was studied by Raman spectroscopy before and after the tribological tests.

EP-8 Role of Carbon Nanotubes in Reducing Friction between Steel/Steel Contacts, ***Zaixiu Yang****, S Bhowmick,* University of Windsor, Canada*; F Sen,* Argonne National Laboratory, USA*; A Alpas,* University of Windsor, Canada

Carbon materials such as graphene and carbon nanotubes (CNT) are increasingly used to reduce the friction. By performing sliding tests on steel against steel immersed in ethanol solutions with 0.005 mg/ml of CNT added, the coefficient of friction (COF) was reduced from 0.27 (in absolute ethanol) to 0.16. Once the CNTs were oxidized, the partially unzipped CNT showed reduced agglomeration in ethanol. Moreover, the partially unzipped CNT in ethanol led to the elimination of the running-in stage of friction and more stable COF curves. Examination of the worn surfaces indicated that the deposition of CNT to the steel surfaces, which was confirmed by the micro-Raman spectroscopy, was responsible for the reduced COF. Density Functional Theory simulation results were used to reveal the effect of the partially unzipped structure of CNT on the improved friction properties as will be discussed in the presentation.

EP-11 Microstructure Change, Element Diffusion and Tribological Properties of Chromium Oxide from RT to 1000 °C, ***Huidi Zhou****, N He, X Liu,* Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

The demands of reusable solid lubricants with continuous lubricating properties from room temperature (RT) to 1000 °C or even higher temperatures become increasingly urgent with the development of high-tech industries, especially that of aerospace industry. In our work, chromium oxide was investigated as a primary coating because it possesses high melting point and excellent thermal stability. The chromium oxide coatings were deposited on Ni-based high-temperature alloy substrates through an arc ion plating system and then annealed at 1000 °C in air for 2 h. The effects of annealing on the structure and tribological properties in wide temperature range of Cr_2O_3 coating were researched in detail. The phase change and elements diffusion behavior of Cr_2O_3 coating annealed at 1000 °C were also discussed. Main results and conclusions are as-followed:

Ti and Cr atoms in the Inconel 718 alloy matrix diffuse to the coating surface and react with oxygen in atmosphere, thereby generating the mesh-like heave structure that endues the annealed coating an excellent self-lubricating behavior in wide temperature range. The friction coefficients are all lower than 0.3, and the wear rates maintain at a magnitude of 10^{-7} mm^3/Nm from RT to 1000 °C. Particularly, the excellent self-lubricating performance could be maintained even in five-thermal-cycles test. Moreover, while the mesh-like heave structure damaged by friction, Ti and Cr atoms in the matrix tend to diffuse to the damaged locations and react with oxygen in air. This phenomenon results in the reproduction of composite-phase heave structure of Cr_2O_3 and $Cr_2Ti_4O_{17}$ at the damaged locations. Consequently, the self-supplement ability of the mesh-like heave structure could prolong the wear life in wide temperature range.

EP-12 Sliding Wear Behaviour of Infiltrated Self-lubricating Polymer Matrix Composites Studied by in-situ Tribometry, ***Yinyin Zhang****,* McGill University, Canada*; R Schulz,* Hydro-Québec Research Institute (IREQ), Canada*; R Chromik,* McGill University, Canada

The hydropower industry routinely makes use of thermally sprayed coatings and solid lubricating polymer coatings in their operations to enhance the lifetime of their infrastructure, especially those components subjected to sliding wear. Often these two coating systems are used independent of one another but in this study, we examine the feasibility of a duplex coating where a self-lubricating polymer composite was infiltrated into a porous SS316 substrate. This resulted in coatings consisting of a top layer made of a self-lubricating polymer composite and a bottom layer made of a polymer composite infiltrated into a porous metallic structure. This paper presents the tribological behaviour of the polymer composite and the transition when wearing reaches the infiltrated metallic porous substrate.

Addition of graphite (Gr) to a thermoset bismaleimide (BMI) significantly reduced coefficient of friction and wear rate. An in-situ tribometer that uses a transparent sapphire hemisphere as counterfaces permits microscopic observation and video recording of the sliding contact. Interfacial sliding dynamics such as material transfer, formation of transferfilms and wear debris were examined and therefore wear mechanisms of BMI + Gr and BMI + Gr + SS316 were observed. A stable transfer film that was rich in Gr was formed when sliding on the top layer of BMI + Gr, while participation of metallic material in the sliding contact contributed to deposition of transfer film onto wear tracks and transfer film reformation. Raman spectroscopy was used to detect formation of Gr-containing tribofilms and transferfilms in the running-in and steady-state regimes. X-ray photoelectron spectroscopy (XPS) testing on the wear tracks and transferfilms revealed possible tribochemical reactions such as polymer decomposition and interaction with Gr and/or SS316 induced by sliding wear. Mechanical properties of the as-received polymer composites and worn materials were also investigated using nanoindentation.

EP-13 Sputtered B-C-W-Coatings: Composition – Properties – Stability, ***Heidrun Klostermann****,* Fraunhofer FEP, Germany*; J Poetschke,* Fraunhofer IKTS, Germany*; O Zywitzki,* Fraunhofer FEP, Germany

Coatings in the material system B-C-W have been synthesized by pulsed magnetron co-sputtering of a boron carbide and a tungsten target. The bipolar co-sputtering process enables fine tuning of the composition through variation of sputtering pulse times. In the range of composition from pure boron carbide to 70 at-% tungsten content, the hardness of the coatings as determined by nanoindentation changes only little, typically in the range of 24 GPa to 28 GPa. However, in contrast to completely amorphous pure boron carbide, the x-ray diffraction pattern of B-C-W

coatings exhibit broad peaks, indicative of extremely small crystalline domains that cannot clearly be attributed to a single phase for tungsten content below 50 at-%. Corresponding to a smooth transition in structure, scanning electron microscopy investigation reveals very homogeneous coatings with extremely smooth surfaces, even at a thickness of several microns. Consistently, EDX mapping reveals a very homogeneous element distribution. Thermal stability has been tested up to a temperature of 600°C in vacuum and in air. While no degradation is observed in vacuum, the oxidation rate in air depends on the tungsten content of the coatings.

In contrast to many other hard coatings, the stress level of the B-C-W layers is very low and the material seems to be rather resistant to crack propagation, as far as scratch test analysis can reveal. The coatings have been tested on cutting tools for cemented carbide cutting, where they abrade rather rapidly. However, the combination of properties still makes them interesting as hard and tough coatings.

EP-14 Comparison of Tribological and Electrochemical Properties of Titanium Oxided Films Produced on Cp-Ti by Sol-Gel and Silar Methods, *O Çomaklı,* Erzincan University, Turkey*; M Yazıcı,* Erzurum Technical University, Turkey*;* ***Halim Kovacı,*** Atatürk University, Turkey*; T Yetim,* Erzurum Technical University, Turkey*; A Yetim,* Erzurum Teknik University, Turkey*; A Çelik,* Atatürk University, Turkey

Cp-Ti is commonly used in different applications because of its good structural properties but its low mechanical and tribological properties restricts its usage areas. Therefore, different surface modifications based on TiO_2 formation on material surface are applied to enhance its surface properties. In this study, TiO_2 films were produced on Cp-Ti substrates by sol-gel and successive ionic layer adsorption and reaction (SILAR) methods in order to compare the performance of different coating methods. The structural, morphological and mechanical features of TiO_2 films were investigated by XRD, SEM and microhardness tester. The tribological properties of films were characterized using a pin-on-disc tribotester. The electrochemical behavior of TiO_2 films were determined by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) analyses. The structural and mechanical analyses showed sol-gel method caused the formation of more stable and hard film structures with good adhesion in comparison to SILAR method. For that reason, TiO_2 films produced by sol–gel method exhibited better wear and corrosion resistance than the films produced by SILAR.

EP-18 Mechanical and Tribological Properties of W–C–N Films Using Unbalanced Magnetron Sputtering Assisted by Linear Ion Source, ***Hyundong Kim,*** *S Heo, E An, I Park,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Ternary W–C–N films were deposited on 2618 aluminum alloy and 304 stainless steel substrates by a hybrid deposition process combining d.c. unbalanced magnetron sputtering and linear ion source system using pure tungsten targets in an $N_2/(N_2+Ar)$ gas mixture for diesel engine pistons applications. The influence of the carbon content and deposition conditions, i.e. substrate bias voltage and temperature, on the microstructure, mechanical properties and tribological properties of the W–C–N films was systematically investigated in this study. The microstructure for the films was characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscope (XPS), and high-resolution transmission electron microscope (HRTEM). Nano-indentaion was conducted to assess the nanohardness and Young's modulus of the W–C–N films. Wear resistance and tribological behavior of these films also were evaluated using a micro-tribometer with wear debris analyses and coefficient of frictions. Moreover, morphological analysis with surface roughness was calculated by using atomic force microscope (AFM).

EP-19 The Influence of Feedstock Powders on Microstructure and Tribological Properties of WC-Co-Cr HVAF Coatings, *K Szymański, G Moskal, D Niemiec,* ***Aleksander Iwaniak,*** *J Wieczorek,* Silesian University of Technology, Poland

The basic goal of presented investigations is comparison of feedstock powders of WC-Co-Cr type in area of its chemical and phase compositions as well as morphological parameters, size distribution and shape. Those parameters have direct transfer on technological properties of powders such as followability etc., what is essential form high velocity spraying process point of view. In this part of article the X-ray and EDS analysis of powders were made, additionally scanning electron microscopy observation was carried out too. The size distribution was analysed by laser diffraction method. Obtained data gives the possibility to comparison of powders from different sources from technological properties point of view.

The second part of paper related with microstructural characterization of coatings deposited by high velocity air fuel (HVAF) method. The standard procedure for those kind of powders was used. The gun of Kermetico of K5 type was used. The range of investigations included characterization of coatings top surface with descriptions of roughness, as well as the stress state was analysed by X-ray method. Phase analysis was made after deposition and obtained data were compared to initial phase composition of powders as well as theirs chemical compositions. In area of mechanical properties basic parameters such as hardness and fracture toughness were measured and analysed. The final part of investigations is related with characterization of tribological properties of coatings with the same chemical and phases constituent buy deposited from different feedstock materials

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EP-20 Microstructure and Mechanical Properties of CuSn10 Alloy Coating Manufactured by Cold Spraying, ***Weihuang Liu,*** *J Cao, Z Yin, H Li, G Gao,* Shanghai Jiao Tong University, China

In order to achieve compact and low oxidation of Cu-10wt.% Sn (CuSn10) alloy coating, the cold spraying is used to deposit a coating on the bearing material substrate. The coating is analyzed by its morphology, hardness, metallographic, porosity and finite element analysis. Results show the mechanical performances of CuSn10 coating that are excellent. The microstructure of coating is compact and its hardness is appropriate for the requirement of embeddability and machinability. The sizes of grains of CuSn10 are uniform. There are no obviously grain boundary cracks. The porosity ratio is 0.07 %. Stress and deformation show that coating has excellent ability of reducing vibration and absorbing energy. With coating protection, results of fatigue life show that life is improved 173.32 %. The microstructure and mechanical properties of CuSn10 are outstanding that the cold spraying coating is very suitable for bearings.

EP-22 Scratch Induced Thin Film Buckling for Quantitative Adhesion Measurements, *A Kleinbichler,* KAI – Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*; J Zechner,* KAI - Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*;* ***Megan Cordill,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

The adhesion of thin films is one of the most important factors for the reliability of microelectronic devices and the semiconductor industry requires quantitative testing methods to effectively compare these interfaces. Several techniques have been developed over the last decades such as four point bending, budge testing, micro cantilever tests, spontaneous buckling and scratch induced delamination. For compressively stressed films on rigid substrates the scratching can cause buckling failure ideal to be used to determine the adhesion quantitatively by modeling the delaminations according to the Huchinson and Suo model. Two different sample systems, a tungsten-titanium film on a silicate glass and a silicon nitride film on a silicate glass with a tungsten-titanium overlayer, have been tested using a ramp load method in the range of 100-500mN. This study demonstrates that the scratch induced delaminations resulted in parallel and spontaneous buckles. The parallel buckles developed directly beside the scratch trace and were the result of fracture events at the interface and deformation left by the passing indenter tip. The spontaneous buckles, on the other hand, originated from the parallel buckles and propagated according to the stress distribution in the film forming telephone cord delaminations. Using the geometric dimensions of the induced buckles the adhesion energies of the interfaces were quantitatively calculated. It was shown that the adhesion energy of the tungsten-titanium film increased with annealing time from 2.7 J/m² for the as-deposited to 4.7 J/m² for the 2 hour annealed film at 400°C. The adhesion of the silicon nitride film was determined to be 1.4 J/m² and was in good agreement with previous nanoindentation experiments. The results illustrated that the scratch test can be utilized for quantitative adhesion testing of thin films in cases where other methods are not applicable or sample preparation would change the nature of the interface and suggest that scratch induced delamination is a valuable addition to established adhesion measurement techniques.

EP-23 Study of the Mechanisms of Built-up Edge Formation during Machining of Super Duplex Stainless Steel, ***Yassmin Seid Ahmed***, *G Fox-Rabinovich, B Bose, D Covelli, J Paiva, G Dosbaeva, S Veldhuis,* McMaster University, Canada

Tool wear is a very important factor determining tool life and surface quality of a machined workpiece surface. So, it is necessary to minimize tool wear to maximize tool life and to optimize the manufacturing performance. Different mechanisms can cause the tool wear in a specific machining process, adhesion onto the cutting tool frequently observed during machining of stainless steels, generate damage on the tool rake face. Adhesion of the workpiece material causing built-up edge (BUE) formation tends to promote tool chipping, since BUE is never completely stable, but it periodically breaks off leading to tool failure. The phenomenon of BUE formation can lead to poor machined surface texture and accelerated tool wear, subsequently leading to increased manufacturing costs. An experimental study was undertaken in order to study the formation and the cutting mechanism of the BUE. In this paper, the mechanisms that trigger the formation of BUE during the machining of super duplex stainless steel alloys—Grade UNS S32750 with PVD AlTiN/TiSiN coated carbide tool has been investigated. The process parameters were chosen so that the BUE formation was provoked. The BUE formation and tool wear was evaluated throughout the cutting tests using an Alicona Infinite Focus microscope and a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Tribo-film formation on the worn rake surface of the tool was analyzed using X-ray Photoelectron Spectroscopy (XPS). Comprehensive characterization of the BUE mechanisms of PVD AlTiN/TiSiN coated vs. uncoated cutting tool wear was performed using SEM, electron backscatter diffraction (EBSD) and nanohardness tester. This paper investigates the deformation mechanisms and plastic behavior of austenite and ferrite phases in BUE cross section. Nonohardrness distribution and EBSD phase mapping of BUE cross section samples revealed a built-up of austenite bands are collected at the tool-chip interface and ferrite bands collected on the top. Moreover, SEM images of BUE cross section samples show micro-cracks which act as BUE initiators were identified in this region of austenite.

New Horizons in Coatings and Thin Films
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Symposium F Poster Session

FP-2 Adjusting the Oxidation Behaviour of Arc Evaporated $Al_{1-x}Cr_x$ Intermetallics and Substoichiometric Oxides, ***Valentin Dalbauer,*** CDL-AOS at TU Wien, Austria*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C Koller,* CDL-AOS at TU Wien, Austria*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Initiated by our recent works on intermetallic Al-Cr-Fe droplets [1–3], which indicate the ability to trigger the nucleation of corundum-structured $(Al,Cr,Fe)_2O_3$ crystallites, the oxidation behaviour of intermetallic Fe-doped $Al_{0.70}Cr_{0.30}$ coatings and corresponding substoichiometric oxides was investigated. The structure and composition of the outermost oxide scale and the oxidation temperature at which it forms is determined by the initial microstructure. Columnar intermetallic coatings, for instance, oxidise via an outermost metastable Al_2O_3 scale, which transforms into the thermodynamically stable corundum-phase starting at 1000–1050 °C. However, nano-composite–like structures, present in substoichiometric coatings, show a more diverse oxidation at the surface and complex elemental separation within the unoxidised material In the present work, we extent our studies on the oxidation and oxide phase formation to intermetallic and substoichiometric coatings prepared from powder-metallurgically produced $Al_{1-x}Cr_x$ cathodes with nominal compositions of x=0.10, 0.25, 0.30, 0.50, and 0.75. The structural evolution of the outermost scale and coating underneath—studied by X-ray diffraction and cross-sectional electron microscopy—is related to the Cr content, oxygen flow rate during the synthesis process and the oxidation conditions.

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FP-3 Distribution of Dislocations in ZnO Thin Films Grown on a-plane Sapphire Substrates using a Reaction Between Dimethylzinc and High-temperature H_2O Generated by a Catalytic Reaction, *T Saito, R Ibe, A Kato,* Nagaoka University of Technology, Japan*; A Hashim,* MJIIT, Universiti Teknologi Malaysia, Malaysia*;* ***Kanji Yasui,*** Nagaoka University of Technology, Japan

ZnO is highly useful for applications such as short-wavelength optoelectronics and transparent conductive electrodes [1]. We have developed a new CVD method for ZnO film growth using a reaction between dimethylzinc and catalytically generated high-temperature H_2O. ZnO films grown on a-plane (11-20) sapphire (a-Al_2O_3) substrates at temperatures of 773-873 K exhibited excellent optical and electronic properties [2]. However, the electronic properties were dependent on the film thickness: ZnO films thinner than 500 nm showed inferior electrical properties, namely, a low Hall mobility (<100 $cm^2V^{-1}s^{-1}$) and a high residual carrier concentration (>10^{18} cm^{-3}). The room-temperature electron mobility increased from 30 to 190 $cm^2V^{-1}s^{-1}$ as the film thickness increased to ~3 µm. The mobility also increased significantly as the temperature was decreased to approximately 110-150 K, but decreased at temperatures below 100 K for films thicker than 500 nm. On the other hand, the mobility was almost independent of temperature for films thinner than 500 nm. These results suggest that a region with a high defect density exists near the film-substrate interface. To evaluate the crystal quality of the ZnO film along the growth direction, cross-sectional transmission electron microscopy was performed and the defect density was determined. The ZnO epitaxial film that was studied had a thickness of 4.5 µm and a room-temperature electron mobility of 187 $cm^2V^{-1}s^{-1}$. The dislocation density estimated using Ham's method [3] was found to be lower near the film surface than near the film-substrate interface. The combined density of all dislocations (edge, screw, and mixed) in the top 1.5 µm of the film was approximately 1.1×10^9 cm^{-2}, while in a 30-nm-thick region near the interface, it was approximately 1.6×10^{11} cm^{-2}.

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FP-4 Structural and Optical Properties of ZnO Films Grown on Ion-Plated Ga-Doped-ZnO-Based Buffer Layers by Atmospheric-Pressure Chemical Vapor Deposition using Zn and H_2O as Source Materials, ***Tomoaki Terasako,*** *Y Ochi,* Ehime University, Japan*; M Yagi,* National Institute of Technology, Kagawa College, Japan*; J Nomoto, T Yamamoto,* Kochi University of Technology, Japan

Zinc oxide (ZnO) with a direct band gap energy of ~3.37eV at RT and a large exciton binding energy of ~60 meV is one of the promising materials for the optoelectronic devices. Chemical vapor deposition (CVD) is an effective way for obtaining films with good crystalline quality over large area. We have reported the successful growth of highly oriented ZnO films on *c*- and *r*-plane sapphire substrates by atmospheric-pressure CVD (AP-CVD) using Zn powder and water (H_2O) as source materials [1,2]. In this paper, we demonstrate AP-CVD growth of undoped ZnO films on ion-plated Ga-doped-ZnO (GZO)-based buffer layers and discuss their structural and optical properties in terms of substrate temperature, source supply ratio of Zn to H_2O and growth time.

The 200-nm-thick GZO films/quartz substrates deposited by ion-plating with dc arc discharge were used as substrates [3]. The AP-CVD apparatus had a horizontal furnace and a vaporizer for H_2O. The horizontal furnace consisted of two temperature zones: one was used for heating the substrate and another for vaporizing high purity Zn powder. Substrate temperature (T_S) was changed in the range from 550 to 725 ºC. Temperatures of zinc source and the H_2O vaporizer were kept at 700 and 54 ºC, respectively. Both the vapors of Zn and H_2O were transported onto the substrate with nitrogen carrier gaseous.

With increasing T_S from 550 to 700 ºC, the growth rate increased exponentially from 13 to 68 nm/min. The analysis of XRD measurement results showed that the ZnO (002) peak was dominant for all the samples, indicating highly *c*-axis orientation. The FWHM value of the (002) peak

increased with increasing T_S. SEM observation revealed that the surface morphology strongly depended on T_S. The films grown at T_S of 550 and 575 ºC composed of round-structure grains with the average widths of 161 and 244 nm, respectively. With increasing T_S, the grains became less round and more angular in their shape together with an increase in the average width. At a T_S of 650 ºC, the average width of the grains was 410 nm. Further increase in T_S from 650 to 675 ºC enhanced the lateral growth of the grains.

Photoluminescence (PL) spectra of the films grown at T_S of 550 and 575 ºC were dominated by the near-band-edge (NBE) emission at wavelength of ~380 nm. The PL intensity of the green band emission at wavelength of ~480 nm relative to that of the NBE emission increased with increasing T_S, suggesting that the film composition became more oxygen deficient.

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FP-5 Synthesis and Optical Characterization of Nickel Oxide Thin Film obtained by SOL-GEL Method using Nickel Acetate and Citric Acid as Precursors, ***Jhonathan Castillo**, D Mateos, B Valdez, N Nedev, M Curiel, N Rosas, O Pérez,* Universidad Autónoma de Baja California, Mexico

Nickel oxide (NiO_x) has attracted much attention because it is a promising p-type semiconductor with excellent chemical stability and attractive optical and electrical properties as transparent conductive film. This material can be used in thin film transistors, electrochromic devices, batteries and gas sensors, among others. There are several methods to obtain NiO_x. However, most of these methods are expensive because typically the films are deposited in vacuum, e.g., reactive sputtering, High Power Impulse Magnetron Sputtering (HiPIMS) and Chemical Vapor Deposition (CVD).

In this work we obtain pure NiO_x thin films via sol-gel method, employing nickel acetate, citric acid and ethyleneglycol as main precursors. The synthesis consist in mixing 1:1 of $Ni(OCOCH_3)_2 \cdot 4H_2O$ and citric acid in DI water. The pH was adjusted to 8.0 and finally ethyleneglycol was added. The solution was stirred vigorously at 90°C until light green colored gel was formed. The sol-gel solution was deposited on quartz substrate by spin-coating technique and annealed at 410°C in air atmosphere. The annealing temperature was determined previously by thermogravimetric analysis.

EDS analysis reveals the presence of Ni and Oin the deposited thin films. Raman spectroscopy indicates the characteristic peak of NiO_x at 520 cm^{-1}. FTIR measurements show two characteristic peaks at 405 cm^{-1} and 1041 cm^{-1}, which correspond to the Ni-O stretching vibrational modes. UV–VIS absorption spectrum measured after heat treatment corresponds to NiO_x. The transparency and film thicknesses were determined by Spectroscopic Ellipsometry.

The obtained results prove that high purity NiO_x thin films may be obtained at low-cost by sol-gel method. The deposited layers are attractive for application in electronic and optoelectronic devices as transparent and semi-conductive materials.

FP-8 Exploring the Visible Light Photocatalytic Activity of the ZnO - RGO Hybrid - Nanostructures by Sol-gel Process, ***Chih-Chiang Wang**,* National Chung Hsing University, Taiwan*; H Shih,* Chinese Culture University, Taiwan

Carbon-based material, like the graphene, exhibits the unique 2-D structures, e.g., sp^2-conjugated C atoms, highly electronic conductivity, larger specific surface area, better chemical stability. Hence, it attracts various attentions in many fields, like the photocatalysts, solar cells, energy storage, etc. ZnO is an n-type semiconducting material with a wide direct band gap (3.3eV), hexagonal wurtzite structure and higher exciton binding energy (60meV), and has been applied in the field of photocatalyst, gas sensors, and solar cells. In this study, the pristine and ZnO-RGO hybrid-nanostructures were fabricated by sol-gel method at the ambient environments. Subsequent baking was conducted at the 500℃ under $4x10^{-3}$torr.

XRD showed that peaks of (100), (002), (101), (102) and (110) planes belonged to the pure ZnO as the wurtzite structure, but no RGO-related peaks appeared at 24˚ of the ZnO-RGO hybrid-nanostructures. The SEM images revealed that the sheet-structures appeared in the adding RGO samples and TEM-SAD showed the RGO patterns, suggesting that the RGO was covered by the ZnO nanoparticles which has confirmed the XRD results. Raman spectra exhibited the decreasing ratio of I_D/I_G from 1.2 to 0.8 while the ZnO combined with the RGO, meaning that ZnO fixed the defects inside the RGO and increased the sp^2-carbon domain.

UV-vis. spectra revealed the characteristic peak of ZnO at 375nm, and the absorbance increased with the increasing RGO concentrations. PL spectra exhibited two emission regions at NBE and DLE, and displayed the decreasing tendency while the RGO contents increased, indicating that the recombination of electrons and holes was hindered by the adding of RGO. The specific surface area (BET) showed the increasing profile from 4 to 18.5m^2/g while the RGO contents was from 0 to 6400ppm, while the grain size decreased from 31 to 26nm. The results suggested that the RGO could inhibit the grain growth of ZnO, therefore, the BET values increased. The visible light photocatalytic tests revealed that the efficiency of pristine ZnO, ZnO-RGO_{400ppm}, ZnO-RGO_{800ppm}, ZnO-$RGO_{1600ppm}$, ZnO-$RGO_{3200ppm}$, ZnO-$RGO_{6400ppm}$ were 10%, 50%, 94%, 95%, 96%, and 94%, respectively, after 15min illuminating time. Furthermore, the rate constant was smaller than 0.012min^{-1} while the RGO was lower than 400ppm. On the other hand, the rate constant larger than 0.04min^{-1} while the RGO was higher than 800ppm. Both of which confirmed the results of photocatalytic efficiency. In summary, the RGO should be able to inhibit the recombination of electrons and holes, and increase the BET values, as followed by the enhancing of the photocatalytic efficiency under the visible light.

FP-9 Suppression of Moisture-induced Electrical Instabilities in High-mobility ZnON TFTs Fabricated from HiPIMS-made ZnON Films, *K Thorwarth,* ***Rajesh Ganesan**,* EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Trant,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; H Hug,* EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Bilek, D McKenzie,* The University of Sydney, Australia

The effects of water absorption on the Thin Film Transistor (TFT) devices fabricated from zinc oxynitride (ZnON) films deposited by direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS) have been investigated. When exposed to moisture at room temperature, DCMS-made ZnON TFTs exhibited a smaller mobility, lower threshold voltage, increased carrier concentration and higher subthreshold slope with a deteriorated electrical stability under positive gate voltage. However, for the set of similar conditions, TFT devices made from HiPIMS-deposited ZnON films exhibited relatively stable electrical characteristics than that of the ones made by DCMS. The enhanced performance of ZnON films deposited by HiPIMS could be attributed to the high film density and the amorphous nature which is free of crystallographic defects. Such film characteristics reduce the formation of oxygen vacancies and the bonding of zinc and nitrogen, and thus hold the efficiency of electrical behavior of the films intact.

FP-12 Tribo-mecanical Characterization of Ti/TiN/AlN Thin Film Produced by HiPIMS, ***Joaquin Oseguera**, D Melo-Máximo,* ITESM-CEM, Mexico*; L Melo,* TRAMES S.A. de C.V., Mexico

High power impulse magnetron sputtering (HiPIMS) has the capability of yielding a highly ionized flux of gas and sputtered materials by applying high power in short pulses to the targets. Ti/TiN/AlN thin films were deposited using a homemade reactor with two non-balanced magnetrons by reactive sputtering; co-deposition was produced on a 4140 T tool steel AISI-SAE designation. From the process, optical emission spectroscopy was performed and the combination of voltage pulses and the current was measured, the parameters process were changed (temperature, gas composition, and adhesion layer). The microstructures of thin solid films were characterized by X-ray diffraction and scanning electron microscopy, scratch tests, hardness and friction coefficients were determined.

FP-13 Synthesis and Characterization of Bismuth Cuprate Thin Films Produced by Co-Sputtering, *D Franco-Pelaez, O Depablos-Rivera,* ***Sandra Rodil**,* Universidad Nacional Autonoma de Mexico, Mexico

One of the most important challenge of the humanity is the production of sustainable energy, the increase in energy consumption and the use of coal reserves could come several environment problems and high cost solutions. Semiconductors based on bismuth oxide present a band gap in the visible light, so is possible to use these materials in the production of hydrogen by photoelectrochemical water splitting. We report the synthesis of cuprate bismuth thin films deposited by reactive magnetron co-sputtering, metallic copper and bismuth oxide (Bi_2O_3) targets were used to deposit cuprate bismuth on FTO (fluorine doped tin oxide), glass (fused silica) and silicon substrates. For the copper target it was necessary to vary the applied power (DC) from 3 to 60 Watts finding that the best option is 10 Watts, while at the bismuth oxide target 30 Watts (RF) were applied. The coatings were grown under reactive environment with Ar: 28 sccm and O_2: 12 sccm and heating the substrates at 200 ˚ C. However, the as-

deposited coatings were amorphous and it was necessary to perform a heat treatment at 500 ° C in static air for 2 hours to obtain the tetragonal structure. The X-ray diffraction confirmed the formation of the tetragonal phase ($CuBi_2O_4$) coexisting with copper oxide, the optical and electronic properties were measurement by UV-VIS spectrometry and Mott- Schottky plots, finding that the optical band gap is ~ 1.4 to 1.6 eV and the films presented an p-type conductivity with a flat band potential of 0.4 eV. The photocurrent was evaluated as a function of the thickness.

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FP-14 Synthesis of Zn /ZnO Nanoparticles using Atmospheric Plasma Discharge in Solution to Mitigate the Stress Corrosion Cracking in the Simulated Primary Water Environment, ***Sang-Yul Lee***, *S Kim, M Song,* Korea Aerospace University, Republic of Korea*; S Kim,* Korea Institute of Industrial technology, Republic of Korea*; J Kim,* University of Incheon, Republic of Korea

Zn injection is known to cause changes in composition as well as in crystalline morphology of the oxide layers, which is responsible for mitigating corrosion on the Ni-based alloys in the simulated primary water [1]. Conventionally Zn precursors such as dimethyl zinc, diethyl zinc, zinc hydroxide, zinc carbonate, and zinc acetate are used for Zn injection and this, however might cause additional problem due to the formation of other corrosive ions (OH^- , CO_3^{2-}, and CH_3COO^-) [2].

To eliminate this problem, in this study, pure Zn nanoparticles were synthesized by atmosperic plasma discharge process in aqueous solution for the mitigation of primary water stress corrosion cracking (PWSCC). Zn nanoparticles with various sizes were synthesized using SPP and were applied for the treatment of Ni-based alloy samples at simulated primary water environment (300ºC, 150 bar). The Zn treatment duration was controlled in the range from 0 to 240 hours. As-obtained oxide films after various Zn treatment durations were investigated using X-ray diffractometry (XRD) analysis. The Zn-treated and non-treated U-bend type Ni-based alloy samples were subjected to very harsh corrosion test under simulated PWR environments, i n which the conditions were Na_2S of 1.0 M and NaOH of 1.0 M. To measure the corrosion behavior of Zn-treated and non-treated Ni-based alloy samples, electrochemical potential analysis was performed by Potentiostat/Galvanostat. Diffraction patterns exhibited that stable oxide films with a spinel structure of $ZnCr_2O_4$ would form with increasing Zn treatment duration. It is postulated that the exchange reaction between Zn and Fe/Ni cations occurred extensively so that the dense and compact Zn spinel structure responsible for the corrosion inhibition formed [1]. Zn treated Ni-based alloys exhibited a low electrochemical potential (ECP) value comparing with non-treated Ni-based alloys. In addition, the results from U-bend test showed that the PWSCC in Zn-treated Ni-based alloy samples was much retarded comparing with non-treated Ni-based alloys.

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FP-15 Vanadium Nitride Thin Films Grown by High Power Impulse Magnetron Sputtering, *H Hajihoseini,* ***Jon Tomas Gudmundsson,*** University of Iceland, Iceland

Thin vanadium nitride films were grown on SiO_2 by reactive high power impulse magnetron sputtering (HiPIMS). The film properties were compared to films grown by conventional dc magnetron sputtering (dcMS) at similar conditions. We explored the influence of the stationary magnetic confinement field strength on the film properties and the process parameters. Furthermore, for both dcMS and HiPIMS the deposition rate is lower for strong magnetic confinement. Structural characterization was carried out using X-ray diffraction and reflection methods as well as atomic force microscopy (AFM) and scanning electron microscope (SEM). For reactive growth of vanadium nitride the HiPIMS process produces denser films with lower surface roughness than dcMS does. Lowering the magnetic field strength increases the deposition rate significantly for reactive HiPIMS while it increases only slightly in the reactive dcMS case. The films grown by HiPIMS with strong magnetic confinement exhibit higher density and lower roughness. We find that the operating pressure, growth temperature, cathode voltage and film thickness has influence on the properties of HiPIMS grown vanadium nitride films. The films are denser when grown at high temperature and cathode voltage and low pressure < 1 Pa. Density of those films are inversely proportional to its thickness and thicker films consist of larger grain size. In all conditions, higher density coincide with lower surface roughness. Thus, the deposition method, the magnetic field strength, growth temperature, cathode voltage, film thickness and growth pressure have a significant influence on the film quality and structural properties, including the grain size for the various orientations.

Surface Engineering - Applied Research and Industrial Applications
Room Grand Hall - Session GP
Symposium G Poster Session

GP-2 Laser-clad Induced Reaction Synthesis of TiC/WC Reinforced Co-based Composite Coatings on Copper Alloy, ***Hua Yan****, P Zhang, Z Yu,* Shanghai University of Engineering Science, China

Co-based composite coatings reinforced by nickel coated WC (Ni/WC) and in-situ synthesized TiC particles has been fabricated from precursor mixtures of HG-Co01(Co-based alloy), Ni/WC, graphite and pure titanium powders by laser cladding on Cr-Zr-Cu alloy substrate. The microstructure, phase and wear properties were investigated by means of optical microscopy (OM), X-ray diffraction (XRD) and scanning electron microscopy (SEM), as well as dry sliding wear test. Results show that reinforcements dispersed uniformly in the Co-based matrix. TiC showed the morphology of dendritic and particle. During laser-clad processing, the laser heating effect caused inter-diffusion action between the precursor mixtures and generated TixCy and some Ti element diffused into Ni/WC particles formation of TiWC2 alloyed layer. The laser-clad TiC/WC reinforced Co-based composite coatings exhibited higher microhardness and better wear resistance than copper alloy. The highest microhardness was up to 1007 HV0.2 which was improved 8 times comparing to the Cr-Zr-Cu substrate. The friction coefficients of the laser-clad composite coatings were reduced significantly to about 0.15 and relatively smooth wear surface could be observed.

GP-5 The Study of Mechanical Strength on the Injection Molding Parameters of PMMA/TG Composite Bipolar Plates, ***Ai-Huei Chiou,*** National Formosa University, Taiwan

Recently, green energy technology is developing in the world and fuel cell is one potential energy resource of renewable energy technologies. Now fuel cell is facing the challenges of popularization and miniaturization. The bipolar plate is a key component in this device, so to develop highly conductive, lightweight, and low cost bipolar plate for fuel cell is important goal. Besides, the design of fuel cell assembly plays an important role in the performance. Therefore, the primary goal of this study is improving process, material selection and mechanical properties of bipolar plate. To make a breakthrough the bottleneck of science and technology in fuel cell and create more economic value in the future.

Therefore, weight and cost of bipolar plates were important research project for improvement. In this study, light-weight composite bipolar plates were prepared by injection molding. The thickness of the lightweight composite bipolar plates were thinner in this study. After the injection molding bipolar plate may havepoor strength caused affection [to fuel cell assembly and battery efficiency. In order to make it have good strength, take the tea graphites(TG) as reinforcing materials that were made of recover tea leaves and mixed with Polymethylmethacrylate. The experimental parameters were planned by Taguchi method to improve strength and warping quality.

The experimental results showed that the increase of TG content decrease the PMMA flow and transmittance, but the bending strength and heat resistance increased in PMMA / TG composites.The Single quality optimization of bending strength of the PMMA / TG composite bipolar plate was about 35.64 ±1.9 Mpa, which was improved about 7.6% higher than the maximum bending strength of L_8 (33.13±1.4Mpa)in the orthogonal table.Results showed that the composite of interest qualified under the Department of Energy (DOE) requirements for weight and flexural strengthfor fuel cell bipolar plates.The study concludes that the process of PMMA/TG bipolar plates by injection mold may be used in fuel cell applications.

GP-6 Real-time Analysis of Neutral Species from Atmospheric Plasma, ***Peter Hatton***, *A Rees, C Greenwood, S Bort,* Hiden Analytical Ltd, UK

Electrical plasmas at atmospheric pressures find increasing application in materials processing and other fields. Generation of the plasmas is not necessarily more difficult than at low pressures, but the plasmas can involve a wider range of particle species, produced through an increase in interactions at the elevated pressures. Identification of the active species assists the characterisation of the plasmas and the evaluation of equilibrium pathways involved, thus aiding the optimisation of particular systems. The work reported here is for two simple RF atmospheric plasmas studied using a Hiden HPR20 EPIC quadrupole mass spectrometer. The measurements were made in real-time using the instrument's capillary inlet system to couple to the reactor. Test data for a mixture of helium and carbon dioxide clearly show the plasma dissociation of the carbon dioxide. The reaction was monitored either through observing the intensities of CO^+ and CO_2^+ ions produced in the source of the HPR20 EPIC from the sampled gas or the intensity of the negative oxygen ions produced by selecting the electron energies in the source to be those corresponding to the peaks in the dissociative electron attachment for the two gases.

Data from tests using a methane/helium plasma show clearly the wide range of high mass products produced by the plasma, and their rapid response to changes in plasma conditions. Negative ions such as H^- and $C_2H_2^-$ were monitored as well as high –mass positive ions. The data illustrate some of the potential of instruments such as the HPR20 for the study of high pressure plasmas, for example in the production of hydrophobic surfaces.

GP-8 Correlation of HPPMS Plasma and Coating Properties using Artificial Neural Networks, *K Bobzin, T Brögelmann, N Kruppe,* ***Martin Engels***, Surface Engineering Institute - RWTH Aachen University, Germany

The development of industrial coating processes for tool coatings by means of physical vapor deposition (PVD) is usually extremely complex. This is caused by the large number of necessary coating batches and associated coating analyses until suitable process parameters are found. Artificial neural networks (ANN) are basically capable of describing complex relationships between various characteristic process values. Hence, within the scope of this paper the capability of describing complex correlations was tested on the example of a reactive high power pulsed magnetron sputtering (HPPMS) (Cr,Al)ON process. Selected process parameters pulse frequency and process gas composition were chosen, since they exhibit strongly non-linear cause-effect relationships. The ANN was used in order to correlate selective results from efficient substrate-oriented plasma diagnostics and coating analyses. Regarding the plasma properties the Al/Cr ratio and the metal-to-gas ion flux ratio were considered. With respect to the coating properties the Al/Cr ratio and the universal hardness were examined. From the correlation of these results, conclusions on the process parameters for desired coating properties were deduced and successfully proven for the investigated HPPMS (Cr,Al)ON process. Hence, the ANN exhibits a great potential to supplement the fundamental understanding of PVD processes in order to contribute to a simplification of the development of industrial coating processes.

GP-9 Linking Erosion and Sputter Performance of a Rotatable Target to Microstructure and Properties of Mo Thin Films, *A Hofer-Roblyek, K Pichler,* Montanuniversität Leoben, Austria*; C Linke,* Plansee SE, Austria*; R Franz,* Montanuniversität Leoben, Austria*; J Winkler,* Plansee SE, Austria*;* ***Christian Mitterer***, Montanuniversität Leoben, Austria

The use of molybdenum in large area thin film deposition includes back contact layers for thin film solar cells as well as diffusion barriers and source/drain electrodes in microelectronics and relies on its excellent thermal stability and chemical inertness as well as low electrical resistivity. A constant high quality of sputter deposited thin films during the entire target lifetime is of vital importance for these applications. Thus, this study addresses the sputter performance, i.e. changes of current, voltage and arc rate, recorded during erosion of a rotatable Mo target as well as the quality of thin films deposited at different erosion stages. The enhanced target erosion and the thus reduced target wall thickness cause an increase of the magnetic field strength in front of the target and yield a slightly reduced voltage and increased current. Increased arc rates could be related to venting the vacuum chamber during interruptions in target erosion which were needed for thin film depositions. Both, microstructure and electrical resistivity of the films deposited are widely unaffected by the progressing target erosion. In contrast, the different substrate carrier oscillation modes determine film topography, stress and electrical resistivity. The end of target life is determined by the pronounced sputter grooves formed at both ends of the rotatable target due to the shape of the permanent magnetic field at the turnarounds rather than changes in the quality of the films deposited.

GP-10 Surface Profile Analysis as an Investigative Tool for Electrolytic Plasma Polishing, ***Nicolas Laugel***, *A Matthews, A Yerokhin,* University of Manchester, UK

Electrolytic Plasma Polishing (EPPo) is a finishing method for the smoothing of conductive workpieces. Based on the electrodissolution of metals at electrical potentials lying in the hundreds of volts range, it presents the advantages of electropolishing. The absence of a tool, for example, means independence from macroscopic surface geometry as well as the avoidance of tool wear. Yet in contrast with traditional electropolishing, it requires lower material removal for a given target roughness and makes uses of mild electrolytes, for a very low negative environmental impact.

In EPPo, just like in electropolishing, material is typically thought to be removed through anodic dissolution. The high energy discharge at the interface leads however to several simultaneous phenomena limiting the rate of material removal. A gaseous vapour hull enveloping the treated surface, hallmark of plasma electrolytic processes, is an example as it limits drastically the current flowing through the cell. So is the production of soluble ions and oxides significantly modifying the effective electrolyte composition at the surface's immediate vicinity. The eventual topological properties of the treated surface are a direct result of these competing phenomena.

Careful characterisation of interfacial features thus allows to gather information on the process itself. Power spectral density analysis of height maps, obtained by laser confocal profilometry over wide areas and with varying resolutions, underline the characteristic lengths of surface features of a given surface. Comparing its results before and after EPPo, on pieces made of different materials and with varying original roughness distributions, sheds a unique light on the material removal process. Contrasting them with the results form other characterisation techniques, both *in* and *ex situ,* builds on a picture showing EPPo as a chain of processes each indispensable to the whole and to a large extent independent of one another.

GP-11 Evaluation of the Oxidation of Cr-W-N Coating on Ferritic Steel as Bipolar Plates for Solid Oxide Fuel Cell, *S Yang,* ***Chi-Ju Tsan***, National University of Kaohsiung, Taiwan*; Y Chang,* National Formosa University, Taiwan*; Y Pan,* China Steel Corporation, Taiwan*; D Lin,* National University of Kaohsiung, Taiwan

Ferritic stainless steel is the one of materials of choice for SOFCs bipolar plates, because of high electrical conductivity, suitable thermal expansion compatibility, excellent mechanical properties and oxidation resistance. It has been reported that Crofer 22 H has excellent electrical conductivity and oxidation resistance with additions of Nb and W, whcih are better than those of Crofer 22 APU. Even though Laves phase in Crofer 22 H improves creep property, the oxidation rate is not sufficiently low to enable uncoated Crofer 22 H interconnects to meet the current 40,000 h SOFC lifetime requirement. Therefore, Crofer 22 H also requires a protective coating both to retard the oxidation rate and to prevent the volatile chromium species.

In this study, Cr-W-N coating was deposited on high-chromium ferritic stainless steel as protective coatings by using cathodic arc evaporation. Oxidation kinetics of the Cr-W-N -coated sample was evaluated through isothermal tests in an atmospheric furnace at 800 °C for 1000 h. Morphology and cross sections of scales were examined under a field-emission scanning electron microscope in both backscattered and secondary electron modes. Coating phase assemblies were assessed using X-ray diffraction. High resolution transmission electron microscopy was utilized for a close examination of the coating/alloy interfacial chemistry. After oxidation at 800 °C for 1000 h, the results showed that the dominant oxidation mechanism transfer is the growth of Cr_2O_3 and $(Mn,Cr)_3O_4$ spinel. Moreover, the doping of W benefited the formation of a χ phase to precipitate at the oxide/coating interface, which acted as a diffusion barrier retarding the reaction rate between Cr and O.

Advanced Characterization Techniques for Coatings and Thin Films
Room Grand Hall - Session HP
Symposium H Poster Session

HP-1 Temperature Dependence of Nanocrystalline Aluminum Thin Film Elastic Constants by In-situ Brillouin Light Scattering and Picosecond Ultrasonics: Comparison to Molecular Dynamics, ***Philippe Djemia,*** LSPM-CNRS, France*; L Belliard,* INSP-UPMC, France*; H Zhang, Q Hu,* IMR-CAS, China*; F Challali, N Girodon-Boulandet, D Faurie,* LSPM-CNRS, France

We investigated the effective elastic constants in the temperature range [20°C, 600°C] of a polycrystalline aluminum thin film deposited on a silicon substrate by rf magnetron sputtering from Al target in Ar plasma discharge. From x-ray diffraction, Al polycrystalline film did not show strong crystallographic texture. The Brillouin light scattering (BLS) and the picosecond ultrasonics (PU) were complementary employed in combination with a furnace under high –vacuum (~10^{-5} mbar) or inert gas, to measure their acoustic and elastic properties. At room temperature, the Al film could be considered as nearly isotropic while increasing the temperature until 600 °C led to a continuous decrease of the elastic constants and an increase of the elastic anisotropy that was evaluated by a C_{11}/C_{33} ratio greater than one, of the in-plane (C_{11}) and out-of-plane (C_{33}) longitudinal effective elastic constants. Our results are found to be in a good agreement with previous experimental studies on bulk Al using standards ultrasounds equipment and our molecular dynamics theoretical estimates.

HP-2 High Resolution Full-field Curvature Measurement, *S Grachev,* ***Quentin Herault,*** *J Wang, I Gozhyk,* Saint-Gobain Recherche, France*; R Lazzari,* INSP-UPMC, France

A novel approach to curvature measurement will be presented. It allows for measuring curvatures below 10^{-7} m^{-1}. The method was successfully applied to observation of the first stages of growth of Ag by sputtering with unprecedented detail. The full-field capability allows for observation of complex forms resulting in variation of local curvature. The method was applied to a Mo film with inhomogeneous thickness distribution, which provided the curvature distribution maps. The poster will present the details of the method as well as its applications.

HP-4 In-situ High Temperature Characterization of DLC Films Using an Integrated Synchronized System, *M Rouhani,* National Chung Cheng University, Taiwan*; F Hong,* National Cheng Kung University, Taiwan*;* ***Yeau-Ren Jeng,*** National Chung Cheng University, Taiwan

An integrated synchronized system capable of mapping of depth-sensing indentation, spatially synchronized with a Raman spectrometer was applied to analyze microstructure, mechanical properties and surface roughness of DLC films over a specific area of the surface simultaneously. This integrated system was equipped with a high temperature chamber coupled with feedback control to make it possible to study the temperature effects on the mechanical properties and the microstructure evolution of the films, in ambient air up to 450°C. A series of DLC films with different sp^3 content were deposited on Si substrates using filtered cathodic arc vacuum (FCVA) deposition system. Our study confirms the previous results that the thermal stability of the a-C films depends on their initial sp^3 content. The results show that the structural change is accompanied with profound increase in surface roughness of the films. The hardness of the films decreases with temperature increasing even before any changes in the microstructure of the films could be detected using Raman spectroscopy. The capability of the synchronized system enabled us to explore surface sensitive phenomenon of a-C film due to temperature rise that was not known before. Hence, our *in-situ* study showed for the first time that the surface sensitivity to temperature is greater than for the bulk of a-C films.

HP-6 Novel Methodology for the Evaluation of Mechanical Properties of Specific Crystalline Phases Present in Alumina Layers Formed by Plasma Electrolytic Oxidation (PEO) of Aluminium Alloys, ***Etienne Bousser,*** *A Yerokhin, A Gholinia, P Withers, A Matthews,* University of Manchester, UK

Aluminium alloys are widely used for their high specific strength but because of their lower hardness, these alloys often present a less than ideal resistance to surface wear. In order to improve the tribo-mechanical behaviour of these materials, electrolytic processes have been used for many years to promote the formation of protective oxide layers. More recently, Plasma Electrolytic Oxidation (PEO) has been shown to offer excellent wear performance through increased hardness due to the formation of hard crystalline phases during the oxide growth process at near-to-ambient bulk metal temperatures. However, the evaluation of the mechanical properties of the constituent phases in such oxide layers is difficult due to their complex microstructure. Indeed, these coatings are typically non-uniform with a shallow porous top layer which sits on a thicker, relatively dense layer comprising of a mixture of polycrystalline and amorphous oxide phases. In addition, complex multi-scale crack and pore networks are present over the entire thickness of the layer, making the evaluation of mechanical properties problematic using standard depth-sensing indentation methodologies. In this study, we present a novel approach for the precise evaluation of the mechanical properties of individual crystalline phases in the Al_2O_3 layers formed on aluminium alloys using Pulsed Bipolar PEO processes. The methodology presented in this poster is based on the statistical analysis of highly spatially-resolved mechanical property mapping of oxide layer cross-sections combined with high resolution characterization of the crystalline phases using Electron Back-Scattered Diffraction (EBSD). The EBSD was carried out on cross-sections prepared by Xe^+ ion Plasma FIB serial-sectioning and broad Ar^+ ion beam milling. In order to gain deeper insights into the processing effects on structure-property relationships, layers formed at different process times were evaluated.

HP-7 In situ High Temperature Fracture Toughness Evaluation of Hard Thin Ceramic Coatings by Means of a Micro-pillar Splitting Technique, ***Juri Wehrs,*** Platit AG, Switzerland*; J Best,* University of New South Wales, Australia*; M Polyakov, X Maeder,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Wheeler,* ETH Zürich, Switzerland*; M Morstein, B Torp,* Platit AG, Switzerland*; J Michler,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The fracture toughness at elevated temperatures is currently quite a difficult property to measure, but is a useful engineering variable for knowledge-based hard coating design. Most relevant applications of hard coatings, for example for metal cutting and forging tools, require usage at elevated temperatures. However several difficulties exist concerning toughness elucidation of small-scale specimens, mainly due to size effects, plasticity, residual stress effects and the influence of ion penetration from the sample fabrication process. Measuring at elevated temperatures magnifies the complexity of this task even further. Hence only few examples of high temperature fracture toughness measurements at high temperatures exist for small-scale samples.

In this study we explore the fracture toughness of a variety of arc-PVD coatings (CrN, AlTiN, AlCrTiN, and a AlCrN/SiNx nanocomposite) by means of a pillar splitting technique in the temperature range from RT to 500°C. The pillar splitting method for small-scale fracture toughness evaluation is inherently advantageous as the fracture event occurs under a sharp nanoindentation tip and in a region of material not significantly influenced from ion penetration and implantation. Therefore such a method is interesting for the study of brittle small-scale samples where ion implantation effects may be problematic. Further, unlike for other direct indentation techniques used to measure fracture toughness, the interface between coating and substrate does not interfere with the cracks that form, keeping the physics relatively simple.

Topical Symposia
Room Grand Hall - Session TSP
Symposium TS Poster Session

TSP-1 Enhanced Hardening and Damage-tolerance Nanotwinned Medium Entropy Alloy CoCrNi Coatings Deposited by Magnetron Sputtering, ***Fuyang Cao,*** *P Munroe,* University of New South Wales, Australia*; Z Zhou,* City University of Hong Kong, China, Hong Kong*; Z Xie,* University of Adelaide, Australia

High entropy alloys (HEA) are defined as alloys consisting of at least five or more equiatomic elements, such as FeNiCoCrMn, commonly with a single FCC (or BCC) crystal structure. HEAs are reported to have promising mechanical properties, high thermodynamic stability, as well as excellent fracture toughness at cryogenic temperature. Herein we have investigated a series of equiatomic medium entropy alloy coatings, containing only three elements, Co, Cr, Ni. These coatings were deposited onto M2 steel substrates using a DC magnetron sputtering system with a CoCrNi alloy target (1:1:1 at.%). The microstructure and mechanical properties were examined by a number of techniques, including transmission electron microscopy (TEM) and nanoindentation. TEM results showed that the

coatings were composed of elongated grains containing fcc {111} nanotwins. Such coatings exhibited a very high hardness, ~10 GPa as well as exceptional damage-tolerance under contact loading. It is believed that the nanotwinned structure is responsible for the high hardness and damage tolerance in these coatings.

TSP-4 Hvof Coatings Modified With Polymers To Reduce Ice Accretion For Use In Aerostructures Components, ***Raúl Muelas Gamo**, A Agüero Bruna, J Mora Nogues, P García Gallego,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Accretion of ice on aerostructures affects airplanes as well as rotorcraft as it constitutes a severe security issue and requires certified anti-icing technologies. Moreover, icing increases the aerodynamic drag on an aircraft and thus increase fuel burn. Most ice protection technologies presently in use have inherent negative effects such as high energy consumption, increased weight, a negative environmental impact, and the need for frequent reapplication among others.

Surface engineering can contribute to reduce ice accumulation in a durable manner. An attractive approach to this issue is the development of hard icephobic coatings applied by thermal spray in particular High Velocity Oxyfuel (HVOF), using highly resistant coatings to the different atmospheric aggressions and doping them with polymers particles, which can provide the icephobic properties necessary to complete the demanded functionality.

The inclusion of the polymer in the high resistance coating improves the hydrophobicity and the ice accretion behavior without affecting its structural properties. This polymer-doped cermet coating has been tested on an ice wind tunnel and compared with an anti-icing commercial paint, and has improved the properties in terms of ice accretion behavior.

The proposed solution is environment-friendly, will contribute to the reduction of energy consumption, and will help eliminate the need for frequent on-ground de-icing procedures. This in turn will contribute to the reduction of cost, pollution and flight delay.

TSP-5 The Electro-Mechanical Properties of Cathodic Arc Deposited High Entropy Alloy Thin Films on Polymer Substrates, *A Xia,* Montanuniversität Leoben, Austria*; O Glushko, M Cordill,* Erich Schmid Institute of Materials Science, Austria*; **Robert Franz**,* Montanuniversität Leoben, Austria

In recent years a new class of materials has emerged in the field of metallurgy: high entropy alloys (HEAs). These metallic alloys consist of 5 to 13 metallic elements in an approximately equimolar ratio. Studies conducted on HEA bulk materials revealed promising combinations of properties, such as strength, ductility, corrosion resistance, wear resistance, hardness, diffusion and thermal conductivity. While research on bulk high entropy alloys has seen quite a boost over the past years, investigations on thin films are still a relatively unexplored area.

The focus of this report lies on the cathodic arc deposition (CAD) of two different HEA thin films and the characterization of their electro-mechanical properties, in particular their fracture behavior. The MoNbTaVW and AlCuCrTaTi thin films were synthesized by CAD with an Ar pressure of 4.9 Pa and a current of 120 A to a thickness of 200 nm on polyimide foils and silicon substrates. While the MoNbTaVW film revealed a smooth surface with columnar microstructure, the AlCuCrTaTi film showed a high number of droplets on the surface and a coarse microstructure. In-situ characterization techniques were used to examine the mechanical and electrical properties of the films, while the adhesion energies were calculated using the geometry of buckles formed due to the presence of compressive stresses. The films were exposed to uniaxial tensile straining, while simultaneously measuring the change in electrical resistance. Additionally, the crack formation during straining was investigated with optical microscopy. The results showed that both films remained electrically conductive up to 3% strain. At higher strains MoNbTaVW revealed brittle behavior as seen by straight through thickness cracks and an abrupt increase in resistivity, whereas AlCuCrTaTi showed a more ductile fracture and a less steep resistivity increase.

TSP-6 Synthesis and Characterization of Multicomponent Nitrides in the Al-Cr-Nb-Y-Zr System, ***Kristina Johansson**,* Uppsala University, Sweden*; P Soucek,* Masaryk University, Czech Republic*; A Srinath, D Rehnlund, E Lewin,* Uppsala University, Sweden

Nitride based thin films are commonly used as protective coatings for e.g. cutting tool applications due to their excellent properties regarding high hardness, thermal stability as well as corrosion and oxidation resistance. Recently, multicomponent nitrides with five or more principal elements have attracted a lot of attention due to their interesting material properties. In this regard they can outperform their respective binary nitrides. Multicomponent nitrides are based on the high entropy concept, where the high entropy of mixing caused by including at least five elements will favor the formation of a solid solution. Whereas binary nitride materials, such as Cr-N, Nb-N, Zr-N and Cr-Al-N, have been widely studied for their high hardness and corrosion resistance, multicomponent nitrides have not been studied to the same extent. Also, by addition of yttrium corrosion and oxidation resistance can be improved as previously studied for the Cr-Al-Y-N and Ti-Cr-Al-Y-N systems [1-2]. In this study, multicomponent nitride thin films of the Al-Cr-Nb-Y-Zr system were deposited in order to study their mechanical and electrochemical properties. The films were synthesized by dc magnetron reactive sputtering using elemental targets of the respective elements and a gas flow of Ar and reactive N_2. Both the substrate temperature and the target powers were varied to study their effect on the structure and the material properties.

All films were found to have a nitrogen content of about 40 at.%, indicating substoichiometric films with respect to N. From XRD it was found that all coatings were of single solid solution phase with NaCl-type structure. The lattice parameter ranged between 4.29 to 4.38 Å depending on both the composition and the substrate temperature, where is it was found that the unit cell size decreased with increased temperature and also increased with increased Nb and Zr content. SEM cross section images revealed a columnar microstructure, which became finer with increased temperature and with decreased Al and Cr content. The hardness increased from 17 GPa up to 27 GPa with increased substrate temperature and with decreased Al and Cr content. Corrosion resistance, studied by polarization measurements between -0.2 V to +1.5 V in a 1.0 M HCl aqueous electrolyte, showed improved corrosion resistance for all the studied samples, i.e. increased corrosion potential and lower current densities, compared to an industrial stainless steel reference sample. Thus, this material system shows a potential for the use as hard and corrosion resistant coating.

References

1. F. Rovere et al., Surf. Coat. Technol. 202 (2008)

2. L.A. Donohue et al., Vacuum, 55 (1999)

Coatings for Use at High Temperatures
Room California - Session A1-3

Coatings to Resist High Temperature Oxidation, Corrosion, and Fouling

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Shigenari Hayashi, Hokkaido University, Sebastien Dryepondt, Oak Ridge National Laboratory, USA

8:00am **A1-3-1 A Framework for Modelling the Nanomechanical and Nanotribological Properties of High Temperature HfB_xC_y Coatings**, ***Mohammad Humood***, *T Ozkan,* Texas A&M University, USA*; E Mohimi, J Abelson,* University of Illinois at Urbana-Champaign, USA*; A Polycarpou,* Texas A&M University, USA

High aspect ratio conformal HfB_xC_y coatings were synthesized using low-temperature chemical vapor deposition (CVD). The carbon content was varied in the aggregates, which resulted in thin films with different compositions and mechanical properties. A framework was developed based on mixing of different aggregates to predict the nanomechanical properties of these films. Under this framework, we assumed the growth to be either diffusion or nucleation controlled. Different volume fractions of aggregates were considered. Certain mixing rations agreed well with the instrumented nanoindentation and provided further insights to better understand the results of and nanoscratch experiments. Nanoscratch experiments revealed the coefficient of friction (COF) to diminish to a superlubricity level of 0.05 when the carbon content increases in HfB_xC_y thin films. This value is comparable to DLC, and underlines the immense potential of HfB_xC_y hard thin film coatings for tribological applications. However, due to the shortcomings of C-based coatings such as a-C and DLC, which all experience graphitization and degradation under tribological contact conditions at elevated temperatures above 350 °C, there is a potential need for using ultra-high temperature ceramic coatings such as HfB_xC_y as an alternative for tribological applications.

8:20am **A1-3-2 Characterization of Thermal Properties of Different Pyrochlore Ceramic Materials Dedicated for Application as an Insulation Layers in Thermal Barrier Systems**, *M Mikuskiewicz,* ***Damian Migas***, *G Moskal,* Silesian University of Technology, Poland

The basic direction of thermal barrier coatings (TBC) systems development is related to new materials solutions dedicated for bond-coats and ceramic insulating layers. From technological point of view this development consists mainly new conceptions in internal architecture of ceramic sublayer in the form e.g. of segmented, composite or multilayered morphology. In the case of new materials concepts the most interesting areas of investigations are related to strongly defected systems such as pyrochlore ceramic with overall formula RE2(Zr,Hf,Ce)2O7, perovskites or hexaaluminates materials of REZrO3 and (A,B)Al11O19 type respectively, or defected cluster zirconia based materials with two rare earth elements (with high cations ionic size differences) and formula ZrO2-Y2O3-RE12O3-RE22O3.

In presented article thermal properties of different types of pyrochlore material based on zirconia, hafnia and ceria of samarium are presented. Analyzed materials were synthesized by solid state reaction method form mixture of feedstock nano-sized powders of zirconia, hafnia, ceria and samaria. Synthesized materials were analyzed from its chemical and phase constituent point of view. The crystallite size was determined as well by X-ray diffraction method. Additionally the crystallite size and theirs orientations were analyzed by EBSD method. The morphological characterization of used feedstock powders was showed as well. The basic range of investigations was related to thermal parameters such as thermal diffusivity, specific heat and coefficient of thermal expansion analysis. Those data were obtained by laser flash analysis, calorimetric and dilatometric investigations respectively. On the base of those data the thermal conductivity was calculated in temperature range 25 to 1500°C. Obtained value of thermal parameters were compared to analogous data for usually used zirconia based ceramic of 8YSZ type.

The research has been supported by National Science Centre within Sonata scheme, under contract UMO-2016/21/D/ST8/01687.

8:40am **A1-3-3 Development of High Performance Corrosion Resistant Coatings using Graphene**, ***Anand Khanna***, *K Aneja,* IIT Bombay, India

Graphene based high performance coatings have been developed using a graphene powder prepared in our lab using a new pressure based exfoliation method. Three kinds of coatings were made: (i) pre-treatment coatings on steel substrates using a new patented method of functionalizing graphene. The thin five micron coating has excellent adherence and very low permeability. (ii) graphene dispersed epoxy primer whose properties appear superior than a epoxy zinc rich coating or inorganic zinc rich coating and (iii) a graphene based polyurethane top coat with superior UV blocking properties. Combining all the individual coatings as conversion coating, primer and top coat, it becomes an excellent high performance coating with very high corrosion resistance, mechanical properties and weathering resistant. Each individual coating has its independent application for example pre-treated graphene can be an excellent replacement for electrolytic coating for automobile bodies and graphene dispersed epoxy can be a good replacement for epoxy based zinc rich coating or inorganic zinc rich primers.

9:00am **A1-3-4 Wide-range and Enhanced Filtration of Polyacrylonitrile Membrane for Water Purification by Coating with Thin Film Metallic Glass**, ***Shewaye Kassa***, *Y Liao, J Chu, J Chen,* National Taiwan University of Science and Technology (NTUST), Taiwan

We have successfully fabricated comprehensive thin-film metallic glass (TFMG) coated polyacrylonitrile (PAN) membrane for wastewater purification. Several PAN-based membranes, synthesized via electrospinning were compacted into a single membrane through Zr-based TFMG coating by a means of magnetron sputtering deposition. TFMG coatings with various thicknesses ranging from 200 nm to 320 nm were grown on the membranes with no external heating. After coating with TFMG, the water purification performance of the membrane for synthetic wastewater, contaminated with toxic heavy metals (Cr and Cd), vegetable oil and microorganisms (E. coli and P. aeruginosa), was found to be higher than 95% with a pure water flux rate of 814 L $m^{-2}h^{-1}$. TFMG-coated PAN membrane exhibited extraordinary selectivity and a remarkable fouling recovery rate in comparison to the bare polyacrylonitrile membrane, which can be as a result of significant enhancement in the strength as well as the thermal and chemical stability of the membrane through the TFMGs coating.

9:20am **A1-3-5 The Effect of Surface Aluminizing to Enhance High-temperature Air-oxidation Resistance of Equimolar FeCoNi and FeCoNiCr Alloy**, ***Wu Kai***, *F Cheng, F Chien, R Huang,* National Taiwan Ocean University, Taiwan*; J Kai,* National Tsing Hua University, Taiwan

The effect of surface aluminizing treatment on air-oxidation behavior of equimolar FeCoNi-based alloys (FeCoNi and FeCoNiCr) was studied at 950°C. The results showed that the oxidation kinetics of the aluminized alloys followed the two-stage parabolic rate law. The optimal aluminized parameters were to heat the alloys at 850°C for 4 h in 63% Al_2O_3-30% (Fe-Al)-7%AlF_3 powders under an Ar-gas flow-rate of 200 cm^3/min. The oxidation rates of the aluminized alloys were significantly lower than those of the untreated alloys by 3 to 5 orders of magnitude. The scales formed on the aluminized alloys consisted of an exclusive thin-layer of a-Al_2O_3 whose formation is responsible for the significant reduction of the oxidation rates with respect to the ternary and quaternary substrates.

9:40am **A1-3-6 TEM Study of Hf-B-Si-C-N Coatings Microstructure at High Temperatures**, ***Yi Shen***, *M Zhang, J Jiang,* University of Texas at Arlington, USA*; J Vlček,* University of West Bohemia, Czech Republic*; E Meletis,* University of Texas at Arlington, USA

Amorphous $Hf_7B_{23}Si_{22}C_6N_{40}$, $Hf_7B_{23}Si_{17}C_4N_{45}$ and $Hf_6B_{21}Si_{19}C_4N_{47}$ coatings were synthesized by reactive pulsed dc magnetron co-sputtering. These coatings possess a hardness of ~ 20 GPa and a Young's modulus of ~170 GPa, and exhibit superior high-temperature oxidation resistance. The microstructures of the coatings annealed up to various temperatures from 1100 °C to 1600 °C in helium and in air were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM) to understand the effect of slight composition tuning on their microstructure evolution at high temperatures. All annealed films were found to have a two-layered structure composed of the original film followed by a nanocomposite oxidized surface layer involving HfO_2 nanoparticles embedded in a SiO_x-based matrix. Slight changes in the nitrogen content of the coatings were found to result in significant microstructure difference and oxidation resistance at high temperatures.

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Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-3-1 Nano-Structural Ni Matrix Films Synthesized byElectrochemical/Chemical Composite Depositions**, ***Zhixiang Zeng,*** Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In this study, the chemical deposition was introduced into the electrochemical deposition system to tailor the micro-structures of Ni matrix films. The structures and micro-hardness of films were characterized by transmission electron microscopy and nano-indenter, respectively. Results show that not only nanocrystalline and amorphous films but also amorphous/nanocrystalline composite films could be one-step synthesized by electrochemical/chemical composite depositions. The crystalline size of Ni films could be refined to about 5 nm, which leading to the micro-hardness of about 12GPa.

8:20am **B4-3-2 NbC-Ni Coatings Deposited by DC Magnetron Sputtering: Effect of Ni Content on Mechanical Properties, Thermal Stability and Oxidation Resistance**, ***Luis Varela,*** University of São Paulo, Brazil; *F Fernandes, A Cavaleiro,* University of Coimbra, Portugal; *A Tschiptschin,* University of São Paulo, Brazil

Hard coatings have been widely used in the machine tool industry to increase the wear resistance and hence to improve their service life-time, as a result of their better mechanical properties. Most of the studies focused more in nitrides and less in carbides. In this study, we evaluated the effect of Ni additions on the properties of NbC films deposited by magnetron sputtering. In particular, we investigated the microstructure, structure, mechanical properties, oxidation resistance and thermal annealing of films. The properties of Ni rich coatings were compared to a NbC film deposited as reference. All the films displayed a columnar morphology with columns extending from the substrate up to the surface. Increasing the Ni content decreases the columns size of films and consequently, their level of compactness. Excluding the substrate contribution, all the diffraction peaks could be generally assigned to the f.c.c NaCl type structure. The introduction of Ni to the NbC film shifts the (111) and (200) diffraction peaks to higher and lower angles, respectively. A progressive decrease of grain size is observed with Ni additions, reaching a quasi-amorphous from Ni contents higher than 17 at.% Ni. TGA measurements showed that Ni additions increased the oxidation performance of the coatings.The onset point of oxidation of films is higher by 100 °C for Ni containing films independently of the Ni amount. The hardness of films increased to Ni content in the range of 0<at.% Ni<12 and then progressively decrease with further Ni additions. Annealing performed at 600 and 800 °C increased the hardness and Young´s modulus of films. Elastic strain to failure (H/E) and plastic deformation resistance H^3/E^2 parameters showed a growing trend with Ni additions.

8:40am **B4-3-3 Stress-Dependent Elasticity of TiAlN Coatings**, ***Marcus Hans,*** RWTH Aachen University, Germany; *U Hangen,* Bruker Nano GmbH, Germany; *L Patterer, D Holzapfel, D Music, S Evertz,* RWTH Aachen University, Germany; *V Schnabel,* Laboratory for Nanometallurgy, ETH Zurich, Switzerland; *A Eriksson, J Ramm, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Switzerland; *J Schneider,* RWTH Aachen University, Germany

In this work we compare the elastic properties of TiAlN coatings synthesized by cathodic arc on sapphire substrates with and without substrate rotation. Elastic properties as well as residual stress states are investigated as a function of temperature by *in situ* nanoindentation and X-ray diffraction up to temperatures of 500°C. Room temperature elastic modulus values of 459 ± 26 GPa and 501 ± 5 GPa were obtained by nanoindentation for coatings grown with and without substrate rotation (stationary), respectively. The elasticity enhancement by 9% due to stationary processing under otherwise identical deposition parameters can be understood by the formation of compressive residual stresses on the order of -5 GPa. The coatings grown utilizing substrate rotation are characterized by a tensile residual stress state of +1 GPa.

9:00am **B4-3-4 Evaluation of the Open Porosity of PVD-Coatings through Electrochemical Iron Detection**, ***Juan Vega,*** *H Scheerer, G Andersohn, M Oechsner,* Technische Universität Darmstadt, Germany

The open porosity of Plasma vapour deposition (PVD) coatings, namely the existence of open paths between the substrate and the environment through the coating is a critical factor that can lead to failure of the coatings in corrosive environments. Most of the coatings create a physical barrier by covering the surface of the substrate. Because of the open crystalline structure of some PVD-Coatings and the presence of imperfections, some parts of the substrate can be expose to corrosive environments. Corrosion takes place preferably on the substrate, due to the superior corrosion resistance of many PVD-Coatings. Corrosion processes underneath the coating could lead to delamination of the coating or even failure of the coated part. Electrochemical methods based on the measurement of the current density as response to the polarisation of the sample have been widely used to characterize the porosity and corrosion behaviour of PVD-Coatings, however the presence of metallic interlayers create a mixed electrochemical potential with the substrate, the results are in this case combined information about interlayers and substrate.

The present investigation uses the electrochemical ion detection to evaluate the open porosity of PVD-Coatings. In order to validate the method, samples with different open porosities and interlayers thicknesses were deposited on steel substrates. The method is based on the assumption that corrosion will occur on the substrate surface if open paths through the coating exist. A platinum mesh located on the sample´s surface, held at oxidation potential of Fe^{2+} to Fe^{3+} is used to detect and quantify iron ions coming from the substrate. The current density on the platinum mesh will be increased if iron ions are available to be oxidized. By comparing the current densities of the coatings it is possible to classify them according to their open porosity. Because not polarisation of the sample is required, unlike other electrochemical methods used to evaluate the porosity, the method can be considered as non-destructive. The detection is not affected by metallic interlayers. The measurements can be done under free corrosion potential conditions, making long-term evaluations possible. In cases where the current densities without polarisation are similar, the sample can be polarised to increase the corrosion processes and the associated iron detection. The results show a good agreement with the microscopic inspection and microstructural characteristics of the samples.

9:20am **B4-3-5 Structural and Optical Properties of Si-Nb-N Composite Thin Films**, ***Cristian Orozco,*** University of Texas at El Paso, USA; *N Murphy, L Sun,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *R Chintalapalle,* University of Texas at El Paso, USA

Nitride nanocomposite thin films have generated significant attention as a result of their robust mechanical and good corrosion stability. Due to their excellent hardness (~40 GPa) and high wear resistance NbN coatings have found use in a wide variety of applications such as the coating of cutting tools and to strengthen the surface mechanical properties of superconducting cavities. The mechanical properties of NbN can be further improved through mixing with Si_3N_4, leading to the formation of a nanocomposite structure. NbN-Si_3N_4 nanocomposite coatings have been actively studied due to their high hardness, high elastic modulus, and high resistance to oxidation. In this work, efforts were made to synthesize Nb-Si-N nanocomposite films with variable Nb-N and establish a correlation between structural and optical properties. The Nb-Si-Nfilms were deposited by pulsed DC and DC magnetron sputtering onto silicon substrates. Pulsed DC was used to ensure the stability for dielectric Si_3N_4 and remained at a constant power of 150W concurrent with variable power DC sputtering (0-150 W) for NbN. The N_2 flow rate was selected via hysteresis monitoring with the co-deposition at 150W Si and 150 Nb related to maximum nitrogen uptake and seeing the metallic, transition, and poisoned modes. X-ray diffraction (XRD) studies indicate that all the films were amorphous. Chemical analyses using X-ray photoelectron spectroscopy (XPS) indicate a progressive reduction in Si content with increasing Nb. Corroborating with structural and optical data, mechanical characteristics also indicate a change in elastic modulus and hardness of the Nb-Si-N films. A structure-composition-property relationship in Nb-Si-N films is established.

9:40am **B4-3-6 HIPIMS Cr/CrN Multilayer Structure for Corrosion Resistant Decorative Coating**, ***Yen-Chun Liu***, *S Hsiao, W Lo, Y Chen, J He,* Feng Chia University, Taiwan

Physical vapor deposition (PVD) processes have long been considered for decorative applications, as alternatives for electroplating processes. However, relatively little progress has been made due to corrosion issues brought by the existing defects in the coating structure resulting from the conventional PVD film morphology. By combining highly ionized PVD and multilayer structure, it is anticipated that corrosion protectiveness shall be improved further due to more effective barrier property to corrosive environment.

This study employs high power impulse magnetron sputtering (HIPIMS) to deposit Cr/CrN multilayer coatings on copper alloy substrates. The main advantages of HIPIMS are much denser, and smoother coatings compared to conventional PVD thin film deposition techniques. This paper briefly describes the corrosion resistance of the obtained HIPIMS Cr/CrN multilayer coatings characterized by electrochemical technique. Microstructures of these coatings are also examined to correlate their respective corrosion protective effectiveness.

10:00am **B4-3-7 Hardness-independent Extraordinary Wear Resistance in Magnetron Sputtered Cr-Si-N Coatings: The Importance of Fracture Toughness**, ***Feng Huang***, *F Ge, C Jia,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

A central problem of tribological hard coatings is to understand the relationship between wear resistance and mechanical properties (such as hardness, elastic modulus, fracture toughness, etc.). When high wear resistance is sought for brittle hard coatings, existing models all suggest a positive correlation with the coating hardness (H) or the hardness-to-modulus ratio (H/E). Here we report experimental observation showing a constantly high wear resistance, independent of the hardness, in brittle ceramic coatings. Nanocomposite Cr-Si-N coatings were prepared by magnetron sputtering under the assistance of energetic bombardment (by 10-60 eV ions) at a moderate ion-to-atom flux (about unity). We find that these coatings, with various amounts of nanopores but no uninterrrupted column boundaries along the growth direction, achieved high wear resistance (i.e., wear rate approaching 10^{-17} m^3/N m level) over a wide hardness range (12-36 GPa). Microscopic examination of the wear tracks reveals noticeable energy relief by limited inelastic deformation, such as crack propagation followed by crack bridging and crack deflection, in a localized to widespread manner with decreasing hardness. Contrary to previous models, the present results demonstrate that the wear resistance of brittle hard coatings is governed by fracture toughness (a measure of resistance to crack extension) rather than hardness (a measure of resistance against permanent deformation), and highlight the importance of energy absorption by limited inelastic deformation in achieving high wear resistance.

Fundamentals and Technology of Multifunctional Materials and Devices

Room Sunrise - Session C2-3

Novel Oxide Films for Active Devices

Moderators: Marko Tadjer, Naval Research Laboratory, USA, Vanya Darakchieva, Linkoping University, Sweden

8:00am **C2-3-1 Improved the PI Transmittance and ITO Conductivity by Supercritical CO_2 Fluid Treatment**, *G Chen,* ***ChienYu Lin***, *T Chang,* National Sun Yat-Sen University, Taiwan*; S Lin, M Yu, Y Chuang,* HannStar Display Corp, Taiwan

In the flexible display, PI is often selected as the substrate, to achieve the requirement of foldable devices. The electrode of the display must be made of transparent metal. In this paper, the PI transmittance and ITO conductivity was improved the by supercritical CO_2 ($SCCO_2$) fluid technology. The advantages of supercritical fluid treatments are high penetration and high solubility can easily take away impurities and doped the film at room temperature. Supercritical fluid technology can bring out the monomer molecules and eliminate defects in PI substrate, inducing to higher transmittance. Hydrogenation $SCCO_2$ increase the conductivity of ITO to improve device performance.

8:20am **C2-3-2 Improving Performance by Inserting an In_2O_3 Layer into HfO_2-Based Resistive Random Access Memory**, ***Cheng-Hsien Wu***, National Sun Yat-Sen University, Taiwan*; S Lin,* National Tsing Hua University, Taiwan*; T Chang, T Tsai, Y Lin, Y Tseng,* National Sun Yat-Sen University, Taiwan

This letter investigates the characteristics of inserting an indium-oxide (In_2O_3) layer in HfO_2-based resistive random access memory (RRAM). Inserting In_2O_3 layer in the Pt/HfO_2/TiN structure not only reduces the forming voltage and the operating current, but also enlarges the memory window. The fitting result of the current-voltage (I-V) curves shows that the conduction mechanisms in high resistance state (HRS) are dominated by Schottky emission conduction for both structures. However, in low resistance state (LRS), the conduction mechanism is Ohmic conduction in Pt/HfO_2/TiN, but Poole-Frenkel emission mechanism in Pt/HfO_2/In_2O_3/TiN. Based on the material analysis and the current fitting result, a physical model is proposed to explain this phenomenon.

8:40am **C2-3-3 Halide Vapor Phase Epitaxy of Ga_2O_3**, ***Ken Goto***, *Q Thieu, D Wakimoto, K Sasaki,* Novel Crystal Technology, Inc., Japan*; K Konishi, H Murakami, Y Kumagai,* Tokyo University of Agriculture and Technology, Japan*; A Kuramata,* Novel Crystal Technology, Inc., Japan*; S Yamakoshi,* Tamura Corporation, Inc., Japan **INVITED**

Gallium oxide (Ga_2O_3) has been actively researched and developed as one of the wide-bandgap semiconductors for next-generation power devices in recent years, and literatures on high-voltage operation of SBDs and FETs were reported. However, in order to introduce Ga_2O_3-based power devices to the market, it is inevitable to establish mass production technologies, especially manufacturing technology for large-diameter wafers with thick and conductivity-controlled epitaxial films on them. Epitaxial growth of single crystal Ga_2O_3 films is reported, which is achieved by using several growth methods such as MBE, PLD, CVD (including MOCVD and mist-CVD) and halide vapor phase epitaxy (HVPE). Among them, HVPE method has demonstrated high-speed growth and doping control over a wide range, and it is suitable for a commercial use because it has a simple hardware structure without using a vacuum system, for instance.

It was thermodynamically analyzed that HVPE growth of β-Ga_2O_3 is possible by using gallium mono-chloride (GaCl) and oxygen (O_2) as precursors, and a high-purity single crystal homoepitaxial film can be grown at a high temperature of 1000 °C in a hot-wall reactor. The growth rate increased in proportion to the input partial pressure of GaCl gas, achieving 20 μm/h or more. Si doping into the epitaxial film was carried out by simultaneous supply of $SiCl_4$ gas into the reactor during the growth, and Si concentration in the range of 3E+15 to 1E+18 cm^{-3} can be controlled. It was confirmed that the Si-doped films show n-type conductivity and their carrier concentration (measured by Van der Pauw method) equal to Si concentration in the epitaxial films (measured by SIMS analysis). The mobility at room temperature was nearly 150 cm^2/Vs when carrier concentration was 1E+16 cm^{-3}.

By applying those findings, we demonstrated homoepitaxial growth by HVPE on a 2-inch-diameter substrate for the first time. Single crystal film was grown on the entire surface of the substrate: mean value (uniformity) of the film thickness and the carrier concentration in the 2-inch-diameter wafer were 10.9 μm (± 16.5 %) and 2.7E+16 cm^{-3} (± 19.7 %), respectively. It was demonstrated that any SBDs fabricated on this wafer worked normally and fluctuation of on-resistances was 3.8-7.7 mΩcm^2. Relatively good uniformity was obtained in an early stage of film growth development on the 2-inch-diameter wafer. By optimizing the gas flow, the film thickness uniformity improved to 8.0 %. Currently, we devote much effort on improving uniformity.

9:20am **C2-3-5 Severe Positive Bias Temperature Instability in N-type MOS Device with Dipole Doped HfO_2 Dielectric Layer**, ***FuYuan Jin***, *T Chang, H Liu, C Lin,* National Sun Yat-Sen University, Taiwan*; J Liao,* National Tsing Hua University, Taiwan*; F Ciou, W Hung,* National Sun Yat-Sen University, Taiwan

In this work, we found severer positive bias temperature instability (PBTI) in N-type MOS device with dipole doped HfO_2 dielectric layer than N-type MOS device with pure HfO_2 dielectric layer. In addition, both electron trapping and defect generation are also more severer in dipole doping device. This phenomenon can be due to the lowering of the conduction band in HfO_2 with higher electric field which is induced by dipole at interface.

9:40am **C2-3-6 Physical Mechanisms of Negative Bias Illumination Stress in InGaZnO Thin Film Transistors with Different Metal Gate Structure**, ***Chung-I Yang,*** National Chiao Tung University, Taiwan*; T Chang,* National Sun Yat-Sen University, Taiwan*; W Chou,* National Chiao Tung University, Taiwan

In this study, the electrical analyses and physical mechanisms of structure-depended reliability tests in InGaZnO thin film transistors are investigated. First, the difference of shielded area between IGZO layer and metal gate is discussed. Under the different metal gate length devices, an abnormal rise in capacitance at the off-state in capacitance-voltage characteristics curves can be observed. It is attributed to edge effect-induced high electrical field when the metal gate length is shorter than IGZO layer length. Under light illumination measurement, the behaviors of subthreshold-leakage current can be observed whether the lengths of metal gate are larger than IGZO layer or not. After the negative gate bias illumination stress (NBIS), it is found that the devices which have edge effect caused the more severe hole injection into the gate insulator.

10:00am **C2-3-7 Fabrication of MSM UV Photodetector Based on ZnO/TFMG/UNCD Nanostructures**, ***Markos M. Yenesew,*** *B Huang,* National Taiwan University of Science and Technology, Taiwan*; J Chu,* National Taiwan University of Science and Technology (NTUST), Taiwan

In this study, we demonstrate the fabrication of a high performance photodetectors using a multilayer of ZnO nanotubes (NTs), thin film metallic glass(TFMG), and ultra-nano crystalline diamond (UNCD). The device is fabricated by depositing UNCD and TFMG on a glass substrate in microwave plasma enhanced-CVD and RF magnetron sputtering systems respectively. Finally, ZnO NTs are grown by two-step hydrothermal technique. Systematic device performance investigations have shown a high on/off ratio and a fast response speed at 5 V external bias. The developed fabrication design opens up possibility for gas sensor applications.

10:20am **C2-3-8 Effect of Cadmium Chloride Treatment on Poly-crystalline Thin Films of CdTe/Cd-Zn-Te/CdTe Structures**, ***Tushar Shimpi,*** *C Reich, K Barth, W Sampath,* Colorado State University, USA

By varying the composition of zinc in the ternary alloy of $Cd_{(1-x)}Zn_xTe$ (Cd-Zn-Te), the band gap can be adjusted. This enables optimizing the Cd-Zn-Te top cell depending upon the number of junctions in the multi-junction solar cell.

In this study, sublimated poly-crystalline thin films of Cd-Zn-Te with a band gap of 1.70 eV was sandwiched in between two 100 nm CdTe films. The overall superstrate structure was glass/tin oxide doped with fluorine/Mg-Zn-O/CdTe seed layer/Cd-Zn-Te/CdTe cap. In the previous studies of 1-micron Cd-Zn-Te films and devices, the well-known $CdCl_2$ defect passivation treatment caused zinc loss in the film through the formation of volatile $ZnCl_2$. The loss of zinc reduced the high band gap thin film of Cd-Zn-Te to a lower band gap CdTe (1.48 eV). The objective of this study was to prevent this stoichiometry change by providing a zinc barrier in the form of CdTe cap prior to treatment. The CdTe seed layer was used to prevent delamination of the Cd-Zn-Te films after the $CdCl_2$ treatment and have a better band alignment at the front interface. After the passivation treatment, electrodes were deposited, and devices fabricated.

From the external quantum efficiency graph, the current generated was more than 60% including the optical losses in the wavelength range of 350 nm to 700nm. The band edge did not shift towards the longer wavelength region indicating that the band gap did not significantly change, and zinc loss was prevented from the Cd-Zn-Te thin film. The devices exhibited a rectifying curve in the current density and voltage graph. The line scans and the elemental maps collected from the cross-section viewed under a transmission electron microscope further confirmed that most of zinc was retained in the bulk of Cd-Zn-Te. Some diffusion of zinc was seen in the CdTe seed and capping layer. The chlorine decorating the grain boundaries of Cd-Zn-Te and accumulation at the front interface of Mg-Zn-O/CdTe seed layer, seen in effective $CdCl_2$ treatment of CdTe films was also observed.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 1-3 - Session H3

Characterization of Coatings in Harsh Environments

Moderators: JeffreyM. Wheeler, ETH Zürich, James Gibson, RWTH Aachen University

8:00am **H3-1 Zr/Nb Nano-multilayers – Structural and Mechanical Response to Radiation Damage**, *M Callisti,* University of Cambridge, UK*;* ***Tomas Polcar,*** University of Southampton, UK

Zr/Nb nanoscale metallic multilayers (NMMs) with a periodicity (*L*) in the range 6 – 167 nm were prepared by magnetron sputtering studied by a combination of transmission electron microscopy analyses and nanomechanical measurements to reveal deformation and strengthening mechanisms. Electron diffraction analyses revealed a change in the crystallographic orientation of α-Zr when *L* 27 nm, while Nb structure retained the same orientations regardless of *L*. For *L* > 60 nm, the strengthening mechanism is well described by the Hall-Petch model, while for 27 < *L* < 60 nm the refined CLS model comes into picture. A decrease in strength is found for *L* < 27 nm; plastic strain measured across compressed NMMs revealed a change in the plastic behaviour of α-Zr, which experienced a hard-to-soft transition. Multilayers were subject to high energy implantation (He, C, Si, Cu), gamma and proton irradiation, and the effects of radiation damage on mechanical properties were studied in detail. DFT simulations were used to identify helium diffusion and agglomeration in pristine and radiation-damaged Zr/Nb interfaces.

8:20am **H3-2 Nanoindentation of Commercial PVD Hard Coatings at Elevated Temperatures**, *W Oliver,* Nanomechanics, Inc., USA*; M Romach,* Advanced Coating Service (ACS), USA*; R Anthony,* ***Kurt Johanns,*** Nanomechanics, Inc., USA

Ten different commercial PVD hard coatings have been characterized with nanoindentation experiments. The thickness of each film has been measured along with a pass/fail test for adhesion. The results from polished surfaces and the rougher as deposited surfaces have been compared. High-speed (NanoBlitz) experiments and statistical analysis have been used to understand the relationships between polished surface and as deposited results. The number of tests required to properly characterize the as deposited surface has been determined. In addition, a selection of the samples have been characterized with high speed, high temperature experiments. The hardness and modulus distributions at room temperature and high temperatures will be presented.

8:40am **H3-3 Elevated Temperature Micro-impact Testing of TiAlSiN Coatings**, ***Ben Beake,*** *A Bird,* Micro Materials Ltd, UK*; L Arrom,* Cranfield University, UK*; F Jiang,* Huaqiao University, China

In developing advanced wear-resistant coatings for tribologically extreme highly loaded applications such as high speed metal cutting a critical requirement is to investigate their behaviour at elevated temperature since the cutting process generates frictional heat which can raise the temperature in the cutting zone to 700 °C or more. It has been shown previously that high temperature nanomechanical characterisation can be a valuable tool in understanding coating properties and how they will perform in different types of cutting tests with different requirements [1]. High temperature micro-tribological tests, such as micro-scratch and nano-impact extend the characterisation capability and have provided severe tests for coatings and correlate well to cutting tool life [2].

In this study we report the development of a novel micro-scale elevated temperature impact capability capable of producing repetitive impacts at significantly higher strain rate and energy than in the nano-impact test. With the new experimental test capability it is possible to study coating fatigue with less sharp spherical indenters than in the nano-impact test.

Micro-impact, nanoindentation and micro-scratch tests have been performed to 600 ºC on monolayer and nanolaminate TiAlSiN coatings on WC-Co. The key role of the elevated temperature nanomechanical properties in the impact behaviour of the coatings is discussed and correlations to elevated temperature micro-scratch tests to 600 ºC are investigated.

[1] *Progress in high temperature nanomechanical testing of coatings for optimising their performance in high speed machining*, B.D. Beake and G.S. Fox-Rabinovich, Surf. Coat. Technol. 255 (2014) 102.

[2] *Elevated temperature repetitive micro-scratch testing of AlCrN, TiAlN and AlTiN PVD coatings*, B.D. Beake, J.L. Endrino, C. Kimpton, G.S. Fox-

Rabinovich and S.C. Veldhuis, International Journal of Refractory Metals and Hard Materials (2017).

9:00am **H3-4 Fracture Testing of Transition Metal (Oxy)Nitride Coatings**, ***James Gibson****, S Rezaei, H Rueß, M Hans, D Music, O Hunold, S Wulfinghoff, J Schneider, S Reese, S Korte-Kerzel,* RWTH Aachen University, Germany

Transition metal (oxy)nitride coatings are used in polymer forming operations for a combination of outstanding wear resistance and chemical compatibility with the polymer materials. Varying the chemical composition and deposition parameters for the coatings will optimise mechanical properties by a combination of chemistry and microstructural optimisation. By developing a representative model for these materials, these materials can be rapidly and efficiently prototyped and improved. However, as both chemistry and microstructure play a role in the material properties, both of these variables must be taken account of in this model. This work demonstrates the first steps in linking quantum-mechanics, micro-mechanics, and meso-scale finite element models together in order to fully understand the behaviour of these coatings.

The effect of thin film composition and temperature on the elastic, plastic and fracture properties of transition metal nitride and oxynitride coatings was invested by nanoindentation, micro-cantilever bending and micro-pillar compression. Vanadium and titanium aluminium nitride and oxynitride coatings were manufactured by high-power impulse magnetron sputtering on silicon substrates. A focused ion beam was used to cut notched micro-cantilever beams to determine values of fracture toughness and micro-pillars were cut to try and obtain plastic deformation in otherwise brittle coatings. Tests were carried out to 500˚C in-situ using a Nanomechanics inSEM system. Results are explained via DFT modelling of the coating chemistry, and integrated into a cohesive-zone element finite element model.

9:20am **H3-5 In-situ Study of Deformation and Fracture Processes in Nanostructured Metals at Elevated Temperatures**, ***Daniel Kiener****,* Montanuniversität Leoben, Austria **INVITED**

Understanding the mechanical deformation and failure processes that take place in nanostructured bulk materials or for thin films on substrates is of prime importance for further improvement of the related material performance.

Miniaturized experiments provide the possibility to specifically test thin layers, individual phases, or interfaces, thereby extending our material understanding. In this presentation, recent developments using quantitative in-situ deformation testing and in-situ fracture experiments within scanning and transmission electron microscopes at ambient and elevated temperatures will be presented. The detailed observations accessible by such advanced experimental setups will be addressed in several case studies concerning the deformation and fracture behavior of, for example, nanostructured bcc metals and layered structures.

10:00am **H3-7 Cryogenic Micropillar Compression Transient Tests at the Lower Limit of Crystallinity Case Study: Nanocrystalline Palladium-Gold**, ***Juri Wehrs****,* Platit AG, Switzerland*; J Schwiedrzik,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Deckarm,* Universität des Saarlandes, Germany*; J Wheeler,* ETH Zürich, Switzerland*; X Maeder,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R Birringer,* Universität des Saarlandes, Germany*; J Michler,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The plasticity of nanocrystalline metals is governed by a complex ensemble of deformation mechanisms which strongly depends on the materials grain size. Smaller grains are less effective in generating dislocations and hence their ability to interact across intercrystalline domains is reduced. Therefore it is instructive that, in particular for that case that grain sizes approach the limit of crystallinity towards the amorphous regime, grain boundary-mediated deformation processes gain influence while dislocation-mediated processes fade. Mechanisms which essentially emerge from the core regions of grain boundaries, such as grain boundary sliding, grain boundary migration, dislocation nucleation and shear transformation zones are under debate. Consequently, both thermally activated and inelastic, stress-driven deformation processes can be simultaneously operative in these materials. All of these mechanisms contribute towards the increased time dependent plasticity of nanocrystalline metals, manifesting itself as a high degree of strain-rate sensitivity and susceptibility to load relaxation and creep even at room temperature.

In this study we explore the strain rate sensitivity of a highly pure nanocrystalline $Pd^{90}Au^{10}$ alloy with an extremely fine nominal grain size of d~10nm by means of dynamic micropillar compression experiments in a temperature interval from -55°C to 250°C. First we introduce and discuss the novel testing technique, our experimental considerations and data analysis methods. Then we focus on the applicability of this type of micromechanical experiment for probing activation parameters in nanocrystalline materials. The extracted activation parameters (i.e. strain rate sensitivity, activation volume and activation energy) are discussed and compared to literature data to gain insights into the possible rate controlling deformation mechanisms at the lower limit of crystallinity.

10:20am **H3-8 Surface Roughness Effects of Hard Coatings under Three-body Abrasive Sliding Conditions**, ***Reza Gheisari****, A Polycarpou,* Texas A&M University, USA

Three-body abrasive laboratory experiments were conducted using two different hard coatings intended for abrasive conditions for electrical submersible pumps (ESP) used in the oil and gas industry. The coatings used were specifically made for the above-mentioned application namely chromium carbide, and Diamonize coatings. These coatings have different surface topographies as well as different mechanical properties. Abrasive slurry of laboratory size-controlled silica sand in hydraulic oil was used to simulate the operational lubrication condition for the ESP. A specialized tribometer was used that simulated temperature, pressure, and velocity conditions encountered in ESPs and uses a pin-on-disk configuration, submerged in the slurry. In–situ measurements of the normal and friction forces were performed. A contact pressure of 6 MPa at a sliding velocity of 1.92 m/s was applied on the contact for 3×10^4 cycles, corresponding to 3500 meters. The focus of the study was to investigate the synergistic roles of the mechanical and roughness properties of the coatings on the wear and friction under three-body abrasive conditions. SEM and EDS analyses on the surfaces, as well as surface profilometry of the wear tracks were employed to gain more detailed perspective of the tribological mechanisms active at the macro and micro levels. It was concluded that while the effect of hardness ratio of the coating to the abrasive is righteously highlighted in previous studies, an RMS roughness close to 1 µm could significantly enhance the wear and friction performance of the coatings. In addition the ratio of abrasive size to surface roughness was proposed as an important factor to be taken into consideration while selecting the optimized coating for an abrasive condition.

Topical Symposia

Room Royal Palm 4-6 - Session TS2

High Entropy and Other Multi-principal-element Materials

Moderators: Ulf Jansson, Uppsala University, Angstrom Laboratory, Diederik Depla, Ghent University

9:00am **TS2-4 Novel Properties and Nitriding Behavior of CoCrMnFeNi High-Entropy Alloy Prepared via Mechanical Alloying and Spark Plasma Sintering**, ***Akio Nishimoto****, T Karimoto, C Nishi,* Kansai University, Japan

An equiatomic CoCrMnFeNi high-entropy alloy (HEA) exhibiting unique chemical and physical properties was synthesized via mechanical alloying (MA) and spark plasma sintering (SPS). The phase evolution, microstructure, mechanical properties, and nitriding behaviors of the HEA were investigated. The 30-h ball-milled alloy powder demonstrates excellent chemical homogeneity and a face-centered-cubic-structured solid-solution-refined morphology. The 30-h MA powder was subsequently consolidated via SPS at 700 °C–900 °C for 10 min. The sintered sample exhibits 93%–97% in relative density and 400–550 HV in Vickers hardness. The wear properties of the sintered sample improved compared with those of the casted sample. The effects of plasma nitriding at 500 °C–550 °C on microstructure and the mechanical performance of the HEA processed via MA-SPS were also investigated. The nitrided layer has a thickness of approximately 30 µm and a peak hardness level of 1300 HV near its surface. The nitrided sintered HEAs exhibit superior wear resistance compared to the casted HEA sample.

9:20am **TS2-5 Structural, Phase Stability, Thermodynamic and Elastic Properties of CoCrCuFeNi-(Nb_x, Al_x) High-entropy and Other Thin Films: Experimental and Ab Initio Investigations**, *C Li,* LSPM-CNRS, France*; B Braeckman, R Dedoncker,* Ghent University, Belgium*; Q Hu,* IMR-CAS, China*; L Belliard,* INSP-UPMC, France*; L Vitos,* KTH - Royal Institute of Technology, Sweden*; D Depla,* Ghent University, Belgium*;* ***Philippe Djemia****,* LSPM-CNRS, France

High entropy alloys are new class of multicomponent materials that renewed the metallurgy concepts by alloying several elements, at least five, with nearly equal concentrations. High mixing entropy can enable stabilization of one phase material by avoiding the formation of several intermetallic compounds. Among them, bulk CoCrCuFeNi solid solution with FCC structure has been among the first. Nevertheless, elaborating and characterizing their thin film counterparts is of newly increasing interest, providing different microstructures inherently due to a different process. Addition of a supplementary element can either increase the lattice distortion and/or favoured strong bonds formation with transition metals. These both effects on phase stability, structural and elastic properties are experimentally and theoretically studied with Nb and Al addition, respectively. Furthermore, as Nb is heavier than base elements, its addition also alters the growth conditions by the atomic peening effect. Fully dense films are then obtained with no modification of their mass density while mass density continuously decreased as a function of Al concentration.

Assessing the elastic properties of polycrystalline multicomponent alloys remains challenging as they relate on many attributes: the phase composition, texture, existence of lattice defects, impurities and porosities, grain size. Strategies should be employed to tackle this challenge by varying microstructure in a control manner and considering both single crystalline and polycrystalline materials.

This is the aim of the present work dedicated to polycrystalline cubic CoCrCuFeNi-(Alx, Nbx) films deposited by magnetron sputtering under Ar plasma discharges on a silicon substrate. In parallel, ab initio calculations were performed in the framework of the density functional theory using EMTO program providing theoretical data for the single crystal. Mass density r was determined by x-ray reflectivity measurements, while x-ray diffraction pole figure was employed to study texture effects and determine lattice parameters. Brillouin light scattering technique allows measuring sound velocity of surface acoustic waves (V_{SAW}) in thin films and thus estimating effective elastic constants (ρV^2). It can be conveniently combined with picosecond ultrasonics technique that measures the sound velocity of longitudinal waves (V_L) that are travelling forth and back within the film along the direction perpendicular to the film plane. We used this combination of techniques to measure the effective elastic constants C_{11}, C_{33}, C_{13} and C_{44} of our nanocrystalline and amorphous films.

9:40am **TS2-6 Carbon-containing High Entropy Alloys - A New Pathway to High-performance Materials?**, ***Stefan Fritze****, P Malinovskis, L Riekehr, D Rehnlund, L Nyholm, E Lewin, U Jansson,* Uppsala University, Angstrom Laboratory, Sweden

High entropy alloys (HEAs) are a promising pathway to achieve new high-performance materials. While HEA thin films have been studied to some extent by experimental and computational materials science, there is only limited information available about the influence of carbon on HEA thin films, especially when prepared with physical vapor deposition techniques. In this study, we report on the influence of carbon on the structure and properties of three different HEA alloys in the CrNbTaTiW system, which are based on only strong carbide-forming transition metals. The metal composition of these alloys includes an approximately equimolar alloy, a Nb-rich alloy and finally a Ta/W-rich composition.

We have successfully deposited highly textured Cr-Nb-Ta-Ti-W-Cthin films by non-reactive unbalanced magnetron sputtering using one carbon and five metal targets. The films were characterized with SEM, XPS, XRD, TEM and nanoindentation. XRD analyses of these coatings show that all carbon-free Cr-Nb-Ta-Ti-W films crystallize in a simple bcc structure with a strong (110) orientation. The addition of 7 at.% carbon lead to an expansion of the unit cell, while retaining the bcc structure without formation of any additional carbide phases in the as-deposited state. As more carbon is added (40 at.%) a transition metal carbide (NaCl-type) structure is obtained.

The best mechanical properties were achieved for a Ta/W rich metal sublattice for all three carbon concentrations. An as-deposited $Cr_2Nb_8Ta_{44}Ti_2W_{44}$ films, exhibited a hardness of 14 Gpa. This is more than two times higher than expected from rule of mixture. The high hardness can be explained by a significant lattice strain due to large differences in atomic radii. Upon the addition of 7 at.% carbon the hardness increased by ~40 percent to 21 Gpa. The formation of a multicomponent carbide film at a carbon concentration of 40 at.% C, leads to a further hardness increase to 27 Gpa. Potential mechanisms for the formation of these extremely hard bcc alloys with carbon will be discussed. Finally, the effect of carbon addition on the corrosion properties was likewise investigated in 0.6 M NaCl environment. High pitting corrosion resistance was found for the $Cr_2Nb_9Ta_{40}Ti_2W_{40}C_7$ composition, with a corrosion potential of 0.23 V (vs. Ag/AgCl) and a transpassive region equal to hyper-duplex stainless steel (i.e. SAF3207HD).

10:00am **TS2-7 Radiation Hardness Of FeCrMnNi High-Entropy Thin Films**, ***Vladimir Vishnyakov****, M Tunes, G Greaves, S Donnelly,* University of Huddersfield, UK

Thin films in the FeCrMnNi system were prepared by ion beam sputter deposition from elemental targets, which were deposited onto silicon, Zircaloy-4 and Ni superalloy (type 718) substrates at a temperature of approximately 350 K. Energy Dispersive X-Ray Spectroscopy and Transmission Electron Microscopy (TEM) were used to determine the elemental composition and the nanocrystalline structure respectively. In order to simulate neutron radiation damage the samples with closest to equimolar (±2 at%) composition were irradiated with 30 keV Xe^+ ions within a TEM at the MIAMI facility at the University of Huddersfield. The irradiation was performed at 573 K up to a fluence of approximately $1x10^{17}$ ions/cm², this corresponds to a damage level of 150 displacements per atom (dpa).

As the composition approaches the equimolar value, large grains were observed with sizes of hundreds of nanometres. The deviation from equimolar composition in the films only affected nanocrystallites size without traceable intermetallic presence.

During ion irradiation, the films have not shown any elemental segregation or dislocation loop formation. While the formation and growth of xenon bubbles was significantly suppressed. It is thus proposed that a fast defect recombination rate and slow defect diffusion in high-entropy alloys are responsible for the high radiation hardness of the high-entropy FeCrMnNi system.

10:20am **TS2-8 Reactive Sputtering of High Entropy Alloys with Nitrogen – Tuning the Unit Cell**, ***Robin Dedoncker****, D Depla,* Ghent University, Belgium*; G Radnóczi,* Centre for Energy Research, Hungarian Academy of Sciences, Hungary

High entropy alloys are a new class of materials with at least 5 different metals in near-equimolar concentrations with promising properties such as a high degree of corrosion resistance and mechanical strength. When deposited with magnetron sputtering, these alloys form solid solution thin films with a (111) out-of-plane fibre texture. In this present study, the effect on nitrogen addition on the growth of two different high entropy alloys, i.e. CoCrCuFeNi and CoCrFeMnNi is discussed. Thin layers were deposited from powder targets which were mounted on a two inch magnetron. Powder targets allow to design fast and in all desirable concentrations the high entropy alloy-thin films and derived compounds. The nitrogen uptake results in an enlargement of the unit cell. Gradually increasing the nitrogen/argon ratio produces a steady growth towards a stoichiometry nitride with the NaCl (B1)-structure. Other deposition parameters such as current discharge, target-substrate distance and pressure also have an influence on the arriving metal-to-nitrogen ratio and thus influence the size of the unit cell. The results can be summarized in a model for fine-tuning the unit cell of high entropy nitrides.

10:40am **TS2-9 Improved Resistance of Senary AlCrTaTiZrRu Under Bump Metallization to Interdiffusion and Reaction at Solder Joints**, ***Wen-Yu Chen****,* National Tsing Hua University, Taiwan*; K Cheng,* National Chung Hsing University, Taiwan*; S Chang,* National Tsing Hua University, Taiwan

A thin layer of under bump metallization, e.g. Ni/Au, at solder joints is used to improve the wettability of molten solder to Cu pads but also to inhibit the rapid interdiffusion and over reaction between solder and the substrates. Under bump metallization needs to prevent solder joints from forming excessive brittle and detrimental intermetallic compounds, and plays an important role in the reliability of electronic devices. Multicomponent high-entropy alloys have been found to present excellent thermal stability and high diffusion resistance in recent years. Therefore in this study, an AlCrTaTiZrRu senary alloy was developed as under bump metallization to reduce the consumption rate and improve the lifetime of under bump metallization. Experimental results indicated that, after the reflow process of solder at 230-250°C, uneven intermetallic compounds

obviously formed on a traditional Ni/Au substrate, and their thickness increased with reflow temperature. In comparison, only a thin interfacial reaction layer of only several tens of nanometers, rather than abundant intermetallic compounds, was observed between solder and the senary under bump metallization, revealing the high thermal stability of the AlCrTaTiZrRu high-entropy alloy. The wetting balance test suggested a good wettability of molten solder to the Ni/Au substrate, while the wetting of molten solder to the senary alloy was reduced. After dipping in molten solder at 250°C for one hour, a Cu substrate completely dissolved in the molten solder. However, the Cu substrate coated with the senary alloy layer remained, without an obvious loss, also suggesting the high thermal stability of the senary alloy.

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