Monday Morning, May 23, 2022

Plenary Lecture
Room Town & Country A - Session PL-MoPL

Plenary Lecture: The Fundamental Physics of Spray Coatings and Surface Impacts: Unit Process Studies of Hypersonic Particle Impacts

Moderator: Samir Aouadi, University of North Texas, USA

8:00am **PL-MoPL-1 PLENARY LECTURE: The Fundamental Physics of Spray Coatings and Surface Impacts: Unit Process Studies of Hypersonic Particle Impacts***, Christopher A. Schuh (schuh@mit.edu)*, MIT, USA **INVITED**

Many surface treatment processes involve impact events, including abrasive spray, peening methods, or spray coatings. The fundamental physics behind such processes, including deformation, bonding, and coating development, however, remain mysterious; the impacts are extremely fast and involve microscopic particles, so that they are challenging to resolve. This talk will review a new line of research aimed at understanding the unit process of particle impacts at velocities into the supersonic range—we study individual ~5-50 µm particles and record their approach and impact with a substrate using an all-optical single-particle test method with nanosecond time resolution. For hard particles, this method leads to quantitative measures of plasticity at extreme rates (>10^7 s^{-1}). For metallic particles, it quantitatively reveals the changes in plasticity that occur as particles approach the threshold velocity for bonding, as well as other deleterious transitions such as impact-induced melting and erosion. When combined with post-mortem characterization, details on microstructural evolution in extreme conditions can be discerned, including, e.g., dynamic recrystallization by a new mechanism that emerges at high rates, or the fracture and delamination of nanoscopic surface oxide layers.

Coatings for Use at High Temperatures
Room Pacific E - Session A1-1-MoM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderators: Shigenari Hayashi, Hokkaido University, Japan, **Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

10:00am **A1-1-MoM-1 Performance of Innovative High-Temperature Coatings after Exposure in a Pilot Plant Burning Biomass***, **Alina Agüero Bruna (agueroba@inta.es)**,* Instituto Nacional de Técnica Aeroespacial INTA, Spain*; P. Audigié, S. Rodriguez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; M. Gutiérrez,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain*; M. Benito, A. Bahillo,* CIEMAT, Spain **INVITED**

To increase the efficiency of biomass power plants, the operating temperature must be raised with a consequent increase in corrosion rates. New materials and/or coatings are required, and testing is needed to evaluate the corrosion resistance of these new materials under various and very complex atmospheres resulting from the different types of available biomass. However, there is no general agreement regarding the methodology to carry out biomass corrosion tests, which can allow realistic ranking of materials and coatings. A 0.5 kWth simple pilot plant based on fluidised bed combustion was implemented allowing constant fed of biomass pellets. Several alloys with and without coatings were tested at 600-620º C for 1000 h while burning eucalyptus forestry residues pellets. The results were compared to those obtained in a laboratory test carried out under KCl deposits and a model atmosphere containing H2O, O2 and N2. Newly developed Super VM12 ferritic steel was tested with and without coatings, which included slurry aluminides, modified FeCr and NiCr based alloys deposited by HVOF and weld cladded IN625. In both the pilot plant and the lab, uncoated Super VM12 showed a very high degree of corrosion, and evidence of a high extent of spallation, whereas all coatings exhibited protective behaviour at different levels. In general, it was observed that the degree of corrosiveness in the plant was similar to that obtained in the lab and in all cases the coatings protected the substrate. For instance, according to the results of both

pilot and lab scale tests, weld cladded IN625 (700 µm) showed a low degree of corrosion in both environments whereas the best behaved HVOF deposited coating was a 325 µm hard steel alloy modified with Al, that from the initial stages developed an approximately 50 µm corrosion product layer which appears to be protective as no significant thickness variations were observed. On the other hand, the slurry coatings showed non uniform degradation in the pilot plant. Indeed, in some areas typical microstructure changes could be detected due to interdiffusion with the substrate, as well as the development of voids. In addition, some degree of widening of the through thickness cracks originally present in the coating was observed (Figure 1a). These cracks self-healed by forming Al-rich oxides which are protective. The coating exposed in the lab shows a lower amount of voids when comparing with the pilot exposed specimen (Figure 2). Other zones of the coating showed important degradation of the aluminide phases after exposure in the pilot plant (Figure 1b). The causes of the difference in behaviour were analysed and will be discussed.

10:40am **A1-1-MoM-3 Surface Coatings for Improved Corrosion Resistance of Steels in Heavy Liquid Metal Coolants***, J. Kulczyk-Malecka,* Manchester Metropolitan University, UK*; N. Barron, S. Ortner,* National Nuclear Laboratory Limited, UK*; **Peter Kelly (peter.kelly@mmu.ac.uk)**,* Manchester Metropolitan University, UK

A key challenge for systems cooled by molten lead is that the cladding materials must resist the harsh environmental conditions that they are exposed to; namely, chemical corrosion by molten lead-based coolant; oxidative corrosion at temperatures above 650°C; and neutron irradiation at doses up to 250 dpa. Austenitic and ferritic-martensitic (FM) steels have been identified as good candidates for cladding materials in molten lead environments. Nevertheless, these steels are susceptible to corrosion in oxidised molten lead and, therefore, their properties need to be improvedeither by alloying with corrosion protective elements or by depositing a corrosion protective barrier coating on the surface of a steel. The ability of alloying elements, such as aluminium and chromium, to form protective oxides is well known. Thus, the aim of this work was to investigate the deposition of protective barrier layers consisting of Al, Al_2O_3 and FeCrAl on austenitic stainless steel type 316L coupons. The coatings were deposited by mid-frequency pulsed DC unbalanced magnetron sputtering in reactive (Al_2O_3) and non-reactive modes (Al, FeCrAl). Individual layers were investigated, as well as multi-layer FeCrAl/Al/AlOx coating stacks. Coatings were characterised by SEM and EDX and then subjected to a corrosive environment of molten lead at elevated temperatures (up to 800ºC) and varying oxygen contents to investigate and compare the corrosion resistance of the deposited layers to allow the best performing corrosion barrier coatings for HLMC FRs applications to be nominated and further developed.

11:00am **A1-1-MoM-4 Improving the Intermediate Temperature Oxidation Resistance of Refractory Metals and Mo-Based Systems***, **Katharina Beck (katharina.beck@dechema.de)**, A. Ulrich,* DECHEMA-Research Institute, Germany*; F. Hinrichs, M. Heilmaier,* Karlsruhe Institut of Technology, Germany*; M. Galetz,* DECHEMA-Research Institute, Germany

Refractory metals and their alloys are interesting materials to be used in high temperature applications. They are characterized by a very high melting point, typically beyond 2000°C, and their good mechanical properties at high temperatures and are therefore promising candidates for novel high-temperature materials. Besides their low oxidation resistance at target temperatures, already at intermediate temperatures, they can be prone to two different attack mechanisms: Pesting and hot corrosion.

Pesting, also referred to as catastrophic oxidation, describes the formation of volatile oxide species at intermediate temperatures and leads to the total disintegration of metal bulk material into powder. Besides pesting another particularly severe corrosion attack is induced by deposits on the surface of compounds, which usually are the result of impurities in combustion atmospheres. In turbine environments sulphates and alkali metal saltsare known to induce hot corrosion.To counteract both attack mechanisms, the formation of protective oxide scales is necessary. As α-Al_2O_3 is commonly known to be very resistant in oxidizing as well as hot corrosion environments, this work aims to make the formation of such an oxide scale possible by the application of Al-coatings.

By means of pack cementation, an *in situ* chemical vapor deposition process, Al-coatings (with thicknesses up to 60 µm) were successfully applied on four different refractory metals (Mo, Nb, Ta and W) and two recently developed Mo-Si-Ti alloys (eutectic Mo-20.0Si-52.8Ti and eutectoid Mo-21.0-34.0Ti) [1]. Using thermogravimetric analysis for 100 h in synthetic air at intermediate temperatures (700 °C and 900 °C), the oxide formation was investigated and the improvement of the oxidation behavior correlated to Al_2O_3 scale formation was confirmed. The formation of these scales results in a substantially decreased oxide growth rate in comparison to the uncoated substrates. Post exposure, Al reservoirs (intermetallic phases) were still present below the formed oxide scale, making healing of the scale possible in the case of crack formation. The applied layers, the formed intermetallic phases and the formed oxide scales were analyzed before and after exposure to the oxidizing atmospheres using optical microscopy, XRD, SEM, EDX and EPMA.

[1] Schliephake, Daniel, et al. "Constitution, oxidation and creep of eutectic and eutectoid Mo-Si-Ti alloys." Intermetallics 104 (2019): 133-142.

11:20am **A1-1-MoM-5 Arc-Evaporated $Ti_{1-x}Al_xN$ Coatings in Hot-Corrosion Settings***, **Oliver Ernst Hudak (oliver.hudak@tuwien.ac.at)**, A. Scheiber,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; L. Shang, O. Hunold, M. Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; S. Kolozsvari,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Hot corrosion is a common phenomenon observed in gas turbine engines, coal gasification plants and waste incinerators. It occurs in high-temperature settings, where a sulfur-rich atmosphere reacts with salt impurities such as Na, Mg, Cl or V, and form high-melting sulfate-salts, that then deposit and adhere on machining component surfaces. There, the salt deposit elicits an accelerated degradation of the material through the formation of non-protective porous oxide scales. Depending on the temperature range, two distinctively different corrosion mechanisms can emerge. At temperatures below the melting point of the salt deposit (~600-850 °C), low-temperature hot corrosion dominates as mechanisms, whereas at temperatures above the melting point, high-temperature hot corrosion predominates (~850-950 °C). For all of the above mentioned fields of application, Ni-, Co-, and Fe-based superalloys have proven to be a reliable choice of material, due to their superior mechanical properties at high temperatures, as well as good oxidation resistance in air. However, if exposed to hot corrosion conditions, their overall oxidation resistant qualities diminish drastically.

From this perspective, this contribution showcases $Ti_{1-x}Al_xN$ as an interesting candidate as protective PVD coatings for extending the lifetime of highly-stressed material components in hot-corrosion environments. $Ti_{1-x}Al_xN$ coatings with varying metal content ratios were arc-evaporated on Ni-based superalloy substrates and tested in an in-house built hot-corrosion testing rig. By applying a sulphate-salt mixture from the alkali and alkaline earth metal group, the samples were corroded in a SO_x-rich atmosphere for a maximum of 30 h according to the HTHC and LTHC conditions, and subsequently analyzed and evaluated for their applicability using a set of high-resolution characterization techniques.

Keywords: Corrosion Resistance; PVD coatings; Diffusion Pathways; Hot Corrosion; HTHC; LTHC;

11:40am **A1-1-MoM-6 High Temperature Oxidation Behavior of Hafnium Aluminum Diboride Thin Films***, Samyukta Shrivastav (ss101@illinois.edu), D. Yun, C. Romnes, K. Canova, J. Abelson, J. Krogstad,* University of Illinois at Urbana Champaign, USA

The integrity of hafnium diboride, a refractory and hard metallic ceramic, is compromised at high temperatures (900-1000°C) when air is present due to oxidation of the boron sublattice to form liquid boron oxide, which evaporates. One potential solution is to deposit a $Hf_{1-x}Al_xB_2$ alloy film, with the expectation that Al can oxidize to form a protective Al_xO_y overcoat.

We use low temperature chemical vapor deposition to deposit the alloys, as described elsewhere in this conference. This approach has the advantage that Al will be distributed throughout the material; by contrast, in conventional hot-pressing of separate HfB_2 and AlB_2 powders the phases may not mix intimately. We previously showed that as-deposited HfB_2 is amorphous and crystallizes upon annealing at temperatures ≥ 600°C. For the alloy, we hypothesize that excess aluminum will be liberated upon crystallization, and will diffuse to the surface and form a passivating oxide.

We show that the oxidation product is strongly temperature dependent. Upon annealing at 700°C for 1 hour, a mixture of hafnium, aluminum, and boron oxides form. But this mixed oxide is not protective, and complete oxidation of films occurs when heated to higher temperatures. At annealing temperatures between 800°C and 900°C, the oxides of boron and aluminum react to form acicular aluminum borate, which is spread uniformly on the surface of the film. TEM cross sections reveal hafnium oxide particles embedded in aluminum borate needles; SEM shows surface roughening; STEM-EDS identifies the composition of the reaction products; and SAED confirms the crystal structures of the products. We conclude that aluminum is not a viable alloying element for the formation of a passivating oxide on diboride thin films. Based on phase diagrams and oxide literature, we suggest using alloying elements like chromium, which forms a passivating oxide but does not react with the oxides of boron and hafnium.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B2-1-MoM

CVD Coatings and Technologies I
Moderator: Raphael Boichot, Grenoble-INP/CNRS, France

10:20am **B2-1-MoM-2 Diamond Coatings for Cutting Tool Applications***, Manfred Weigand (manfred.weigand@cemecon.de), M. Woda, W. Puetz, M. Wegh, C. Schiffers, W. Koelker, O. Lemmer,* CemeCon AG, Germany

Thin film Diamond as pure sp3 bonded crystalline carbon is able to significantly improve cutting tool performance in hard to machine applications. These coatings are typically deposited by the means of hot filament CVD processes on an industrial scale nowadays.

When applying diamond thin films to cutting tools with a cemented carbide substrate and with complex geometries, a large set of work piece materials can be machined including carbon fiber reinforced plastics (CFRP), zirconium oxides, aluminum silicon alloys, graphite or even cemented carbide. This work presents some of the latest results of various case studies revealing the benefits of CVD diamond coatings upon cutting operations on these very demanding work piece materials.

10:40am **B2-1-MoM-3 Deposition of Hard Carbon Films by High Power Pulse Magnetron Sputtering (Virtual Presentation)***, Takayuki Ohta (tohta@meijo-u.ac.jp),* Meijo University, Japan*; A. Oda,* Chiba institute of Technology, Japan*; H. Kousaka,* Gifu University, Japan **INVITED**

Diamond-like carbon (DLC) films, which is an amorphous carbon including both graphite (sp2 bond) and diamond (sp3 bond) structures, has widely used for hard mask for plasma etching and hard coating of the sliding parts. The DLC film containing rich sp3 bond realizes high hardness or low friction coefficient. A bombardment of carbon ions with incident energy of 100 eV into the film is essential to increase the sp3 bond in the DLC film. However, it is difficult to produce the high energy ions in conventional direct current magnetron sputtering (dcMS). High power impulse magnetron sputtering (HiPIMS) is attractive method to obtain large ion flux or high energy ions because the peak power density of HiPIMS is about 100 times larger than that of dcMS under same average power density. A DLC film on Si substrate deposited by HiPIMS shows the hardness of 20 GPa without negative substrate bias voltage[1]. A DLC film on plastic substrate has also deposited by HiPIMS without negative substrate bias voltage. The energy distributions of argon ion (Ar^+) and carbon ion (C^+) were measured using energy-resolved mass spectrometry in HiPIMS discharge in order to investigate the relationship between hardness and ion flux. The total ion flux of HiPIMS was about 100 times larger than that of dcMS under same average power density. The distribution of Ar^+ was composed of low energy component and high energy component whereas C^+ was mainly composed of high energy component. High energy component of both Ar^+ and C^+ simultaneously increased with increasing target voltage in comparison with low energy component of Ar^+. The difference in IEDF is explained by the difference in production process of ions.

The hydrogen-free Si-DLC film was deposited by dual magnetron sputtering method using carbon and silicon targets. The friction coefficient measured with the ball on disc test decreased to be 0.074 with increasing the Si content in the DLC film. At this experimental condition, the hardness was 18.4 GPa measured by the nano-indenter. Si-C bond increased with increasing the Si content from C1s spectra of XPS analysis. The relation among sp3 fraction, hardness, and behaviors of ions will be discussed.

reference

[1] K. Iga et al., Thin Solid films, 672, 104 (2019).

11:20am **B2-1-MoM-5 Ti_3SiC_2-SiC Multilayer Thin Films Deposited by High Temperature Reactive Chemical Vapor Deposition***, Jorge Sánchez Espinoza (jorge.sanchez@grenoble-inp.fr), F. Trabelsi, E. Blanquet, F. Mercier,* SIMAP, Grenoble-INP, CNRS, France

MAX phases have a unique combination of ceramic and metallic properties that make them excellent candidate materials for high temperature applications. They are particularly interesting for their excellent thermal stability up to 1500 °C, their exceptional thermal shock resistance and their damage tolerance. In addition to their good mechanical properties at elevated temperatures and high stiffness, they exhibit optical, electrical and thermal properties similar to metals.

In this work, we report on the preparation of multilayer ceramic coatings based on MAX Phases by Reactive Chemical Vapor Deposition (R-CVD), able to withstand high temperature (T>1000°C) under air while maintaining their structural and functional properties. Computational Fluid Dynamics calculations, thermodynamic and diffusion considerations were developed for the selection and the design of the multilayer experiments.

R-CVD depositions were conducted in a vertical quartz cold-wall CVD reactor in the system $TiCl_x$ - H_2 - SiH_4 - C_3H_8 - H_2 between 1100-1300 °C in order to form multi-layer coatings that consist of stacks of titanium silicon carbide (MAX phase layer Ti_3SiC_2) and silicon carbide (SiC).

The surface morphology and cross-sectional microstructure of as-grown Ti_3SiC_2–SiC layers were characterized by Scanning Electron Microscopy (SEM), and X-Ray Diffraction analysis to identify the different solid phases. High temperature oxidation tests, nano-indentation and emissivity measurements were carried out with the aim of evaluating the potential of this material for high temperatures applications.

11:40am **B2-1-MoM-6 Chemical Vapor Deposition of W(C,N): Process Parameter – Microstructure – Mechanical and Tribological Property Relationships***, **Katalin Böőr (katalin.boor@kemi.uu.se)**,* Uppsala University, Angstrom Laboratory, Sweden*; L. von Fieandt, E. Lindahl,* Sandvik Coromant, Sweden*; M. Fallqvist,* Karlstad University, Sweden*; O. Bäcke,* Chalmers University of Technology, Sweden*; R. Lindblad,* Uppsala University, Sweden*; M. Halvarsson,* Chalmers University of Technology, Sweden*; M. Boman,* Uppsala University, Sweden

There is a constant need to improve the performance of metal cutting tools. A materials research approach is the chemical vapor deposition (CVD) of coatings on the tool insert to enhance some of its properties or to introduce new functionalities. Hexagonal WC is the hard component of cemented tungsten carbide and is expected to have a good performance as a coating as well. Tungsten based coatings deposited by chemical vapor deposition are, however, so far relatively unexplored. The deposition from the gas phase can introduce new microstructures and textures, leading to enhanced mechanical properties. Moreover, the coating is expected to be under a compressive stress after post-deposition cooling if the substrate contains Co and the coating only the hexagonal WC phase. This differs from a tensile stress causing cracks in many conventional CVD coatings on cemented carbide.

The aim of this research was to deposit a new CVD coating, tungsten carbonitride (W(C,N)), which is a solid solution of hexagonal WC and WN, onto cemented carbide. Hexagonal WC and WN are line phases and are difficult to obtain by CVD due to the discrepancy in the reactivity of W-halide and C-precursors or a stable cubic WN_{1-x} phase, respectively. For the W(C,N) synthesis WF_6, CH_3CN and H_2 were used and they proved to have a balanced reactivity for W, C and N incorporation in ratios that enabled the formation of the hexagonal phase.

First, the current understanding on the growth mechanism will be presented. The results are based on a kinetic study and the influence of the process parameters on the coating microstructure and composition. Correlations between the grain size, morphology and orientation will be shown. The coating microstructure was characterized by scanning electron microscopy (SEM), the composition by elastic recoil detection analysis (ERDA) and the texture by X-ray and electron backscatter diffraction (XRD and EBSD). Transmission electron microscopy (TEM) was used to investigate a preferred prismatic texture and the type of defects introduced during the growth. Hard X-ray Photoelectron Spectroscopy (HAXPES) was used to investigate the reason behind a (C+N)-rich composition.

Further, the possibilities to tailor the microstructure and grain orientation of the coatings will be discussed. Nanoindentation measurements, diamond scratch and abrasion tests showed that the coatings were hard or superhard and their mechanical and tribological properties were dependent on the above properties.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-1-MoM

Properties and Characterization of Hard Coatings and Surfaces I

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

10:00am **B4-1-MoM-1 Cathodic Arc Deposition of Chromium Based Coatings***, **Johan Nyman (johan.nyman@liu.se)**, H. Högberg,* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

Chromium is a widely used metal in coating industry with applications as decorative coating and for wear resistant purposes. The dominating Cr coating technique has been and still is electroplating. As health- and environmental concerns of electroplating is receiving ever increased attention, a need arises to develop alternative methods of synthesizing equally well-performing coatings. The multitude of application areas for electroplated Cr means that no universal solution exists to replace it. We investigate cathodic arc deposition of metallic Cr as well as Cr-based coatings alloyed with C and/or N with the purpose to tailor the properties of the coating between metallic and ceramic, seeking a combination of hardness and toughness. Thus, focus is put on determining synthesis-composition-structure relationships and their connection to the resulting mechanical properties of the coatings. We employ nanoindentation to analyze the mechanical properties of the coatings. From applied depositions conditions, transitions between metallic and ceramic properties are identified by determining chemical compositions by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA), bonding structure by X-ray Photoelectron Spectroscopy (XPS), resistivity by four-point probe measurements and phase distribution by X-ray diffraction (XRD) θ/2θ scans.

For Cr-C coatings, ToF-ERDA measurements show an increase in C content from 2 at.% at a C_2H_2 partial pressure of 0.1 Pa to 40 at.% at a C_2H_2 partial pressure of 0.3 Pa, corresponding to a composition of Cr_3C_2. The increase in C content is accompanied by a decrease in deposition rate from 130 to 30 nm/min. In θ/2θ XRD scans, Cr 110, 200, 211 and 220 peaks are clearly visible at C contents below 2 at.% , but where the peak intensities are suppressed with increasing C content. At a C content of 40 at.% there are no discernable peaks, indicating growth of X-ray amorphous coatings. Four-point probe measurements confirm the metallic properties at C contents below 2 at.% where resistivity values are close to values for pure metal Cr coatings with 20 μΩ*cm. At a C content of 7 at.% the resistivity has risen to 35 μΩ*cm and at 40 at.% it is 120 μΩ*cm . Nanoindentation reveals an increase in hardness from about 8 GPa for metallic Cr to 12 GPa already at 2 at.% C, indicating that a window exists for combining beneficial properties from that of a metal and a ceramic. Results from coatings alloyed with N will also be presented.

10:40am **B4-1-MoM-3 Grain Boundary Segregation Engineering in AlCrN Hard Coatings by CrN precipitation***, **Tobias Ziegelwanger (tobias.ziegelwanger@unileoben.ac.at)**, N. Jaeger, C. Mitterer, R. Daniel, J. Keckes, M. Meindlhumer,* Montanuniversität Leoben, Austria

As the modern day race for higher efficiency and machining speed in metal cutting industry asks for steady improvement of both hardness and toughness, this contribution has investigated grain boundary segregation engineering as a viable tool for hard coatings. Wurtzite (w-) AlCrN was chosen as a material of interest due to its favourable decomposition route and precipitation of cubic (c-) CrN. This behaviour was manipulated by alloying with Si in varying content.

A gradient coating $(Al_{0.8}Cr_{0.2})_{1-x}Si_xN$ was deposited by cathodic arc evaporation and annealed at several dedicated temperatures of up to 1100 °C. The Si content was increased with the increasing film thickness. The coating was characterized, in as-deposited and annealed states, by cross sectional X-ray nanodiffraction (CSnanoXRD), in small angle X-ray scattering (SAXS) as well as wide angle X-ray scattering (WAXS) geometries, at the synchrotron source PETRA III at the German Synchrotron (DESY) [Fig1.]. Therein, the formation of a w-AlCrN phase as well as the precipitation of c-CrN was indicated. Furthermore, the formation of periodic nanolayers within the coating in as-deposited state was observed. Their periodicities of 12 and 25 nm, depending on the Si content, were retrieved by the SAXS data.

The collected data from the gradient coating was used for the design of two multilayered coatings each consisting of alternating layers with compositions of $Al_{0,8}Cr_{0,2}N$ and $(Al_{0,7}Cr_{0,3})_{0,9}Si_{0,1}N$ in different layer thicknesses. Additionally, reference coatings of the sublayer materials were deposited as well. The mechanical properties of these four coatings were investigated by in-situ cantilever bending experiments and fracture surface analysis. The multilayered coatings displayed an increase in fracture stress of up to 20% and stable levels of fracture toughness after annealing at 1050°C. A maximum fracture stress of 4.7 GPa and fracture toughness values of 2.7 $MPam^{1/2}$ were measured.

In total it could be shown that the addition of Si to the AlCrN coating enhances its mechanical performance by change of fracture mode. However, the fracture stress did not preserve after heating at 1050°C. The multilayered coatings performed in as-deposited state between the two reference coatings, but exhibited the improved fracture stress after the heat treatment.

11:00am **B4-1-MoM-4 Influence of Deposition Pressure and Gas Mixture on the Microstructure, Phase Composition and Thermal Stability of Arc Evaporated TiSiN Coatings***, Yvonne Moritz (yvonne.moritz@unileoben.ac.at)* [1] *, C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* Ceratizit Austria GmbH, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

Owing to their advantageous properties including excellent hardness and high oxidation stability, arc evaporated TiSiN coatings are frequently used as protective hard coatings for various machining applications in the metal cutting industry. By varying the deposition conditions, microstructural changes and thus also changes of the mechanical or thermal properties can be obtained. Within this work, the influence of a varying N_2 deposition pressure and the addition of Ar to the deposition atmosphere on the microstructure and thermal stability of TiSiN coatings was studied in detail. Scanning electron microscopy and high-resolution scanning transmission electron microscopy investigations revealed a feather-like and fine-grained structure as well as the presence of an amorphous SiN_x phase for all TiSiN coatings. However, at higher N_2 deposition pressures also several larger grains appear. Further investigation of powdered TiSiN coatings by X-ray diffraction (XRD) revealed a significant decrease in lattice parameter for an increasing N_2 deposition pressure, while maintaining an identical chemical composition. These changes in lattice parameter can either be attributed to the formation of a TiSiN solid solution and/or to the formation of vacancies during the deposition process. In addition, the powdered TiSiN coatings were studied by *in-situ* XRD in vacuum up to 1200 °C in order to gain insight into the thermal stability of the coatings. Continuous monitoring of the lattice parameter over the whole temperature range by sequential Rietveld refinement revealed non-linear changes of the lattice parameter upon heating, resulting in a significantly larger lattice parameter for all powdered coatings after annealing. This change in lattice parameter becomes even more pronounced at higher N_2 deposition pressure. It can be assumed that this observation is an effect of Si diffusion out of the crystalline lattice during the annealing process and/or annihilation of vacancies. In order to differentiate between these two effects positron annihilation measurements were performed to evaluate if significantly different vacancy concentrations can be detected for the TiSiN samples deposited at varying N_2 pressure or in Ar/N_2 atmosphere. The presented combination of sophisticated characterization techniques contributed to gain a deeper insight into the microstructure and phase composition of TiSiN coatings synthesized with varying deposition conditions in the as-deposited state as well as at elevated temperatures.

11:20am **B4-1-MoM-5 Grain Boundary Segregation Alters the Fracture Mechanism of an AlCrN Thin Film***, Michael Meindlhumer (michael.meindlhumer@unileoben.ac.at), T. Ziegelwanger,* Montanuniversität Leoben, Austria*; J. Zalesak,* Austrian Academy of Sciences, Leoben, Austria*; M. Hans,* RWTH Aachen University, Germany*; L. Löfler, S. Spor, N. Jäger,* Montanuniversität Leoben, Austria*; A. Stark,* Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Geesthacht, Germany*; H. Hruby,* voestalpine eifeler Vacotec GmbH, Düsseldorf, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; J. Schneider,* RWTH Aachen University, Germany*; C. Mitterer, R. Daniel, J. Keckes,* Montanuniversität Leoben, Austria

Despite having superior hardness and indentation modulus, thin films deposited by physical vapour deposition often lack sufficient fracture strength and toughness, which is related to intercrystalline fracture occurring predominantly along columnar grain boundaries of low cohesive energy. In this study, an $Al_{0.9}Cr_{0.1}N$ thin film was deposited by cathodic arc evaporation and thoroughly investigated. In as-deposited state, a chemical composition modulation within the wurtzite AlCrN grains was detected by transmission electron microscopy and atom probe tomography, where the Al content depleted down to ~0.83, while the Cr-content nearly doubled up to ~0.17 without interrupting the crystallographic structure. These composition modulations exhibited a periodicity of ~35 nm. A heat treatment monitored by *in situ* high-energy high-temperature grazing incidence transmission X-ray diffraction was performed on the $Al_{0.9}Cr_{0.1}N$ film. The heat treatment caused dissolution and promoted the formation of globular cubic (c) Cr(Al)N and elongated c-CrN precipitates with sizes of ~5-30 nm at the position of the former Al-content minima within the grains and at the grain boundaries, respectively, resolved by transmission electron microscopy and atom probe tomography. Additionally, some precipitations of c-Cr were found, which were attributed to macrodefects originating from the arc evaporation process. The X-ray data obtained during the heat treatment partly illuminated the segregation and formation of precipitates along the interlayer interfaces. *In situ* micromechanical testing before and after the heat treatment revealed simultaneous enhancement of Young's modulus, fracture stress and fracture toughness, most prominent enhancing fracture stress from 3.4±0.4 GPa to 5.1±0.4 GPa. Together with the strengthening of the film's mechanical properties, the fracture morphology altered from (typical) intercrystalline to transcrystalline fracture, proving enhanced grain boundary cohesion. The experimental results represent a new and cost-effective way to increase mechanical properties and thus reliability of transition metal nitride thin films.

Coatings for Biomedical and Healthcare Applications
Room Pacific C - Session D1-1-MoM

Surface Coatings and Surface Modifications in Biological Environments I

Moderators: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, **Phaedra Silva-Bermudez**, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

10:00am **D1-1-MoM-1 Corrosion Evaluation of ZrO_2 Coatings Deposited on Biodegradable MgZnCa Alloy for Orthopedic Applications***, Benjamin Millan (bmillan@ciencias.unam.mx), S. Rodil,* UNAM, Mexico*; J. Victoria-Hernandez,* Helmholtz-Zentrum Geesthacht, Germany

The development of biodegradable of Mg-based devices for orthopedic applications has been limited due to its high corrosion rate in biological media, which is accompanied by hydrogen (H2) evolution. This could lead to alkalization of the media and H2 accumulation can cause osteolytic lesions. In a previous work, we reported that a ZrO2 coating deposited by RF magnetron sputtering on a MgZnCa alloy enhanced the corrosion resistance and reduced the H2 evolved. However, an optimization of the deposition parameters to enhance the protectiveness offered by the coating was not done. Therefore, we propose an experimental design that involves power, deposition time and oxygen flux fraction as independent variables. The effect of these variables on the corrosion performance of the coated samples was evaluated using electrochemical impedance spectroscopy (EIS) and H2 evolution assessment with gas chromatography. The charge transfer resistance R can be obtained from the impedance modulus at medium frequencies (0.99Hz). In Fig. 1d, R is summarized as function of the thickness including all the deposition conditions. The conditions A and C deposited at 400 W during 30 and 90 min improves substantially the R (refer to Table 1 for labels). According to H2 results, the corrosion process of the coated samples does not change significantly as the deposition power increases, Fig 2a. But, the higher the deposition time the lower the H2 evolved, Fig. 2b. Increasing the O2 flux fraction is detrimental for the corrosion resistance for the coated samples since the H2 evolved raises, Fig. 2c. Thus, the combined effect of deposition time and O2 flux fraction plays an important role in the amount of H2 evolved. However, the tendency observed in H2 evolution measurements in Fig. 2c does not corresponds to the R in Fig. 1d. We think that H2 evolution measurement with gas chromatography can determine more accurately the short-term corrosion resistance of the coated/uncoated samples since electrochemical techniques have some limitations for corrosion rate assessment of Mg alloys. In conclusion, the effect of the deposition parameters of a ZrO2 coating on the corrosion resistance of MgZnCa alloy was studied. The higher R corresponds to the B43, B49, C43 and C49 samples. The results form H2 evolution measurements indicate that the deposition time and O2 flux fraction are determinant parameters. The O2% flux fraction may induce different growth rates which can contribute to change the coating compactness. This is visible in Fig. 2c, where the ZrO2 coating deposited at 20% of O2 flux fraction shows a reduction of 44 % in the amount of H2 evolved.

[1] **Graduate Student Award Finalist**

10:20am **D1-1-MoM-2 Novel Duplex Treatments Prepared by HiPIMS and HVOF/Solgel on Biodegradable Magnesium Alloy for Biomedical Applications**,
Adrián Claver (adrian.claver@unavarra.es), Universidad Pública de Navarra (UPNA), Spain*; I. Fernandez, J. Santiago,* Nano4Energy SL, Spain*; I. Quintana,* Fundación Tekniker, Spain*; L. Mendizabal,* Fundación Tekniker , Spain*; J. García,* Universidad Pública de Navarra (UPNA), Spain

Magnesium-based biomaterials have become a great candidate to be used in biomedical implants due to their great biocompatibility, biodegradability, and their mechanical properties similar to those of bones. However, Mg-based alloys corrode rapidly in aggressive environments such as human bodily fluids, losing their mechanical properties because of the uncontrolled corrosion and with the risk of infection in the body. In this study, duplex treatments consisting in TaN or TiN doped with Cu and Ag coatings deposited via high power impulse magnetron sputtering HiPIMS with positive pulses followed by a hydroxyapatite (HA) deposited via High Velocity Oxygen Fuel (HVOF) or Solgel top layer, were applied on biodegradable ZK60 magnesium alloy in order to improve the corrosion resistance, antibacterial properties and osteointegration properties of the substrate. Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) were used to characterize the coatings. Scratch test and nanoindentation were performed to study the adhesion and hardness of the coatings, while contact angle measurements were carried out to compare the wettability of the surface. The samples were immersed in SBF to study the corrosion resistance, mass change and hydrogen evolution. Electrochemical tests were performed to estimate the corrosion behaviour of the samples. Furthermore, antibacterial tests were carried out. The treated surfaces showed better hydrophilicity than the uncoated samples, which improves the ability of cell attachment. The results of in-vitro corrosion tests showed that the duplex treatments improved the corrosion resistance of the uncoated magnesium alloy samples, while antibacterial tests showed an improvement of antibacterial properties of the treated samples. Duplex treatments exhibit suitable properties including high corrosion resistance, osseointegration capability, antibacterial properties, and biocompatibility, so that they can be considered as a promising option to be used in biodegradable magnesium implants.

10:40am **D1-1-MoM-3 Surface Properties Control Immune Response to Implanted Biomaterials**,
Rene Olivares-Navarrete (ronavarrete@vcu.edu), Virginia Commonwealth University, USA **INVITED**

Implanting a material into the body generates an immune response, both from the surgical procedure and in response to the material surface. Following this initial insult, wound healing begins with the onset of hemostasis. Due to the range of physical and chemical properties of implanted biomaterials, the initial interactions between biological tissues and biomaterials are not fully understood. Following homeostasis, the inflammatory phase, predominated first by neutrophils and then by macrophages, begins. Furthermore, we have recently explored the affect of Ti surface characteristics in neutrophil behavior. Neutrophils are the most abundant immune cell in blood and arrive in scores to the injury site within minutes following trauma or biomaterial implantation. Neutrophils are known for their antimicrobial activity via phagocytosis, degranulation, enzymatic release, and the production of large DNA-based fiber networks called neutrophil extracellular traps (NETs). However, they are understudied in the context of biomaterials. New studies from our lab have demonstrated their key role during the inflammatory phase of biomaterial integration. Macrophages can be activated by biomaterials to release factors that alter the peri-implant microenvironment, directing the activation and recruitment of additional immune cells and/or progenitor cells. Macrophages exist along a broad spectrum with two opposite phenotypes. The pro-inflammatory (M1) phenotype is characterized by the release of factors such as IL1β, IL6, and TNFα that promote inflammation and secretion of chemokines (Ccl2, Ccl4, Ccl7) that recruit additional immune cells such as neutrophils and T cells. On the other end of the spectrum are the alternatively activated macrophages (M2 phenotype), which release immunomodulatory factors to reduce and resolve the inflammatory state and recruit progenitor cells for regenerative process. Biomaterial surface properties can be tailored to improve the healing response following implant placement. In this presentation, I will discuss how material surface properties can be tailored to control neutrophil and macrophage activation following biomaterial implantation and enhance subsequent recruitment of other immune and stem cells to the implant site to aid healing.

11:20am **D1-1-MoM-5 Metal Oxide Thin Films as Osteoinductive Coatings**,
Phaedra Silva-Bermudez (phaedrasilva@yahoo.com), *M. Fernández-Lizárraga, D. Morquecho-Marín,* Unidad de Ingeniería de Tejidos, Terapia Celular y Medicina Regenerativa, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico*; B. Millán-Ramos ,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; J. García-López ,* Unidad de Ingeniería de Tejidos, Terapia Celular y Medicina Regenerativa, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico*; S. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Biomaterials that exert an appropriate biological response and simultaneously meet biomechanical requirements are essential for orthopedic and dental implants. Mechanical properties of materials are mainly determined by the bulk material while the biological response is mainly directed by the surface properties. Thus, biocompatible coatings with functional properties, such as osteoinduction and osteoconduction, are interesting options to tailor the surface of mechanically- and degradation-wise appropriate bulk materials, to develop novel biomaterials for orthopedic and dental implants. ZrO_2, Nb_2O_5 and Ta_2O_5 are of great interest as coatings for orthopedic and dental implants, since they might promote adequate oseointegration, in a similar way as TiO_2.

Nanocrystalline TiO_2 andZrO_2, and amorphous Ta_2O_5 and NO_2O_5 thin films were deposited on Si(100) substrates, from pure metallic targets by magnetron sputtering, under reactive Ar/O_2 atmosphere, and using RF-power. The properties of the coatings were characterized by Optical Profilometry, Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy and Water Contact Angle. To characterize the biological response, human mesenchymal stem cells isolated from bone marrow (BM-MSC) were plated and cultured on uncoated and oxide-coated substrates; TiO_2-coated substrates were used as positive controls (osteoinductive and appropriate oseointegration). Cells were cultured at 37°C, changing the culture media every other day. Cell viability and metabolic activity was assessed at different days of culture by the Calcein-AM/Ethidium homodimer fluorescent kit and the Alamar Blue assay. At 7 days of culture, cells were fixed, dehydrated and evaluated by SEM. Potential cell differentiation towards the osteoblastic phenotype was qualitatively assessed by immunofluorescence assays against characteristic markers of the osteoblastic phenotype such as osteopontin, osteocalcin and Runx2, and quantitatively assessed by immuno ELISA assay against Osteocalcin and osteopontin, and colorimetric assays to evaluate phosphatase alkaline specific activity. All metal oxide coatings were biocompatible; however, results suggested that number of cells adhered on the substrate and cell differentiation was dependent on the coatings.

Acknowledgements to financial funding from CONACYT CB-2016-1-288101 and FOINS-FC-1740 Grants, CONACyT postgraduate scholarship for M. F-L and D. M-M

11:40am **D1-1-MoM-6 Synergetic Effect of Porous Ta_2O_5 Surface With Zn/ZnO Core-Shell Nanoparticles on Antimicrobial Activity and Corrosion Resistance**,
Luísa Fialho (luisafialho@fisica.uminho.pt), *C. Rebelo,* University of Minho, Portugal*; C. Alves,* Instituto Pedro Nunes, Coimbra, Portugal*; J. Castro,* University of Coimbra, Portugal*; P. Sampaio,* University of Minho, Portugal*; S. Carvalho,* University of Coimbra, Portugal

As an alternative to the conventional Ti dental implant surfaces, Ta surface biofunctionalization was investigated using different surface treatments to endow it with the microbicidal ability and enhance corrosion resistance. To achieve this innovative design, the adopted strategy was accomplished in two main steps: i) development of a bioactive surface based on the synergetic effect of anodic Ta_2O_5 with multilevel porosity (nano to micro) with osteoconductive elements incorporated; ii) development of an antimicrobial delivery system by deposition, by magnetron sputtering, of zinc/zinc oxide (Zn/ZnO) nanoparticles deposited onto the anodic Ta_2O_5 structured surface with or without an additional thin carbon layer.

First, a micro/nano-porous calcium phosphate-enriched Ta_2O_5 layer was developed by plasma electrolytic oxidation (PEO, also known as micro-arc oxidation - MAO) mimicking the bone morphology and chemical composition. Secondly, Zn/ZnO nanoparticles were deposited onto the porous Ta_2O_5 surface by DC magnetron sputtering to promote antimicrobial activity. In addition, the Zn/ZnO nanoparticles were encapsulated by a thin carbon layer to ensure the desired mechanical resistance and provide the antimicrobial agent-controlled release, and consequently improving corrosion resistance.

The antimicrobial effect and the molecular mechanisms involved in the antimicrobial action of Zn/ZnO nanoparticles were evaluated using *Candida* *albicans*, which is an opportunistic fungal pathogen present in the oral cavity that shows increased resistance to antifungal treatment agents. All the porous surfaces doped with Zn/ZnO nanoparticles showed a strong capability to inhibit cells growth and proliferation, revealing a significant antifungal activity. The surface with more Zn nanoparticles demonstrated a higher influence on cellular growth.

Morphological and chemical composition properties of the samples' surfaces were correlated with the corrosion behavior in artificial saliva. Right after the immersion, theporous Ta_2O_5 layer slowed the corrosion rate compared with the untreated Ta surface. The deposition of the Zn/ZnO nanoparticles decreased the corrosion rate and increased the corrosion resistance, indicating an improvement in corrosion behavior throughout the immersion time (14 days). OCP results showed an improvement on these surfaces between the first 2 and 24 hours of immersion, stabilizing afterward, which is related to zinc ions release profile.

Attributing to the excellent *in vitro* performance, this work is progress on the strategy to develop a new generation of dental implants surfaces to prevent implant's infection.

New Horizons in Coatings and Thin Films
Room Town & Country B - Session F5-1-MoM

In-Silico Design of Novel Materials by Quantum Mechanics and Classical Methods I

Moderators: David Holec, Montanuniversität Leoben, Austria, **Ivan G. Petrov**, University of Illinois at Urbana-Champaign, USA

10:00am **F5-1-MoM-1 Competition between Plasticity and Brittleness in Refractory Ceramics**, ***Davide Sangiovanni (davide.sangiovanni@liu.se)***, *F. Tasnadi, I. Abrikosov,* Linköping University, Sweden **INVITED**

Understanding the competition between brittleness and plasticity in refractory ceramics is of fundamental importance for screening and design of hard materials with enhanced resistance to fracture from room to elevated temperature.

Ab initio and classical molecular dynamics (AIMD & CMD) simulations are used to investigate fracture mechanisms in defect-free, as well as notched B1 $Ti_{1-x}Al_xN$ ($0 \le x \le 0.75$) supercells subject to tensile and shear deformation as a function of temperature. The interatomic potential employed in CMD – thoroughly validated for several structural, mechanical, and thermodynamic properties of Ti-Al-N systems – accurately reproduces the results of AIMD simulations obtained for *small* (1100 atoms) supercells. Hence, the results of relatively large ($\approx 10^5$ atoms) CMD simulations of notched crystals subject to mode-I tension allow gaining a comprehensive understanding of the competition between unstable crack growth vs plasticity mechanisms at crack tips in Ti-Al-N systems.

The talk also briefly introduces an AIMD database (24 investigated systems) of B1-structure ceramic properties calculated for $300 \le T \le 1200$K. The database includes both raw *ab initio* data – $\approx 10^9$ phase-space configurations with associated energies, forces, total stresses, and magnetic moments – as well as mechanical properties including elastic constants, tensile and shear strengths, moduli of tensile toughness, Schmid vs non-Schmid lattice-slip mechanisms, and strain-mediated lattice transformation pathways. Taking Ti-Al-N systems as representative case, it is illustrated how indicators (determined from the *ideal* properties of single-crystal ceramics) can reliably predict statistical trends in mechanical performance evaluated for systems that contain native structural flaws.

Sangiovanni, Inherent toughness and fracture mechanisms of refractory transition-metal nitrides via density-functional molecular dynamics, Acta Materialia (2018).

Sangiovanni et al, Strength, transformation toughening, and fracture dynamics of B1 Ti-Al-N alloys, Physical Review Materials (2020).

Mei et al, Adaptive hard and tough mechanical response in single-crystal B1 VNx ceramics via control ofanion vacancies, Acta Materialia (2020).

Almyras et al, Semi-Empirical Force-Field Model for the Ti-Al-N System, Materials (2019).

Sangiovanni et al, Enhancing plasticityin high-entropy refractory ceramics via tailoring valence electron concentration, Materials &Design (2021).

Sangiovanni et al, Temperature-dependent elastic properties of binary and multicomponent high-entropyrefractory carbides, Materials & Design (2021).

10:40am **F5-1-MoM-3 Intriguing Deformation Mechanisms in Nanolayered Ceramics**, ***Nikola Koutná (nikola.koutna@tuwien.ac.at)***, TU Wien, Austria; *L. Löfler,* RWTH Aachen University, Germany; *D. Holec,* Montanuniversitat Leoben, Austria; *Z. Chen, Z. Zhang,* Austrian Academy of Sciences, Austria; *L. Hultman,* Linkoping University, Sweden; *P. Mayrhofer,* TU Wien, Austria; *D. Sangiovanni,* Linkoping University, Sweden

Nanolayered ceramic materials exhibit fascinating properties and can easily overshadow their individual layer components. An excellent example are the superhardening and supertoughening effects experimentally shown for series of nitride superlattices, such as cubic-based TiN/VN, TiN/WN, or TiN/CrN films. Advancing applicability of nanolayered ceramics in extreme conditions—including high mechanical loads—calls for atomic-level understanding of their response to stress. In this talk, we employ multi-method/multi-(length)scale approach that combines density-functional ab initio molecular dynamics, classical molecular dynamics, and experiments to identify elementary mechanisms responsible for tensile strength, plastic deformation, and fracture in transition metal nitride superlattices. The AlN/TiN system—a paradigm protective coating for industrial machining and engine components—represents our model platform. The predicted bilayer-period-dependent trends closely relate to different strain-mediated phase transformations initiating in AlN layers. In particular, the B1-to-B3 transformation is clearly confirmed also by transmission electron microscopy analyses of AlN/TiN superlattice films. The key message of our study is that a simultaneous increase in hardness and toughness can be achieved if the superlattice layer thickness is such that slip across the SL interfaces is impeded at initial stages of deformation, while lattice transformations within AlN layers are gradual and/or local, rather than full polymorph transitions. The AlN/TiN system is well-established and widely studied, however, other TiN-based superlattices, e.g. TaN/TiN, offer even better basis for plasticity enhancement: not only via phase transformations but also via vacancy and valence electron concentration engineering. Different deformation mechanisms arising in these superlattices will be discussed, especially in contrast to AlN/TiN.

11:00am **F5-1-MoM-4 In Silico Testing of AlN/TiN Superlattices Using Molecular Dynamics**, ***Lukas Löfler (loefler@mch.rwth-aachen.de)***, Montanuniversität Leoben, Austria; *N. Koutna,* TU Wien, Institute of Materials Science and Technology, Austria; *Z. Chen,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; *G. Nayak,* Montanuniversität Leoben, Austria; *O. Renk,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; *L. Hultman,* Linköping University, Sweden; *Z. Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; *D. Sangiovanni,* Linköping University, Sweden; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria; *D. Holec,* Montanuniversität Leoben, Austria

The mechanical strength and fracture toughness of thin films can be tuned by microstructure. Superlattices, for example, have shown an increase in both hardness and fracture toughness at small layer thicknesses for a variety of materials. The introduced interfaces in these systems govern the mechanical response of the coating. However, their key role during mechanical loading is not yet understood. In this work, classical molecular dynamics simulations were performed to study the behavior of rocksalt cubic-structured AlN(001)/TiN(001) superlattices under mechanical loading in the form of uniaxial tension and indentation.

The tensile loading simulations aimed at revealing mechanisms behind plasticity and crack growth. Cells with layer thicknesses between 1.25 and 10 nm were put under tensile loading in different crystallographic directions. Depending on the load direction different mechanisms for plastic deformation are activated resulting in anisotropic behavior. Tensile loading perpendicular to the (001)-interface shows only minor plasticity accompanied by the nucleation of only a few dislocations and fracture parallel to the layers near the interface. Strain applied along the [100] and [110] directions on the other hand reveals a significant increase in toughness due to B1-to-B3 or B1-to-B4 phase transformations in AlN and later the development of shear bands. Under these load scenarios, networks of dislocations form that can, for small layer thicknesses, span over the interfaces. The findings were supported by ab initio molecular dynamics and nanoindentation and transmission electron microscopy experiments. From the joint results, we could conclude that the layer thickness of superlattices can impede the formation of cracks.

The indentation simulations focused on the intermixing of the alternating layers in superlattices under the load of the indenter. We were able to reveal that with ongoing deformation, a single phase starts to form near the indenter, degrading the coherent interface. The findings were supported by nanoindentation and high-resolution transmission electron microscopy experiments.

These cutting-edge simulations provided novel insights into the deformation mechanisms and processes of thin bi-layer superlattices at the atomistic level, hence complementing information available through high-end sophisticated experiments.

11:20am **F5-1-MoM-5 Advancing Computational Methods for Heterogeneous Material Systems***, **Susan Sinnott (sinnott@matse.psu.edu)**,* Penn State University, USA **INVITED**

Heterogeneous systems are challenging to investigate with high fidelity at the atomic scale across length scales that are not accessible by first-principles methods. This presentation describes recent developments of classical reactive potentials to enable the modeling of phenomena such as metal catalyst absorption to graphene and carbide-derived carbon supports, the interactions of metal catalysts with water, and the growth of thin films on oxide substrates. The classical simulations that are used to investigate these phenomena are complementary to first-principles, quantum mechanical calculations and experimental measurements. The new insights gained from these investigations are key to enabling the design of new materials and their utilization in applications of technological importance.

12:00pm **F5-1-MoM-7 On the Interplay between Stacking and Stability of Transition-Metal Diborides***, **David Holec (david.holec@unileoben.ac.at)**, T. Leiner,* Montanuniversität Leoben, Austria*; N. Koutná, P. Mayrhofer,* TU Wien, Austria

Transition-metal diborides are a hard and brittle type of materials, which, among others, find their use as protective coatings, because

of their excellent heat conductivity, oxidation stability and wear resistance.

In this work, we apply first-principles calculations to investigate the interplay between the structural properties (stacking of metal planes, puckering of the boron planes), mechanical properties (elasticity) and stability. For the latter, we assessed chemical, mechanical and vibrational stability. The investigated diborides XB_2 included X=Cr, Hf, Mn, Mo, Nb, Re, Ta, Ti, V, Zr. We probed (among others) also the three stackings corresponding to the stable structures of our XB_2, namely the A-A-A-A stacking of, e.g. TiB_2, the A-B-A-B stacking of ReB_2 and the A-B-B-A stacking of WB_2.

We could reveal chemical trends (i.e. related to the position of X element in the periodic table of elements) on the stability and transformation barriers between different stackings.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-1-MoM

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces I

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, **Xavier Maeder**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, **Michael Tkadletz**, Montanuniversität Leoben, Austria

10:00am **H1-1-MoM-1 In Situ Observations and Measurements of Plastic Deformation, Phase Transformations and Fracture With 4D-STEM***, **Andrew Minor (aminor@berkeley.edu)**,* UC Berkeley and LBNL, USA **INVITED**

In situ TEM experiments are typically recorded either in real space or diffraction space. However, it would be ideal to have information from both for when transient events occur that cannot be repeated exactly (ie- defect generation or irreversible phase transformations). 4D-STEM can come close to providing simultaneous real-space imaging and diffraction analysis during *in situ* testing, making it possible to perform orientation and strain mapping and defect and phase identification via diffraction pattern analysis during in-situ deformation in a TEM. This talk will highlight recent *in situ* 4DSTEM nanomechanical deformation experiments that explore transient events where both information from diffraction space and real space are used. The diffraction patterns are used to identify different phases, defects, orientations and relative strain, while the images formed by using virtual apertures provide microstructural context for the analysis. Example experiments include defect generation and fracture in multi-principal element alloys and in situ heating and cooling of materials going through phase transformations.

10:40am **H1-1-MoM-3 Real-Time N_2-Mediated Growth Manipulation of Ultrathin Ag Layers***, **Gregory Abadias (gregory.abadias@univ-poitiers.fr)**,* Institut PPrime - CNRS - ENSMA - Université de Poitiers, France*; A. Jamnig, D. Babonneau, A. Michel, Y. Robin,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; A. Resta, A. Vlad, A. Coati,* Synchrotron SOLEIL, France*; K. Sarakinos,* University of Helsinki, Finland*; B. Krause,* Karlsruhe Institute of Technology (KIT), Germany

Noble-metal ultrathin films, with nominal thickness smaller than ~15 nm, are ubiquitous in a wide range of plasmonic devices and other optoelectronic applications. Silver (Ag) layers have recently gained interest as alternative transparent conductive electrode (TCE) candidates for flexible photovoltaics to currently used indium tin oxide, which is inherently brittle and suffers from high cost and poor sustainability. However, Ag films obtained by conventional physical vapor deposition have the natural tendency to self-assemble into 3D agglomerates on weakly interacting substrates, resulting in the formation of rough surface profiles. Therefore, strategies to produce fully continuous, ultrathin and ultrasmooth Ag layers without compromising their electrical conductivity are needed. Among them, the use of gaseous additives, such as N_2 or O_2, appears as an efficient route to shift the continuous film formation thickness to lower values [1,2]. However, to understand the full evolutionary growth regime requires the implementation of *in situ* and real-time diagnostics.

In the present work, the impact of N_2 addition on the morphological and structural evolutions of ultrathin Ag layers is investigated by coupling complementary *in situ* and real-time diagnostics. Lab-scale studies include wafer curvature, surface differential reflectance spectroscopy and electrical resistivity to determine the morphological transition thicknesses (percolation and continuous formation thickness) [3] as a function of N_2 partial pressure. These are augmented by real-time X-ray synchrotron studies (SIXS beamline at SOLEIL) in which the diffraction and reflectivity signals are simultaneously recorded, together with stress evolution. This enable us to explore the influence of N_2 on island shape, texture and stress development, as well as relaxation mechanisms during growth interruptions.

1. Yun, J. *et al.* An unexpected surfactant role of immiscible nitrogen in the structural development of silver nanoparticles: An experimental and numerical investigation. *Nanoscale***12,** 1749–1758 (2020).

2. Jamnig, A. *et al.* 3D-to-2D Morphology Manipulation of Sputter-Deposited Nanoscale Silver Films on Weakly Interacting Substrates via Selective Nitrogen Deployment for Multifunctional Metal Contacts. *ACS Appl. Nano Mater.***3,** 4728–4738 (2020)

3. Colin, J. *et al.* In situ and real-time nanoscale monitoring of ultra-thin metal film growth using optical and electrical diagnostic tools. *Nanomaterials***10,** 2225 (2020)

11:00am **H1-1-MoM-4 Phase Transformation and Solid-State Dewetting of Precious Metal High Entropy Alloy Thin Films on a Sapphire Substrate***, **Xavier Maeder (xavier.maeder@empa.ch)**, A. Sharma, P. Schweizer, J. Michler,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The transition of thin films into isolated particles at a temperature below the melting point of the bulk material is known as solid-state dewetting. So far, most of the literature is limited to dewetting studies on pure metal and binary alloys thin films. The experimental data on dewetting of compositionally complex alloys is rather missing.This work studied the solid-state dewetting behavior of precious metal high entropy alloy thin film deposited on a (0001) single-crystalline sapphire substrate and annealed in a range of temperatures. The combination of dedicated imaging, composition mapping, and diffraction techniques is used to investigate the interplay of grain growth, phase transformations, and dewetting kinetics with the process of in-situ annealing in the TEM.Both X-ray diffraction and the transmission electron microscopy observations revealed the FCC (single-phase) →FCC1+FCC2 (double-phase)→FCC3 (single-phase) phase transformation sequence during annealing. In addition, ex-situ annealing experiments have been performed in the same temperature range to assess the film's dewetting and phase transformation kinetics quantitatively.

11:20am **H1-1-MoM-5 Investigation of Silicon Samples by the Emerging Picosecond Ultrasonics***, F. Faese,* ***Julien Michelon (jmichelon@neta-tech.com)****, X. Tridon,* Neta, France

With the constantly increasing needs in microelectronics, photovoltaic cells, and other high-tech components in specialized industries, characterizing the growth of epitaxial (epi) silicon on silicon or evaluating the quality of Si/Si bonding becomes more and more critical. For instance, managing the epi Si layer paved the way to new generations of devices such as the Metal Oxide Semiconductor devices (MOS, CMOS and MOSFET) [1] as well as high performance photovoltaic cells [2]. Therefore, in order to address these increasing needs, existing characterization tools provide constantly improved performances, and new characterization tools regularly emerge to provide a technological breakthrough that offers more challenging features.

Some of the existing characterization tools that meet the needs are destructive, such as Scanning and Transmission Electron Microscopy, or semi-destructive such as Secondary Ion Mass Spectrometry. Only a few characterization tools can measure the thickness of epi Si on Si and evaluate the quality of Si/Si bonding after the fabrication process and non-destructively. Among these techniques is the emerging Picosecond Ultrasonics (PU) [3]. This communication will present the principle of operation of this technique and describe some of the potentialities regarding the characterization of Si-based samples. First, we will see how PU can measure the thickness of a layer of epi Si on a Si substrate and describe the related advantages of this technique. Second, we will focus on Si/Si bonding applications with an illustration of PU possibilities to evaluate the quality of the silicon direct bonding.

[1] Skibitzki, Oliver. "Material Science for high performance SiGe HBTs: Solid-Phase Epitaxy and III-V/SiGe hybrid approaches." (2013).

[2] Hamon, Gwenaëlle, et al. "Plasma-enhanced chemical vapor deposition epitaxy of Si on GaAs for tunnel junction applications in tandem solar cells." Journal of Photonics for Energy 7.2 (2017): 022504.

[3] Thomsen, C., et al. "Coherent phonon generation and detection by picosecond light pulses." Physical review letters 53.10 (1984): 989.

Topical Symposia
Room Town & Country A - Session TS5-MoM

Sustainable Surface Solutions, Materials,Processes and Applications

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Noora Manninen**, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

10:00am **TS5-MoM-1 Innovative Processes for High Performance Materials for Low Carbon Energy in a Circular Economy Approach***,* ***Frederic Schuster (frederic.schuster@cea.fr)****,* CEA, France **INVITED**

Innovative materials and coatings in particular are at the core of innovation process for energy transition. They are not the sole technological challenges but they are often the link that makes progress happen or not, sustainability possible or not, economically feasible or not, ecologically meaningful or not. Metallurgical coatings and thin films have been developped in the field of low carbon energy since a long time ago. This surface functionalization, more and more integrated from the beginning in the steps of design of efficient architectures having to work in environments sometimes harsh and often complex, is the result of the implementation of surface treatment processes sometimes quite old, sometimes revisited, sometimes much more emerging. In a Green Deal approach, sustainability and in particular durability, are the main drivers for the development of surface engineering in energy field. The coatings must often operate under combined stresses such as: mechanical and corrosion, oxidation and irradiation, corrosion and irradiation. In general, the design of a coating must be done on the basis of precise specifications and the choice of the method of elaboration must be made taking into account a certain number of scientific, technological, economical and environmental criteria. Material efficiency, especially when it comes to using for example critical metals as well as the recyclability of scarce resources can also in some cases become one of the criterion of choice. Hybridation of processes is also a strong driver for breakthrough innovation. Surface engineering has made many advances in the past two decades, making possible applications that were not in the past. This is particularly the case with developments for the nuclear energy sector. In the PVD field, the development of ionized PVD such Hipims technology is now very close to the production of protective coatings for EATF (Enhanced Accident Tolerant Fuels) but is also under development in the field of nuclear fuel reprocessing. This very generic technology is also developped in renewable sector, for example for hydrogen production through electrolysis. In the field of CVD, the great diversity of organometallic chemistry offers real opportunities for the development of DLI-MOCVD or Atomic Layer Deposition, and recent advances concerning the upscaling of technology will be presented as well as the great versatility of the process.As for other development of Materials Science and Engineering, surface engineering benefits greatly from digital technologies progresses, in particular Artificial Intelligence, that makes the optimization of complex processes faster.

10:40am **TS5-MoM-3 Pathways for Sustainable Surface Solutions***, J. Vetter, J. Becker, C. Scholz,* Oerlikon Balzers Coating Germany GmbH, Germany*; F. Rovere,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; A. Barth,* Oerlikon Metco AG, Switzerland*; M. Esselbach,* ***Noora Manninen (Noora.Manninen@oerlikon.com)****,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Surface solutions are enablers of an ecological transformation of production and consumption. The goal is to reach sustainability for instance by product enhancement, efficient materials management, waste reduction, pollution prevention, or energy saving in different applications fields.

Sustainable Surface Solutions are now mostly applied for wear and/or friction reduction, e.g. for tools and automotive components. There are also various deposition or treatment processes which enable different pathways for sustainable solutions for energy conversion and storage. Examples can be found in the field of energy conversion like wind power, fuel cells, electrolyzers, batteries, or supercapacitors. The applications include also thermal insulation, self-cleaning surfaces (e.g. photocatalytic effect, lotus effect), coatings on plastics, optical coatings, medical coatings, decorative coatings, antifouling coatings, corrosion protection coatings, sensoric and electronic coatings.

Also aspects of life cycle assessment "cradle to grave" are of interest for surface solutions beginning with the material selection and ending with the “recycling” (circular economy, cradle to cradle). This analysis has to be intensified besides the pure cost calculations.

The potential and typical dedicated applications of coating solutions based on Oerlikon coating technologies, e.g. for general engineering, emission reduction of cars, including EV and Hydrogen-ICE, and green manufacturing are presented.

11:00am **TS5-MoM-4 Selection of Laser Processing Parameters for Cleaning of Aluminum and FRP Sheets***,* ***Bartłomiej Przybyszewski (Bartlomiej.Przybyszewski.dokt@pw.edu.pl)****, R. Kozera, A. Boczkowska, D. Kuczyńska, H. Garbacz, J. Pura,* Warsaw University of Technology, Poland

This study presents the laser cleaning of grade aluminium alloy sheets as well as Glass Fibre Reinforced Plastics (GFRP) covered with standard paint systems as an alternative for commonly used mechano-chemical stripping methods. A SPI20W laser with wavelength of 1064 nm was applied to remove a variety of painting systems from 2024-T3 alloy sheets with a pure aluminium-clad layer or from composite materials. The paint removing effect from substrates at a laser speed of 500–4000 mm/s, distance of passes of 40-80 µm and different number of passes was studied. Based on detailed substrate examination the best speed for paint stripping was 1000 mm/s with beam distance 40 µm and number of passes strongly depending on the structure of the coating system. The results showed that interaction of laser beam does not cause any significant changes in microstructure or mechanical properties of aluminium alloy, pure aluminium clad or GFRP matrix.

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Special Interest Talks
Room Town & Country A - Session SIT1-MoSIT

Special Interest Session I
Moderator: Samir Aouadi, University of North Texas, USA

1:00pm **SIT1-MoSIT-1 From High Temperature Tribology to Ultrasensitive Biomolecular Detection: The Versatility of Transition Metal Dichalcogenide Thin Films***, Christopher Muratore (cmuratore1@udayton.edu),* Department of Chemical and Materials Engineering, University of Dayton, USA **INVITED**

You can look through the program for this and many other conferences and see talks on MoS_2 and other transition metal dichalcogenides (TMDs) throughout diverse symposia .The extraordinary properties of TMDs are highly anisotropic, so most members of this family of materials are actually like two remarkable materials in one. TMDs demonstrate extremely low shear strength in one direction, and are quite strong in the perpendicular direction. The same can be said for thermal and electron transport properties. These differences arise from types of chemical bonding within a TMD crystal, and also give rise to anisotriopic catalytic properties and chemical reactivity in general. If the thickness of a TMD material is reduced to a few molecular layers, it has completely different optical and electronic properties than its bulk counterpart, with changes in the nature of the bandgap (indirect to direct, or vice-versa) in addition to extreme mechanical flexibility allowing strains greater than 10%.The chemical reactivity and other properties of many TMDs are well-suited for many biological applications, especially biomolecular sensing. To complete the portfolio of desirable attributes of TMDs, some have great natural abundance, with a price close to that of dirt. Some potential applications for stacks of ultra-thin, or two-dimensional (2D) TMDs (less than 5 molecular layers thick) have captured the imagination of materials scientists as a means of creating crystals layer-by-layer with tunable properties and without constraint on lattice parameter matching. The primary barrier for realization of custom crystals is the challenge of processing multilayer materials without introducing property-attenuating defects. Most frequently, multilayer van der Walls stacks entail materials removal and transfer methods from the growth substrate, which is challenging to scale. We have developed a novel approach to obtain van der Waals materials with over 100 individual, chemically distinct layers. To accomplish this, continuous sub-nanometer metal layers are sputtered on oxide substrates as a precursor phase for subsequent reaction in chalcogen gases for conversion to metal selenides or sulfides. To conquer physical limitations inhibiting continuous thin metal layers, the power to the sputtering source was optimized to deposit such thin layers without island formation. Selection of processing temperature allows orientation of reacted van der Waals layers horizontally or vertically. With this novel approach, rapid realization of the new physics promised for over a decade by development of monolayer TMD materials and their heterostructure superlattices is now underway.

Coatings for Use at High Temperatures
Room Town & Country D - Session A1-2-MoA

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling II

Moderators: Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK, **Gustavo Garcia Martin**, REP Energy Solutions, Spain

3:00pm **A1-2-MoA-5 Influence of Dispersed Nano-Y_2O_3 Particles in NiAlY and NiCrAlY MMC Coatings on Microstructure, Oxidation and Wear**, ***Christoph Grimme (christoph.grimme@dechema.de)***, *R. Kupec, F. Schulze, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

State of the art MCrAlY coatings are known to protect structural materials against oxidation and corrosion and are part of TBC systems. Due to their mechanical properties at high temperature, they are commonly applied in the hottest sections of turbine engines and other high temperature environments. High costs for the thermal spraying process of MCrAlY coatings drive forwards cost saving alternatives such as galvanic co-deposition of particles. Co-deposition of particles is influenced by numerous factors, such as particle size, kinetic effects, current density, pH related zeta potential or chemical stability of the particles [1]. In this study, nano-Y_2O_3 particles are co–deposited galvanically alongside with nickel and subsequently pack chromized and aluminized. Y_2O_3 is known to improve both oxide scale formation and oxide scale adherence. Another promising effect of Yttria is the reaction with low melting V_2O_5 to form high melting YVO_4, which reduces the aggressiveness and of corrosive salt deposits and thereby reduces corrosion attack [2].

Subsequent chromium and/or aluminum enrichment(s) after co-deposition using a pack cementation process is shown to lead to microstructural refinement compared to coatings without particles and are able to decrease wear up to high temperature. Additional microhardness measurements revealed an increase of approx. 100 HV1 for MMC NiAlY coatings compared to coatings without dispersed nano–Y_2O_3 particles. Depending on the activity of the pack cementation method to be used, differences in the distribution of dispersed particles are observed and discussed. Besides wear, the oxidation resistance as well as corrosion resistance of the manufactured coatings against molten V_2O_5/Na_2SO_4 salt mixtures at 700 °C in 0.1 SO_2/air gas are tested and compared against bare IN617 alloy.

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[2]N. S. Bornstein,*Vanadium Corrosion Studies***1993**.

3:20pm **A1-2-MoA-6 Reactive Magnetron Sputtering of Al-O-F for High-Temperature Oxidation Protection of γ-TiAl via the Halogen Effect**, ***Stephen Brown (stephen.brown@polymtl.ca)***, *F. Bergeron,* Polytechnique Montréal, Canada*; M. Cavarroc,* SAFRAN Tech, France*; S. Knittel,* SAFRAN Aircraft Engines, France*; L. Martinu, J. Klemberg-Sapieha,* Polytechnique Montréal, Canada

The implementation of γ-based TiAl alloys in aircraft engines is motivated by their low weight and high specific strength at high temperatures compared to conventional nickel alloys. Their mechanical properties, such as yield strength and elastic modulus, match those of Ni-based alloys already employed in aircrafts engines, while their density is significantly lower than current solutions, allowing for the manufacture of lighter turbines and increased thrust-to-weight ratios. Their use, however, is restricted to low-pressure turbines due to the growth of a mixed Al_2O_3/TiO_2 oxide scale at temperatures greater than 750°C. While the dense Al_2O_3 is protective against further oxidation, the porous TiO_2 allows oxygen diffusion to the substrate, voiding the alumina's protective properties.

Of great interest for the protection of TiAl is a surface treatment based on the halogen effect, where a halogen, such as chlorine or fluorine, is used to promote the growth of a protective alumina scale. Aluminum halides are formed at the surface of TiAl and are transported through the oxide scale, where oxygen partial pressure is high enough to lead to the oxidation of these halides, promoting the formation of a protective Al_2O_3 scale.

This work demonstrates the possibility of exploiting the halogen effect through the deposition of Al-O-F films on γ-based Ti-Al48-Cr2-Nb2 substrates via reactive magnetron sputtering. The plasma chemistry of Al sputtered in an Ar, O_2, and CF_4 atmosphere was first measured by mass spectroscopy, and coated samples were deposited under a range of sputtering conditions. Coating microstructure was characterized by Scanning Electron Microscopy (SEM) coupled to Energy Dispersive X-Ray Spectroscopy (EDS), while Rutherford Backscattering Spectrometry (RBS) was used to determine coating composition. A subset of deposited coatings was oxidized at temperatures up to 875°C. Analysis by EDX and X-ray Photoelectron Spectroscopy (XPS) confirmed the transformation from Al-O-F to Al_2O_3 after oxidation, and the coated samples showed mass gains up to 10 times lower than the uncoated TiAl.

3:40pm **A1-2-MoA-7 Development of a New Coating Against High-Temperature Erosion-Corrosion in Fluidized Bed Biomass Boiler Condition**, ***Suzue Yoneda (s-yoneda@eng.hokudai.ac.jp)***, *S. Tanaka,* Hokkaido University, Japan*; Y. Miyakoshi,* Hokkaido Research Organization, Japan*; T. Kogin,* Dai-ichi High Frequency Co., Ltd., Japan*; E. Ishikawa,* EBARA Environmental Plant Co., Ltd., Japan*; M. Noguchi,* EBARA Corporation, Japan*; S. Hayashi,* Hokkaido University, Japan **INVITED**

High-temperature Erosion-Corrosion (E-C) is one of the critical issues for the heat exchanger used in a fluidized bed biomass boiler plant. E-C occurs by not only erosion due to impact of sand particles but also high-temperature corrosion in chlorine containing atmospheres. Current coatings widely used for boiler tubes in fluidized boiler plants are Ni-based protective coating (Japan Industrial Standard: JIS SFNi4 and/or SFNi5). However, E-C resistance of those coatings is still not sufficient. Thus, development of coating which have good E-C resistance is strongly required. SFNi4 contains a lot of alloying elements (Cr, B, Si, C, Fe, Co, Mo and Cu). In this study, effect of Mo, Si, Cr and Fe on E-C resistance was evaluated by using model alloys in order to optimize the Fe content. Mo and Si were found to be detrimental for E-C and Fe addition significantly improve E-C resistance. After E-C, oxide scale consisted of thinner NiO on the alloy without Fe, but thicker Fe-rich oxide on the alloy with Fe. Erosion resistance of Fe-rich oxide could be higher than that of NiO, resulting in higher E-C resistance in the alloy with Fe. Based on the results obtained from E-C test, the new coating which is higher Fe content and lower Mo and Si content was proposed and it was confirmed that E-C resistance of this coating was higher than previous coating in the actual plant.

4:20pm **A1-2-MoA-9 Introduction of Methodologies from Artificial Intelligence Into Slurry Coating Development**, ***Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de)***, *M. Juez Lorenzo, W. Becker,* Fraunhofer Institute for Chemical Technology ICT, Germany

Aluminum slurry coatings are a high-impact and economic technique to protect steels against corrosion at high temperatures and in aggressive media. They are easy to apply using different methods of deposition such as spraying or brushing with a subsequent heat treatment to form the diffusion coating. For optimization as well as for customization to particular applications with different substrate steels and media further development is needed. The use of methodologies and algorithms from artificial intelligence (AI) can significantly accelerate the development and reduce the costs by minimizing the experimental effort. For an AI supported approach the entire system has to be considered and digitalized integrating all components, all process parameters at all processing steps including the models for the different mechanisms such as diffusion.

To digitalize the aluminum slurry coating the entire coating system and its manufacturing process was fully parametrized considering every single parameter having influence. In doing so the coating process was divided into three sections: slurry formulation, slurry deposition and the heat treatment to form the aluminide diffusion layer including the substrate steel data. The parameters comprise the particle size and slurry components, spray characteristics such as distance, particle velocity or angle and heat treatment temperature, time and atmosphere.

The parameters were formatted in computer readable formats: (i) numerical values (numbers x, y, z, …) when specific values can be assigned such as the heat treatment temperature in degree Celsius; (ii) groups of values (x to y), e.g. small, medium, large aluminum particles within a range of µm and (iii) categories with I/0 decision, where specific values or ranges of values are not applicable, e.g. slurry deposition by spraying (yes/no). Target values were defined for the parameters describing the targeted coating properties as well as assessment criteria for their achievement. Algorithms from the field of Design of Experiments were chosen for the first approach elaborating a parameter matrix for a slurry coating system. A set of experimental values from former projects was filled in to train the software for calculating the impact of process parameter variation on the coating properties.

4:40pm **A1-2-MoA-10 Slurry Coatings for Heat Exchangers of Particle Receivers of Solar Towers***, Michael Kerbstadt (michael.kerbstadt@dechema.de), A. Ulrich, M. Galetz,* DECHEMA-Forschungsinstitut, Germany

Diffusion coatings are widely used in high temperature applications to enhance oxidation and corrosion resistance of metals and alloys. Metallic elements (commonly Al, Cr, or Si) are enriched at the surface to form protective oxide scales during exposures at high temperatures. Al, Cr and Si-based diffusion coatings are mostly accomplished by pack cementation, where the deposition occurs via a gas diffusion process. For the pack cementation process the substrates usually have to be fully embedded into a powder mixture, which is laborious and requires a lot of furnace furniture to be heated up. For Al an alternative slurry process is well established, where the slurry is sprayed on the metallic surfaces by air brush. This simple deposition leads to economic advantages compared to other diffusion coating techniques and also to the possibility to coat large technical parts, weldings or to do local repair works. The target application of this work focuses on a new generation of solar power plants, where bauxite particles are used as receiver and heat storage medium instead of the state of the art tubes with molten nitride salts. In this case the coating on the outside of the heat transfer tubes, which are in contact with the particles not only has to withstand oxidizing environments at high temperatures but also abrasion due to the impact of the heat carrying particles. For this application Cr- and Si-rich coatings are very interesting, e.g. because of the hard silicide phases, which are more oxidation resistant than the respective Cr-carbides at the target temperatures.

Due to the higher melting points and limited phase formation, the development of Si- or Cr-based diffusion coatings via the slurry process is more complicated, e.g. the use of Cr-Al pre-alloyed powder leads only to Al diffusion.

In this work novel slurry coatings are presented applied by a water-based slurry. The subsequent heat treatment is conducted in an inert Ar atmosphere at temperatures up to 1200° C. The application of such slurry coatings is demonstrated on Inconel 740 (Ni-base) and Sanicro 25 (austenitic stainless steel). Therefore, different slurry compositions and heat treatment parameters are tested. The coating thicknesses achieved are up to 10 µm on the Inconel 740 and up to 300 µm on the Sanicro 25. For phase determination and microstructural characterization X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) are used. Oxidation exposures in synthetic air at 900°C show the formation of a protective scale and indicate an improved oxidation behavior by the applied coatings of the two investigated substrates.

5:00pm **A1-2-MoA-11 Low Emissivity Thin Films Coatings to Reduce Thermal Emittance of SSA for Evacuated Solar Collectors***, Antonio Caldarelli (antonio.caldarelli@na.isasi.cnr.it), C. D'Alessandro, D. De Maio, D. De Luca, E. Gaudino, M. Musto, E. Di Gennaro,* University of Napoli "Federico II", Italy*; R. Russo,* National Research Council of Italy, Napoli Unit, Institute of Applied Sciences and Intelligent Systems, Italy

Solar energy is the ideal energy source to provide heat at medium temperatures with the aim of transitioning to clean, renewable energy sources. Evacuated flat plate solar collectors (EFPCs) are able to convert solar energy directly into heat with high efficiency. Thanks to the high vacuum insulation, the main mechanism of loss in EFPCs is represented only by the radiative losses from the selective solar absorber (SSA). Thermal emittance plays a more important role than solar absorbance for the efficiency of SSA used in EFPCs working at medium temperature [1].

Once the SSA has been optimized for a maximum efficiency [2,3], further improvement can be obtained by reducing the substrate emissivity. We therefore deposited by electron beam low emissive Cu or Ag thin film on an Aluminium bulk substrate to improve the coating performances by reducing its thermal emittance, keeping the economic advantages of using a substrate as cheap and light as Aluminium. The low emissive coating can be used to reduce the thermal emittance of both the selective coating side and the substrate side of SSA. The thermal emittance was measured as a function of temperature through a calorimetric approach [4]. The thermal stability of the coating and the use of thin films of Cr2O3 as a diffusion barrier were also investigated.

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Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B2-2-MoA

CVD Coatings and Technologies II

Moderator: Raphael Boichot, Grenoble-INP/CNRS, France

1:40pm **B2-2-MoA-1 Synthesis of Rare Earth Silicate Coatings by CVD***, **Arthur Derrien (derrien@lcts.u-bordeaux.fr)**, L. Lager, J. Roger, J. Danet, S. Jacques,* LCTS, CNRS, Univ. Bordeaux, France

Rare earth silicates (RESiO) are increasingly studied due to their optical and electrical properties. They are also chemically inert and have numerous crystalline structures allowing their properties to be adjusted depending on the required application. They are used in various fields such as lasers, sensors, microelectronic components or solid oxide fuel cells.

These applications require a good control of the process during the synthesis of these materials, sometime used as coatings. The methods conventionally used to produce these films, such as sol-gel or PVD, have disadvantages in terms of thickness control, homogeneity and conformity on parts presenting complex geometry. Thus, the production of these thin films by CVD can overcome these disadvantages to obtain coatings with controlled composition and desired crystalline phase, in order to have homogeneous and conformal thin films, by avoiding, for example, the shading phenomena linked to PVD processes oncomplex shaped parts.

Since the crystallized phases of these materials are formed at relatively high temperatures (>1000°C), the most suitable gaseous precursors for the deposition of RESiO are halogen-containing reagents, especially $SiCl_4$ and $RECl_3$, because of their thermal stability. While $SiCl_4$ is liquid at room temperature, rare earth chlorides are solid up to more than 700 °C, complicating their transport to the reaction zone and the control of their flow. The control of the composition, and therefore of the crystalline phase of the produced coating is difficult.

The case of yttrium silicates is studied here. After setting up an in-situ weighing system, the evaporation of YCl_3 could be studied over a pressure/temperature range matching with the CVD deposition conditions that were previously determined by a thermodynamic approach. In this way, the flow rate of chlorinated precursors could be controlled up to 1150 °C in order to lead to the formation of yttrium silicate coatings on alumina substrates. The obtained coatings were characterized using different techniques: Raman spectroscopy, X-ray diffraction, EDS and SEM.

2:00pm **B2-2-MoA-2 Doped Alumina Coatings***, Zhenyu Liu (zhenyu.liu@kennametal.com),* Latrobe, USA

In order to enhance the performance of the conventional alumina coating and meet the needs for high performance and high-speed cutting applications, the definite demands in the improvement of thermal resistance and wear resistance are necessary. Therefore, it is the technique need to develop novel CVD alternative alumina coatings with novel structures or coating architectures. By using doping elements, such as Ti, Zr and/or other group IV elements, the doped alumina with excellent wear resistance and tool life can be achieved.

The doping process will create not only novel grain crystalline structures but also alternative coating structures. We have developed different doping procedures including Ti, Zr, Hf-doping and the co-doping. The previous research showed that dopant such as Ti can modify the surface energy of formed oxide crystalline planes. One good support on this hypothesis and practice is that the Ti-doped CeO_2 particles showing round shape, in contrast to the un-doped CeO_2 having polyhedron crystal structures. the dopant atoms may distribute at single atom level in the oxide metal ion column and enrich at the grain boundary. According to the Goldschmidt's Rules on Thionic substitution, the ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than approximately 15%. (Free substitution can occur if ionic size difference less than 15%; Limited substitution can occur if ionic size difference is 15~30%; little or nonsubstitution can occur if ionic size difference is greater than 30%.) In the systematical doped alumina coatings, the ionic radius of Al^{3+} is ~0.675 Å, Ti^{4+} is ~0.745 Å; Zr^{4+} is ~0.80 Å and Hf^{4+} is ~0.79 Å. The ion size differences from the group IV B is less than 15%, then they should be substituted freely by one another.

At the same time, the dopant atoms can segregate and enrich at the grain boundary. The grain boundary engineering can provide enhanced grain interaction and dopant atoms can function as the pinning atoms or provide pinning effect for grain boundary, leading to enhancement of the thermomechanical properties. It is already accepted that the dopants will markedly strengthen the alpha-Al_2O_3 interface against mechanical deformation.

Keywords: CVD, Al_2O_3, thin films, nucleation, crystal growth

2:20pm **B2-2-MoA-3 Stress Control of AlN-based Multilayer Coatings with Amorphous Intermediate Layers**, *V. Tabouret, R. Reboud, A. Crisci,* ***Frederic Mercier (frederic.mercier@grenoble-inp.fr)***, SIMAP, Grenoble-INP, CNRS, France

Aluminium nitride (AlN) possesses attractive properties like piezoelectricity, high thermal conductivity, low thermal expansion coefficient, high temperature stability, chemical barrier capabilities and ability to develop stable alumina scales at high temperature. Stress control of AlN-based coatings is therefore of high importance for emergence of new applications.

We report in this presentation the possibility to tune the stress in AlN-based multilayers by introducing amorphous intermediate layers. AlN-based multilayer coatings are grown by metal-organic chemical vapor deposition (MOCVD) on 300 µm thick silicium (100) wafer at 900°C. Trimethylaluminium, ammonia and propane were used as Al, N and C precursors. Alternative injection of precursors enables the growth of polycrystalline/amorphous multilayers and the control of the stress in the coatings. In situ curvature, ellipsometry and reflectance measurements are performed simultaneously during growth.

Based on in-situ measurements and ex-situ precession electron diffraction techniques, we demonstrate that the growth of virtually stress free AlN is possible with the introduction of amorphous layers in the multilayer structure.

2:40pm **B2-2-MoA-4 Circumventing Thermodynamic Constraints – A Selective Kinetic Growth of Low Thermal Expansion Al_2TiO_5-coatings by Chemical Vapour Deposition**, ***Sebastian Öhman (sebastian.ohman@kemi.uu.se)***, Uppsala University, Angstrom Laboratory, Sweden

Most materials expand upon heating. Yet, a few are known to behave the opposite way around. Almost exclusively, these may be found among multicomponent transition metal oxides sharing a diverse range of properties. However, their potential applications have remained scarce due to the difficulties faced in their synthesis and their general metastable characters, which typically limits their thermal stabilities.

This talk will present a novel chemical vapour deposition method to prepare such multicomponent phases at low temperatures and with increased stabilities. Specifically, I will demonstrate how aluminium titanate (Al_2TiO_5), a renowned low-to-negative thermal expansion material with favourable heat-resistant properties, can be synthesized at much lower temperatures than predicted by thermodynamics. Examinations of the Al-Ti-O system led us to discover new types of structurally related intergrowth phases, having enlarged unit cells, leading to improved thermal stabilities of these materials. The cause and origin of these intergrowth phases will be discussed based on detailed Raman spectroscopic measurements and in-situ TEM analyses studying their crystallization behaviours.

Materials possessing a low-to-negative thermal expansion are an attractive candidate to improve the thermal resistance of multi-layered coating designs used in applications such as microelectronics, optical engineering, energy harvesting and wear resistance. Thus, this talk aims to not only present a method to fabricate materials for these specific purposes, but also to open the potential of fabricating new multicomponent oxide coatings within other material systems.

3:00pm **B2-2-MoA-5 Atomic Layer Deposition of BN Based on Polymer Derived Ceramics Route: Fabrication of Functional and Protective Coating**, ***Catherine Marichy (catherine.marichy@univ-lyon1.fr)***, *W. Hao, A. Hossain, C. Journet,* University Lyon, France **INVITED**

The scientific interest for hexagonal boron nitride (h-BN) material, especially as thin film and nano-/hetero-structures, is growing owing to its potential use in various domains such as microelectronic, spatial, lubricant, energy and environment. Atomic Layer Deposition (ALD) is a technique of choice for fabrication of such thin films and complex nanostructured material.(*1*, *2*) Despite some limitations of temperature and crystalline quality, ALD already demonstrates suited to fabricate BN layers that can successfully be integrated into electronic devices.(*3*) Based on polymer derived ceramics chemistry, we developed a two-step ALD process of BN that permits access to various BN thin films and complex nano-/hetero-structures. It consists of the growth layer by layer of a preceramic BN films, onto various substrates, at low temperature, and then to its densification into pure BN by annealing process.(*4*)

Herein, the potential of the ALD process based on PDCs route for BN thin films will be discussed. Indeed, BN thin films were successfully deposited in a controlled manner on various inorganic and organic substrates/templates. The application of the developed process for fabricating protective coating towards oxidation and functional quality crystalline BN nano/heterostructures will be presented.

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Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-2-MoA

Properties and Characterization of Hard Coatings and Surfaces II

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

1:40pm **B4-2-MoA-1 Microstructural Simulations on Thin Films**, ***Vinzenz Guski (Vinzenz.Guski@imwf.uni-stuttgart.de)***, *W. Verestek, S. Schmauder,* Universität Stuttgart, Germany **INVITED**

Due to their outstanding mechanical properties, hard coatings possess a wide range of applications as protective layers. However, an experimental determination of the properties of such thin coatings is not only difficult but also cost- and time intensive. In this regard, numerical methods, such as finite element method (FEM), have the ability to reduce the experimental effort, significantly. Usually, for characterisation of hard coatings indentation tests are performed to determine the hardness, the Young's modulus or the adhesive behaviour. With the aid of FE simulations, additional important effects such as residual stresses or the microstructure on the material properties can be investigated.

In the presented work FE simulations of indentation tests using a Vickers pyramid were carried out to investigate the mechanical behaviour of hard coatings in depth. During a sensitivity study, FE models with different coating microstructures, such as equiaxed or columnar grains with different grains size distributions, and coating thicknesses were established and analysed. Besides, the effect of residual stress on the mechanical behaviour are addressed. The performed simulations were validated by indentation test data and cross sections of the coatings. Finally, these simulation results deliver a property-microstructure-relation of the investigated hard coatings and can provide suggestions for optimization.

2:20pm **B4-2-MoA-3 Ab Initio Supported the Development of Tin/Mon Superlattice Thin Films With Improved Hardness and Toughness***, **Zecui Gao (zecui.gao@tuwien.ac.at)**, J. Buchinger, N. Koutná, T. Wojcik, R. Hahn, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Motivated by superior strength and toughness indicators predicted for $TiN/MoN_{0.5}$ superlattices by ab initio calculations, we synthesize a series of TiN/MoN_y superlattice (SL) thin films by DC reactive magnetron sputtering to extract the superlattice effect on hardness and fracture toughness. The SLs crystallise with a single-phase centred cubic (fcc, rock salt) structure. The MoN_y layers are stabilised in their fcc structure by the coherent growth with TiN layers and low N_2-partial pressure, ensuring a close to $MoN_{0.5}$ stoichiometry, favouring fcc. Both hardness and toughness, reveal a distinct dependence on the bilayer period L, featuring a hardness peak of 34.8 ± 1.6 GPa for L = 9.5 nm. The fracture toughness (K_{IQ}) shows a significant enhancement compared to TiN (K_{IQ} ~ 2.2 MPa√m) and Mo_2N (K_{IQ} ~ 2.7 MPa√m) coatings, peaking with ~ 4.1 ± 0.3 MPa√m also at L = 9.5 nm.

2:40pm **B4-2-MoA-4 Effect of Substrate Bias on the Residual Stress Depth Profile and the Mechanical Properties of Ti-Al-N Coatings Prepared by Cathodic Arc Deposition***, **Luis Varela (luis-bernardo.varela-jimenez@polymtl.ca)**, K. Tsoutas, A. Miletic, E. Bousser,* Polytechnique Montréal, Canada*; J. Mendez,* MDS Coating Technologies Corporation, Canada*; J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Ti-Al-N coatings were prepared by the Cathodic Arc Deposition (CAD) onto Inconel 718 substrates. The substrate bias voltage during deposition was varied, and we evaluated its effect on the residual stress (RS) distribution throughout the thickness of the coatings. Structural characterization and RS measurements were performed by classical X-ray Diffraction and synchrotron X-ray radiation measurements. Mechanical properties, namely the hardness and Young's modulus, were measured by depth-sensing indentation. The results indicate a higher compressive RS at the film surface (several GPa) that decays to a lower compressive stress value (hundreds of MPa) at the film/substrate interface. Hardness values significantly increased from 23 GPa to 31 GPa upon substrate bias increase, with a slight reduction of the Young's modulus. Similarly, the average compressive RS increased from 1.0 to 4.7 GPa for coatings deposited at bias voltages of 0V and -100V, respectively. As well, scanning electron microscopy morphological analysis of the cross-sections revealed a pronounced width reduction of the columns with the increase of the bias. The present findings provide a better insight into the impact of the substrate bias voltage on RS, film microstructure, and the mechanical properties of arc evaporated Ti-Al-N coatings. This allows one to select the most suitable coatings for specific mechanical solicitations in different industrial applications.

Coatings for Biomedical and Healthcare Applications
Room Pacific C - Session D1-2-MoA

Surface Coatings and Surface Modifications in Biological Environments II

Moderators: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, **Phaedra Silva-Bermudez**, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

1:40pm **D1-2-MoA-1 Microstructural and Electrochemical Characterization of 3D Printed Biomedical Implants (Virtual Presentation)***, **Mozart Neto (mozart_q_neto@rush.edu)**, R. Pourzal,* Rush University Medical Center, USA **INVITED**

Ti6Al4V is the most used alloy in orthopedic implants such as total hip, knee and shoulder replacements. Implants are conventionally made by cast or wrought alloys, but additively manufactured (AM) implants are increasingly used. Although Ti6Al4V is known for its great corrosion behavior, there are increasing reports of corrosion and fretting-corrosion related implant failures. Currently, it is unknown how alloy microstructure impacts the electrochemical behavior of Ti6Al4V, and its implication on in-vivo corrosion. Therefore, we tested six frequently occurring microstructure types occurring in Ti6Al4V implant components. Our hypothesis was that, despite identical chemical composition, differences in microstructural features can dictate the corrosion behavior of implant alloys. This study included three types of wrought alloys, one cast alloy, and two types of AM alloys: wrought alloys with A) fine equiaxed grains, B) coarse equiaxed grains and C) bimodal grain; D) lamellar dendritic (cast alloys); AM alloys with E) lath-type grains and F) needle-like grains. While A-E exhibited varying degrees of β phase within an α matrix, F exhibited a α' martensitic structure. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were performed within simulated joint fluid (30 g/L protein) at pH 7.6 and 37°C to determine the corrosion behavior. We observed differences in corrosion current (icorr), polarization resistance (Rp) and capacitance (Q), but not in the corrosion potential (Ecorr). The needle-like group had the inferior corrosion behavior attributed to the metastable nature α' and the presence of built defects (local crevice corrosion), followed by equiaxed coarse and lath-type groups attributed to the galvanic coupling between α and β phase, specifically when a difference in Ti and V content of >10%occurred between both phases. Therefore, the microstructure does influence the corrosion behavior of Ti6Al4V implants, however the distribution of alloying elements also played a role.

2:20pm **D1-2-MoA-3 Diamon-like Carbon Coatings with Precise and Localized Silver Doping for High-Performance Biomedical Applications***, **Abdul Wasy Zia (abdul.zia@northumbria.ac.uk)**,* Northumbria University, UK*; M. Panayiotidis,* The Cyprus Institute of Neurology & Genetics, Nicosia, Cyprus*; M. Birkett,* Northumbria University, UK

Diamond-like carbon (DLC) coatings are recognised due to superior mechanical, biomedical, and tribological performance. Therefore, these coatings are actively being used for artificial orthopaedic joints, stents, heart valves, etc applications. Silver is doped in DLC coatings to boost its biocompatibility for superior biological performance. The increasing amount of silver is inferred to deliver better biological performance. However, DLC coatings lose their unique mechanical and tribological characteristics, such as high hardness, low friction coefficient, and low wear rates due to silver-induced-ductility in the coatings. In this work, silver doped DLC coatings are made with magnetron sputtering technique and the deposition process is controlled to dope silver in the form of small isolated nanoparticles at defined depths. The coatings are characterised for microstructure, hardness and Young's modulus, friction and wear, and cytotoxic studies. The preliminary results suggest that the silver nanoparticles are ~17nm in diameter and uniformly distributed in a plane and embedded at control depths. It is observed that ~ 2at.% silver when doped in DLC with the controlled deposition process gives similar cytotoxicity levels as delivered by ~18at.% silver which was doped with conventional co-sputtering methods. Whereas, the baseline DLC has a hardness of ~20GPa which is reduced to ~17GPa and ~10GPa for 2at.% and 18at.% silver doped DLC coatings. The investigations suggest that a relatively small amount of silver will be required to boost biocompatibility without compromising mechanical properties if the coatings are made with the proposed process.

Acknowledgement:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No 885534.

2:40pm **D1-2-MoA-4 Corrosion Resistance and Biocompatibility Evaluation of TiZrNbTaMo High Entropy Alloy Coatings***, S. Hou,* Ming Chi University of Technology, China*; B. Lou,* Chang Gung University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been attracted lots of attentions due to their unique properties compared to conventional alloy coatings. In this study, an equimolar TiZrNbTaMo target connected to a high power impulse magnetron sputtering (HiPIMS) power and a pure Ti target connected to a radio frequency (RF) power were used to fabricate five TiZrNbTaMo (TZNTM) HEA thin films with different Ti contents on the surfaces of cp-Ti substrates.In this study, scanning electron microscope (SEM), electron probe X-ray microanalyzer (EPMA), transmission electron microscope (TEM) and X-ray diffractometer (XRD) were used to analyze the cross-sectional morphology, composition and crystal structure of each thin film. The corrosion resistance of TiZrNbTaMo HEA films was studied using a potentiostat in the Ringer solution. Furthermore, the in vitro biocompatibility of MG 63 human osteoblast-like cells on the HEA films were evaluated. This study found that the corrosion resistance and biocompatibility of TiZrNbTaMo high entropy alloy film were improved with increasing titanium contents in the thin films.

3:00pm **D1-2-MoA-5 Corrosion Risk Evaluation of Carbide-Derived Carbon (CDC) Surface Modification for Hip Implants**, ***Yani Sun (ysun98@uic.edu)***, University of Illinois at Chicago, USA; *K. Kinnerk,* City Colleges of Chicago, USA; *K. Cheng, M. Mathew,* UIC College of Medicine at Rockford, USA; *M. McNallan,* University of Illinois at Chicago, USA

Ti6Al4V is a commonly used alloy for biomedical applications as it has excellent corrosion properties, which are mainly attributed to the oxide layer on the surface. Nevertheless, the early failure of total hip replacements has happened on Ti6Al4V alloys due to its poor tribocorrosion behavior. Previously, we have proved that carbide-derived carbon (CDC) can provide superb protection to Ti6Al4V from tribocorrosive damages[1]. However, the basic corrosion behavior of CDC stills remains unknown. In this work, experiments were conducted to investigate CDC's corrosion behaviors in comparison with the substrate alloy (Ti6Al4V).

Two groups of experiments were designed to evaluate CDC's corrosion performances: (1) Ti6Al4V as the control group, and (2) the CDC. Each group was repeated three times (N=3) to confirm the reproducibility. For Group (1), Ti6Al4V discs (11 mm dia x 7 mm) were ground and polished to a mirror finish. In Group (2), CDC was fabricated by the electrolysis method[2]. Furthermore, a three-electrode corrosion chamber was employed, where the tested sample was used as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. With an aim at the application for hip implants, bovine calf serum (BCS) was selected as the electrolyte, with the temperature maintained at 37˚C. Finally, the electrochemical protocol for the Ti6Al4V was set as open-circuit potential 1 (OCP1) for system stabilization – potentiostatic (PS) for surface cleaning – OCP2 (stabilization) – electrochemical impedance spectroscopy (EIS) – Cyclic polarization. Same protocol without PS was followed for Group (2) as the CDC layer was coated on the surface. After the corrosion testing, JEOL JSM-IT500HR SEM with Oxford AZtec EDS and Bruker-Nano Contour GT-K Optical Profilometer were utilized to examine the sample surface.

The geometric sample area exposed to the solution is 0.1256 cm^2, which was used to calculate the current density and impedance for Ti6Al4V. However, instead of having a smooth surface like the polished Ti6Al4V, the prepared CDC has a rough and porous structure with a large surface area. Therefore, we estimated our CDC area exposed to the solution based on the Brunauer-Emmett-Teller (BET) surface area of Ti-CDC reported by Huang et al.[3]. Consequently, according to the potential dynamic and EIS results, the CDC shows higher corrosion resistance than Ti6Al4V. However, the actual surface area of our CDC products is still needed, which will be achieved in the upcoming studies.

5. Cheng, K *Surf. Coat. Technol.* **2020**
6. Sun, Y *Surf. Coat. Technol.* **2021**
7. Huang, P *Science.* **2015**

3:20pm **D1-2-MoA-6 Enhancing the Mechanical and Biomedical Properties of Super Hard β-Ti_3Au Intermetallic Thin Films by Doping with Known Antimicrobial and Interstitial Elements**, *C. Cherian Lukose ,* ***Martin Birkett (martin.birkett@northumbria.ac.uk)***, Northumbria University, UK; *M. Panagiotidis ,* The Cyprus Institute of Neurology & Genetics, Cyprus

Owing to their excellent mechanical hardness and biocompatibility, Ti_3Au intermetallic materials are being extensively researched as thin film coating systems to protect the surface of load bearing implants and thereby extending their lifetime within the human biological environment. However, bacterial biofilm formation around the newly implanted device and wear of implant devices in the load bearing joint are known to be the leading causes of implant failure. The mechanical and biomedical properties of β-Ti_3Au intermetallic thin films doped with low quantities of a known antimicrobial element like silver and known interstitial element like nitrogen is explored. Thin films of Ti_3Au intermetallic were deposited by magnetron sputtering onto glass and Ti_6Al_4V substrates at elevated substrate temperature to promote development of the super hard β phase. Silver doping was introduced in one set of samples using a titanium-silver mosaic target, whereas, reactive nitrogen gas was introduced into the argon environment in a separate set. Elemental analysis using Energy dispersive X-ray spectroscopy confirms that the required 3:1 ratio of Ti and Au is achieved and the doping concentration of ternary element is below 5 at%. X-ray diffraction of the samples explores the development of β phase of Ti_3Au with addition of ternary element and is corelated to microstructure images captured using electron microscopy across sample surface and cross section. Surface features were also probed by Atomic force microscopy to account for change in surface roughness. Mechanical hardness and elastic modulus of the samples were measured by nanoindentation technique using a Berkovich tip in a displacement control mode. Biocompatibility of the films were evaluated by performing cytotoxicity test on L929 mouse fibroblast cells and measured by Alamar blue assay while concentration of leached ions from thin films were analysed using Inductively coupled plasma optical emission mass spectroscopy technique. Antimicrobial performance was tested using *E. coli* and *S. aureus* and by following the reduction in colony formation. Mechanical hardness better than 12 GPa and a low elastic modulus value of 148 GPa, combined with cell viability better than 95% encourages use of β-Ti_3Au as coating material. Nitrogen acts like a interstitial defect raising the energy of the barrier to dislocation movement thereby enhancing the mechanical hardness. Leached ion concentrations lower than 1 ppm sustains the non-cytotoxic nature, whereas, increased release of silver ions with addition of silver in the thin film matrix lends additional antimicrobial functionality to the material system.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F5-2-MoA

In-Silico Design of Novel Materials by Quantum Mechanics and Classical Methods II

Moderators: David Holec, Montanuniversität Leoben, Austria, **Davide G. Sangiovanni**, Linköping University, Sweden

3:40pm **F5-2-MoA-7 Theoretical Investigation of Sluggish Diffusion in Nitride Films of High-Entropy Alloys**, ***Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at)***, Montanuniversität Leoben, Austria; *A. Kretschmer, P. Mayrhofer,* TU Wien, Austria; *D. Holec,* Montanuniversität Leoben, Austria

The concept of alloying was revolutionized in multi-component or high-entropy alloys (HEA), where five or more elements are distributed randomly on a crystalline lattice in equiatomic or near-equiatomic composition. Thereby, no element acts as a principal component and four core effects have been postulated to stem from this configuration: high configurational entropy, severe lattice distortion, sluggish diffusion, and cocktail effects. Since we still lack a proper quantification of the sluggish diffusion, this work focuses on this topic applied to the case of high-entropy nitrides (HENs). These ceramic materials possess high hardness and good thermal stability and are hence attractive for high-temperature applications.

The HEN systems that have been considered for this ab initio study are non-magnetic and structurally stable systems with the metals distributed on the metal sublattice by special quasi-random structure (SQS) methods. For each HEN system and each species, we determined migration barriers corresponding to vacancy-driven elementary point-defect migration mechanisms for crystalline solids. The change in diffusion w.r.t. migration barrier, while going up from ternary to hexinary systems, will be presented. Our results suggest that the impact of the local composition and increasing high-entropy environment can significantly alter these results. Our analyses focus on comparing low and high entropy systems (as measured by the number of elements) for systems exhibiting low and large local distortions, and similar and different nominal bond lengths of the forming binary nitrides. From our preliminary results, the claimed sluggishness of the diffusion in HENs should be more composition and/or environment-specific rather than generalizing for all high entropy systems.

4:00pm **F5-2-MoA-8 Simulation of Transport and Mechanical Properties of TiSiN:Ag Self-Lubricating Coatings With Machine Learned Force Fields**, ***Veniero Lenzi (veniero.lenzi@fisica.uminho.pt)***, University of Minho, Portugal; *F. Fernandes,* University of Coimbra, Portugal; *L. Marques,* University of Minho, Portugal

The quest for the environmental impact mitigation of aerospace industry passes through the use of lightweight and high-performance novel materials. However, these materials are hard to work/machine with standard tools. In this regard, a promising solution is the use of nanocomposite self-lubricating thin films on cutting and machining tools, which might enhance their lifetimes while reducing the use of lubricant, with clear economic and environmental advantages.

Titanium Silicon Nitride and Silver (TiSiN:Ag) nanocomposite thin films have been shown to provide good performance as self-lubricating coatings.[1,2] Their performance depends critically on the release rate of silver, the lubricating agent, which is influenced by the nanoscale structure of the thin film. Atomistic simulation methods are thus necessary to investigate and understand the Ag diffusion within the coating. [3] Moreover, it is important to consider the effects of the high temperatures and stresses encountered during the operation conditions on the coating's structure and stability.

To tackle the complexity of this material, we are currently employing machine learning (ML) techniques to obtain force fields capable of ab-initio level accuracy while enabling large-scale simulations. In particular, we are using the FLARE package [4] to perform on-the-fly training over ab-initio calculations. In this way, we obtained force-fields for TiN/Ag, SiN/Ag and TiSiN systems, which we used to calculate not only the diffusion constants for the different transport processes of Ag within the coating, but also the evolution of the nanocomposite structure under high temperatures and stresses. The obtained force fields show a very high degree of accuracy, within range of ab-initio calculations.

This work highlights the importance of ML methods for the simulation of complex materials. Our results shed light into the Ag transport in TiSiN coatings and in their mechanical properties, thereby providing a unique tool to optimize the thin film processing parameters to achieve the best possible performance.

References:

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2: D. Cavaleiro, *et al.*, *Surface and Coatings Technology*, 399:126176, 2020.
3: V. Lenzi, *et al., Applied Surface Science,* 556:149738, 2021.
4: Y. Xie,*et al., Nature Computational Materials,* 7:40, 2021.

4:20pm **F5-2-MoA-9 Machine Learning Assisted Ab Initio Thermodynamics of Novel Materials***, **Prashanth Srinivasan (prashanth.srinivasan@imw.uni-stuttgart.de)**,* University of Stuttgart, Germany*; F. Körmann,* Max-Planck Institut für Eisenforschung, Germany*; B. Grabowski,* University of Stuttgart, Germany **INVITED**

Recent developments in machine learning techniques has immensely benefited *ab initio*modeling of materials. Interatomic potentials such as the moment tensor potential (MTP) (Shapeev, 2016) that are trained to high temperature density-functional theory (DFT) data are able to predict energies and forces of atomic configurations highly accurately. They are thus able to statistically sample a much wider part of the phase space in a fast and efficient manner. In combination with a systematic thermodynamic integration method (Direct Upsampling), they can be used to calculate total free energies of even complicated systems such as high entropy alloys (HEAs) to 1 meV accuracy (Grabowski et al., 2019, Ferrari et al., 2020) up to the melting point. Apart from static and electronic energies, this also includes vibrational contributions including anharmonicity which significantly affect thermodynamic properties such as specific heat capacity and bulk modulus at high temperatures.

Here, firstly, we demonstrate these results for a bunch of refractory BCC systems ranging from single- to five-component alloys. We break-down the total free energies into various individual contributions. We compare a contrasting trend in the anharmonic free energies beyond the quasi-harmonic approximation in certain BCC refractories, some of which show a positive contribution and some a negative contribution. We narrow this feature down to the density of states (DOS) and the first- and second-neighbor forces and illustrate a difference in bonding behavior between the two sets of BCC elements. Secondly, we also show the applicability of the MTPs to design novel shape memory alloy materials, where a MTP trained to DFT data predicts the stress- and temperature-induced phase transformations in these alloys.

5:00pm **F5-2-MoA-11 Materials Design Principles of Amorphous Cathode Coatings for Lithium-ion Battery Applications***, **Jianli Cheng (jianlicheng@lbl.gov)**, K. Persson,* Lawrence Berkeley National Laboratory (LBNL), USA **INVITED**

Cathode surface coatings have been the foremost solution to suppress cathode degradation and improve cycling performance of lithium-ion batteries (LIBs). In this work, we carry out an extensive high-throughput computational study to develop materials design principles governing amorphous cathode coating selections for LIBs. Our high-throughput screening includes descriptors to evaluate the thermodynamic stability, electrochemical stability, chemical reactivity with electrolytes and cathodes, and ionic diffusivities in the cathode coatings. We consider the commonly used Li_3PS_4 and $LiPF_6$ as the solid and liquid electrolytes, respectively, and categorize the coating materials based on their chemical reactivity with the electrolytes. We reveal the formidable challenge of mitigating oxygen diffusion when selecting an ideal cathode coating, and suggest a few promising materials that pass all the criteria in our high-throughput study. Combining the screening results and detailed ionic diffusion analysis of the selected cathode coatings, we summarize the general guidelines for selecting amorphous cathode coatings.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific E - Session G4-MoA

Hybrid Systems, Processes and Coatings

Moderators: Satish Dixit, Plasma Technology Inc., USA, **Sang-Yul Lee**, Korea Aerospace University, Korea (Republic of)

1:40pm **G4-MoA-1 Modelling Layered Materials Systems Using the Einstein-Hilbert Action***, **Frank Papa (frank@gpplasma.com)**,* GP plasma, USA*; T. vom Braucke,* GP plasma, World Formula Apps, Canada*; N. Bierwisch,* Saxonian Institute of Surface Mechanics SIO, Germany*; N. Schwarzer,* Saxonian Institute of Surface Mechanics SIO, World Formula Apps, Germany

Complex thin film systems can be simulated by a general approach for any coating system by first characterizing it with a set of properties. Once these properties are allocated to certain aspects, we have a method to holistically simulate it. While such a holistic description is only with words, surprisingly, over 100 years ago the great mathematician David Hilbert already found a way to put a set of properties, attributes, degrees of freedom or – as all these other terms are just coding - dimensions into a mathematical formalism, it being the Hamilton extremal principle [1]. He realized that a given set of attributes is nothing else but a set of dimensions and thus, forms a mathematical space or space-time. However, Hilbert only applied his calculus to ordinary 4-dimensional space-time and to then derive the Einstein-Field-Equations [1, 2]. This methodology was further elaborated and generalized in [3, 4] providing a top-down method to describe a large complex system, that can be fed by measurement data to probe a response at various scales of a system under different scenarios. We provide a preliminary theoretical outlook toward materials science applications.

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2:00pm **G4-MoA-2 Control of Phase Transition of VO_2 Films and VO_2-based Terahertz and Infrared Devices***, **Heungsoo Kim (heungsoo.kim@nrl.navy.mil)**,* Naval Research Laboratory, USA*; D. Lahneman,* National Research Council Fellow , USA*; R. Auyeung, K. Charipar, C. Rohde, A. Pique,* Naval Research Laboratory, USA

Vanadium dioxide (VO_2) undergoes an insulator-metal transition (IMT) at ~67 ˚C, which is associated with a structural phase transition (SPT) between an insulating monoclinic phase and a metallic tetragonal phase. This SPT leads to a sharp change in conductivity and index of refraction, which make VO_2 an ideal material for various active devices. High quality VO_2 epitaxial thin films have been synthesized on various single crystal substrates with various buffer layers via pulsed laser deposition. By adjusting the growth conditions of the buffer layers, we were able to modify the interfacial strain between VO_2 film and buffer layer, and consequently can control the T_{IMT} in VO_2 films. We have exploited the phase transition of VO_2 to modulate terahertz (THz) transmission by combining split ring resonator structures with phase changingVO_2 films. We have also demonstrated a VO_2-based passive solid-state radiator for spacecraft thermal control. In this design, we were able to provide dynamic thermal emissivity control by the thermochromic phase change in VO_2 film, which can vary the amount of emitted power of the multilayer device. We will present details on the properties of strained VO_2 films and results from VO_2-based devices.

This work was supported by the Office of Naval Research (ONR) through the Naval Research Laboratory basic research program.

2:20pm **G4-MoA-3 Hybrid HIPIMS and Controlled Pulsed Arc for Deposition of Hard Coatings***, Jiří Vyskočil (jiri.vyskocil@hvm.cz), P. Mareš,* HVM Plasma, Czechia*; Z. Hubička, M. Čada,* Institute of Physics CAS, Czechia **INVITED**

A new hybrid PVD deposition system was developed based on the combination of HiPIMS pulsed glow discharge and pulsed cathodic arc discharge (HiPIMS+arc). The presence of cathodic arc discharge in the HiPIMS is a typical situation when the glow discharge randomly transits to an arc discharge during the active part of the pulse cycle. In these typical cases, the transition appears randomly and cannot be controlled. The new hybrid HiPIMS+arc discharge works with modified pulsed high power supplies which allow the initiation of pulsed arc discharge during HiPIMS pulse at the defined time. The initiated arc during the active part of HiPIMS pulse is quenched at the end of this active part of pulse when the magnetron cathode is disconnected from the negative voltage of power supply. Several modifications with HiPIMS sequence of active pulses with arc were tested as well. The hybrid HiPIMS+arc was applied for the deposition of ta-C thin films by use of a graphite magnetron target. Carbon ta-C films were deposited on silicon substrates at different working gas pressures and different puls configurations. Deposited films were analyzed by Raman scattering and microhardness measurements and the ratio of sp^3/sp^2 bonds was determined. The surface morphology was obtained by SEM and AFM and the presence of microdroplets was analysed for particular conditions. Achieved ta-C film parameters for this deposition source were compared with other deposition methods.

Plasma diagnostics was done in the HiPIMS+arc system by an energetically resolved ion mass spectroscopy and by a RF ion flux density monitor as both methods worked with the time resolution. Ion energy distribution functions of C^+, C^{++} Ar^{++}, Ar^+ were observed at the position of substrate for different deposition conditions in HiPIMS+arc plasma system. Measured parameters of plasma with energies of ions of carbon and argon and the values of total ion fluxes on the substrates were correlated with properties of deposited ta-C films.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H1-2-MoA

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France, **Xavier Maeder**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, **Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **H1-2-MoA-1 Decomposition of CrN Induced by Laser-Assisted Atom Probe Tomography***, Helene Waldl (helene.waldl@unileoben.ac.at), M. Schiester,* Montanuniversität Leoben, Austria*; M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; N. Schalk, M. Tkadletz,* Montanuniversität Leoben, Austria

It is well known that measurement parameters can significantly influence the elemental composition determined by atom probe tomography (APT). Especially results obtained by laser-assisted APT show a strong dependence of the laser pulse energy on the apparent elemental composition. Within this study laser-assisted APT experiments were performed on $Cr_{0.51}N_{0.49}$ and thermally more stable $(Cr_{0.47}Al_{0.53})_{0.49}N_{0.51}$, applying two different laser wavelengths (i.e. 532 and 355 nm) and systematically varied laser pulse energies. The deduced elemental composition of CrN exhibited a strong increase of the Cr content, when the laser pulse energy was increased for both laser wavelengths. For low laser pulse energies Cr^{2+}, CrN^+, N^{2+}, N_2^+were identified, while the amount of detected Cr^{2+} ions increased and the amount of N^{2+} ions strongly decreased at higher laser pulse energies. Further, increased detection of more complex Cr containing ions such as Cr_2N^{2+} at the expense of CrN^+ was observed at higher pulse energies. At the highest pulse energy levels used within this work the Cr content was > 80 at. %, dominated by the amount of detected Cr^{2+} ions. The change of the spectrum of the detected ions with increasing laser pulse energy led to the conclusion that high laser pulse energies initiate the thermal decomposition of CrN, consistent with the known thermal decomposition path into Cr_2N and subsequently into Cr and gaseous N. On the contrary, variation of the laser pulse energy for the thermally more stable CrAlN resulted only in a slight increase of Cr and a decrease of Al and N with increasing laser pulse energy and no change in the type of detected ions. In conclusion, within the present study the decomposition of a coating material with low thermal stability induced by laser-assisted APT was reported for the first time, emphasizing the importance of the selection of suitable measurement parameters for metastable materials, which are prone to thermal decomposition.

2:00pm **H1-2-MoA-2 Watching Matter Move: Observing in-situ Silver Intercalation in Real Time***, Falk Niefind (Falk.Niefind@nist.gov),* NIST-Gaithersburg, USA*; C. Dong, R. Maniyara, J. Robinson,* Pennsylvania State University, USA*; S. Pookpanratana,* NIST-Gaithersburg, USA

Collective electron oscillations, known as plasmons, respond strongly to electromagnetic radiation and their chemical environment.[1] Therefore, plasmonic materials have great potential in applications such as optoelectronic devices and sensors.[2] Thin silver (Ag) films are a particularly appealing plasmonic material, due to their low ohmic resistance. However, thin metallic films need to be shielded against unwanted environmental interactions to prevent degradation. One option is to intercalate the Ag atoms between an epitaxially grown graphene (EG, as a top layer) and silicon carbide (SiC).[3]

Here, we use photoemission electron microscopy (PEEM) to observe the Ag de- and re-intercalation process between EG and SiC during in-situ annealing directly in real time (~1 s resolution). PEEM is a surface-sensitive, full-field imaging technique that achieves nanometer-scale spatial resolution with topographic and electronic contrast. It's basic operating principle employs the imaging of electrons released from a sample surface via the photoelectric effect.

The samples were prepared by ex-situ confinement heteroepitaxy (CHet)[3] during which Ag atoms diffuse through plasma engineered defects of the top graphene layer towards the EG-SiC interface at ~900 °C. To our surprise, we found the intercalation process to be observable even at moderate temperatures (300 °C) until it eventually ceases, where additional heating will not drive the reaction forward. Kinetic analysis of the real space images indicated that the intercalation is probably defect mediated, as has been observed for the CHet process. In addition, we conducted scanning electron microscopy (SEM)-energy dispersive x-ray (EDX) analysis, atomic force microscopy (AFM) as well as x-ray photoelectron spectroscopy (XPS) to corroborate and aid in proposing a mechanism of our PEEM-based observations.

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9. A. S. Baburin, Optic. Mater. Expr. 9, 611-642 (2019).
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2:20pm **H1-2-MoA-3 In-Situ Study of Plasma Surface Interaction Utilizing a Microplasma in a TEM***, Holger Kersten (kersten@physik.uni-kiel.de), L. Hansen, N. Kohlmann, U. Schuermann, L. Kienle,* Kiel University, Germany

The idea of in-situ investigation of a microplasma in a transmission electron microscope (TEM) was successfully demonstrated in 2013 for the first time [1]. Since then no attempts have been taken to observe the plasma surface interaction in real time. Various technical challenges, e.g. size limitations, gas sealing and handling of high voltages, have to be overcome to enable the in-situ TEM imaging.

A stable atmospheric pressure microplasma discharge was designed and studied ex-situ in advance to gain insight in the plasma surface interaction by several diagnostics [2]. For the experimental studies, a simple setup utilizing parallel plate electrodes with a 50-150 µm interelectrode distance divided by a Kapton spacer with a 1mm diameter hole as discharge region intended for in-situ TEM studies is used. The rather small setup operated in Ar or He, respectively, results in an atmospheric pressure DC normal glow discharge observed by I-V characteristics of the microplasma. Significant differences due to the working gas, electrode material and electrode distance have been found. Currents in the range of 0.5-3 mA resulted in electrode potentials of 140-190 V for most experimental conditions. Optical emission spectroscopy and imaging revealed stable plasma operation and enabled the determination of current densities (approx. 16 mA/mm^{2}for He, or 28 mA/mm^{2}for Ar) independent of the input current as the discharge channel grows in diameter. Sheath thicknesses in the range of a few µm have been calculated by the collision-dominated Child-Langmuir law and trends are confirmed by the optical imaging. Energy flux measurements revealed a pronounced effect of ions on the measurement process and resulted in high energy fluxes locally up to 275 W/cm^2. Effective secondary electron emission coefficients ranging from 1 to 1.6 depending on the discharge conditions have been determined based on the energy balance at the cathode.

Prototypes of the vacuum-proof microplasma cell have been build and preparations for the in-situ studies are successfully ongoing right now. In the present contribution the microplasma and its vacuum-proof encapsulation is addressed and a report on the current state of the in-situ experiments for surface modification will be given.

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[2] L. Hansen et al., Plasma Sources Sci. Technol., 2022, accepted.

2:40pm **H1-2-MoA-4 Detection of Individual Nucleated Dislocation Slip Trace During *in Situ* TEM Tensile Testing by Advanced Image Analysis***,* ***Xiaoqing Li (li_xiaoqing@berkeley.edu)****, A. Minor,* University of California at Berkeley, USA

Nucleation of crystalline defects such as dislocations lies at the heart of mechanical deformation. Here, we demonstrate a technique for observing the nucleation of individual dislocations during *in situ* transmission electron microscopy (TEM) tensile testing and measuring fundamental parameters relevant for plasticity from the individual events. Our method relies on systematic detection of dislocation slip traces with automated image analysis in an oriented single crystal Ni sample. In this work, a method for detecting a nucleated dislocation is presented and a quantitative approach is applied to extrapolate the energetic barriers for the nucleation of surface dislocations in pristine crystals.

The in-situ tensile test on a defect-scarce single crystal Nickel sample with stable plastic deformation consisting of single defect nucleation was performed on a push-to-pull device in a JEOL 3010 microscope. The load-displacement relation, along with simultaneous video of the deformation (24 frames/second) were recorded (Fig. 1). For a nucleated dislocation that quickly sweeps through a perfect crystal, only the dislocation 'slip trace lines' existed but difficult to be caught. In order to detect dislocation slip traces from dislocations moving at speeds higher than possible to detect directly, contract analysis of frames before and after an event was carried out (Fig. 2). By subtracting the brightness value of each pixel in each two consecutive frames, the dislocation slip trace line can be marked out. Also, molecular dynamics (MD) simulation was performed to confirm the nucleation specific type of dislocation operating during the uniaxial loading condition. Using the identification of individual defect traces from *in situ* testing, a cumulative probabilistic function is applied to correlate the relationship between a dislocation nucleation event and the corresponding stress level (Fig. 3). Our analysis allows for the extrapolation of the activation parameters for individual dislocation nucleation events using the data on one sample in one tensile test. Precise and quantitative correlation of activation parameters for dislocation nucleation from *in situ* TEM nanomechanical testing can provide direct quantitative measurements useful for computational models of plasticity.

3:00pm **H1-2-MoA-5 Effect of Film Thickness and Trace Width on Electrical Conductivity of Stretchable Composite Inks Under Monotonic and Cyclic Tensile Loading***,* ***Qiushi Li (gli75@gatech.edu)****, O. Pierron, A. Antoniou,* Georgia Institute of Technology, USA

Flexible and stretchable electronics devices often employ a conductive ink film to transmit electrical signal. As these devices are designed to perform electrically while undergoing large deformation, understanding the electrical conductivity of the ink film under deformation is essential for designing reliable devices. The current work studied the electrical performance of a conductive ink consisting of silver flakes embedded in a polyurethane binder and screen printed on a thermoplastic polyurethane substrate. The effect of ink film thickness (10, 20, 30 mm), differentiated by the number of printing passes and consequently the number of ink layers, for different film trace widths (from 0.25 to 2 mm) was investigated under both monotonic and cyclic tensile loading conditions up to 200% applied strain. *In-situ* experiments under confocal as well as scanning electron microscopes were also performed to examine the evolution of strain localization and damage for specimens with different ink film thicknesses and trace widths. The ink film thickness was found to have a significant impact on electrical performance for smaller trace widths in both the monotonic and cyclic loading cases, but as trace width increased the effect of film thickness was diminished. Based on these findings, a relationship between electrical performance and the geometric design parameters of ink film thickness and trace width was proposed.

3:20pm **H1-2-MoA-6 Exploring Diffusion and Segregation Phenomena on the Nano Scale by *in Situ* Tem Heating Studies (Virtual Presentation)***,* ***Yolita Eggeler (yolita.eggeler@kit.edu)****,* Laboratory for Electron Microscopy, KIT, Germany **INVITED**

At high temperatures, local diffusion and segregation phenomena affect thermo-mechanical properties of high-performance alloys. This is fascinating from a fundamental point of view but also important in view of the exploitable service lives of high temperature components. Therefore, these processes need to be investigated using *in situ* analytical electron microscopy. This can be achieved by combining multiple heating/cooling steps in the transmission electron microscope (TEM). MEMS based heating chips are used to expose micro machined specimen with specific microstructures to well defined temperature intervals, during which local diffusion/segregation phenomena take place. After cooling energy dispersive X-ray spectroscopy (EDXS) detectors allow to capture elemental distributions maps. Maps which are taken after different accumulated exposure times allow to study the kinetics of nano scale diffusion and segregation phenomena. As one key element of the *in situ* study, two elements of the microstructure (a γ' phase particle and the adjacent γ channel) are used as an intrinsic nano-diffusion-couple (NDC). A thermodynamic equilibrium is established at one temperature followed by annealing at a different temperature. The kinetics in which the new equilibrium is reached is studied using STEM-EDXS. The NDC approach is not only well suited to study interdiffusion across interfaces in two phase model systems, as will be demonstrated in the first part of the study, where experimental results shed new light on the predictions of thermodynamic/kinetic modelling procedures. It also allows to study segregation phenomena to linear and planar defects in compositionally complex alloys, the second key topic which will be investigated. It will be shown that chemical segregation to planar defects can be interpreted as a local phase transformation. Kinetic results on how segregation proceeds will be presented. Special emphasis will be placed on discussing the potential and the limitations of this type of *in situ* investigations and areas in need of further work.

4:00pm **H1-2-MoA-8 *In-situ* Spectroscopic Ellipsometry Based Real-Time Growth Monitoring of Metal-Oxide Atomic Layer Deposition Processes***,* ***Ufuk Kilic (UFUKKILIC@UNL.EDU)****, S. G. Kilic, M. Hilfiker, A. Mock, D. Sekora,* University of Nebraska-Lincoln, USA*; G. Melendez,* Polytechnic University of Puerto Rico*; N. Ianno, C. Argyropoulos, E. Schubert, M. Schubert,* University of Nebraska-Lincoln, USA

Within the last decade, Atomic Layer Deposition (ALD) of conformal metal-oxide ultra-thin films has provoked an unprecedented interest due to the materials' potential roles in several applications including on-chip photonic devices, ultra-fast switching systems, and next generation transistors [1]. While downsizing of material dimensions for devices applications is an ongoing demand from industry, the ultra-precise control of growth processes during the fabrication of complex systems is a requirement for advanced manufacturing technologies. The integration of spectroscopic ellipsometry (SE), an optical, contactless, and non-invasive technique, into ALD processes has been demonstrated as a powerful and widely-used tool for in-*situ* thin film growth monitoring [2].

In this study, we successfully optimized the oxygen plasma enhanced ALD growth for three different metal-oxides: ZnO, WO_3, and TiO_2, by employing $Zn(CH_3)_2$, $(tBuN)_2(Me_2N)_2W$, and $Ti(OC_3H_7)_4$ organometallic precursors, respectively. To analyze the *in-situ* SE data which were measured within and across multiple cycles during plasma-enhanced ALD of metal-oxide thin films, *a dynamic dual box model is proposed.* The model consists of five layers (substrate, mixed native oxide and roughness interface layer, metal oxide thin film layer, surface ligand layer, ambient) with two of them acting as dynamic parameters (metal oxide thin film layer thickness and surface ligand layer void fraction) to unravel in-cycle kinetics of the metal-oxide ALD growth process. *In-situ* SE data analysis revealed a dynamic surface roughening process with fast kinetics followed by subsequent roughness reduction with slow reaction kinetics upon cyclic exposure to precursor materials and plasma enhanced chemical surface reactions. The proposed dynamic dual box model may be generally applicable to monitor and control metal oxide growth during atomic layer deposition and can be further implemented for precise feedback control and real-time optimization of deposition parameters.

References:

[1] George, S. M., Chem. Rev. 110.1 (2009): 111-131.

[2] Kilic, U., et al.,J. Appl. Phys.*:1805.04171*(2018).

Topical Symposia
Room Town & Country A - Session TS6-1-MoA

A Session to Acknowledge the Contributions of Joe Greene to the ASED, ICMCTF, AVS, and IUVSTA I

Moderators: Michael Stüber, Karlsruhe Institute of Technology, Germany, **Samir Aouadi**, University of North Texas, USA

1:40pm **TS6-1-MoA-1 Low-Temperature Growth of Epitaxial and Polycrystalline Thin Films Under High-Fluxes of Low-Energy Gas Ions*, Ivan G. Petrov (petrov@illinois.edu),*** Linköping University, Sweden, University of Illinois at Urbana-Champaign, National Taiwan University of Science and Technology, Taiwan*; J. Sundgren,* Swedish Association of Engineering Industries, Sweden*; L. Hultman,* Linköping University, Sweden*; J. Greene,* inköping University, Sweden, University of Illinois at Urbana-Champaign, National Taiwan University of Science and Technology, Taiwan **INVITED**

From its inception the benefits of sputter deposition have stemmed from the presence of plasma in the vicinity of the growing film. Bombardment with charged particles and energetic photons affect the substrate initial condition and all stages of film growth: nucleation, coalescence, competitive growth, and recrystallization. Measuring and controlling the fluxes and energy of the charged particles to the substrate is essential in achieving low-temperature growth of high-quality thin films. Under typical conditions during direct current magnetron sputtering (DCMS), the dominant ion species incident at the growth surface while sputtering with N_2/Ar gas mixtures optimized to obtain stoichiometric films is typically Ar^+, while the ratio of the gas-ion flux to deposited metal flux $J_i/J_{Me} \leq 1$. Densification is achieved by increasing the ion energy $E_i$commonly above 100 eV.[1] However, at higher ion energies, a steep price is extracted in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice.An alternative approach is offered by strongly magnetically-unbalanced magnetron sputter deposition system, which allows ion-to-neutral flux ratios J_i/J_{Me} incident at the growing film to be varied over extremely wide ranges (up to > 20) at very low (below the lattice displacement threshold) ion energies (E_i ~ 10-20 eV).[2] Using high-flux low energy ion irradiation during deposition opens new kinetic pathways to independently control the texture (from completely 111 to completely 200) and microstructure (from underdense to fully dense) in transition metal (TM) nitride films grown on amorphous substrates as well as to achieve low-temperature epitaxy of refractory materials as well as of metastable alloys.

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[2]Greene, J.E., Sundgren, J.-E., Hultman, L., Petrov, I., Bergstrom, D.B., "Development of preferred orientation in polycrystalline TiN layers grown by ultrahigh vacuum reactive magnetron sputtering" Appl. Phys. Let. **67** (1995) 2928

2:20pm **TS6-1-MoA-3 Advanced Materials, A Key for the Green and Digital Transformations and for Industrial Competitiveness (Virtual Presentation)*, Jan-Eric Sundgren (jesundgren@gmail.com),*** Swedish Association of Engineering Industries, Sweden **INVITED**

Large resources are allocated world-wide to the green and digital transitions. It is also obvious that research and development in close cooperation between different sectors in society play a crucial role for this twin transition. Another important part to achieve the necessary change is access to advanced materials and new innovative processes for sustainable production of these materials.

In this talk we will describe a mapping study that have conducted of the Swedish broad field of advanced materials. The results show that the value added for Swedish Industries manufacturing advanced materials has continuously increased in the years studied (2011-2019). The field is also expected to globally grow with 5-10% annually. In addition to the industry sector Sweden has also a strong academic community, with several research groups at the international forefront to which Prof Joe Greene has contributed significantly. Based on the mapping conducted and other recent studies we will present recommendations aimed to further boost the field of advanced materials both in Sweden and elsewhere.For example, an increased coordination and cooperation between different sectors and disciplines as well as the use of computational and AI methods are necessary to reduced lead times for industrial impact and thus to industrial competitiveness in the field.

3:00pm **TS6-1-MoA-5 Industrial Magnetron Sputtering: Interfaces & More*, Wolf-Dieter Münz (W_DM@gmx.at),*** Consultant, Austria **INVITED**

Magnetron sputter deposition of wear resistant hard coatings has found broad acceptance in many industrial applications serving e.g. the automotive, micro mashining, aeronautical and biomedical but also decorative industry. Perfect adhesion is a dominant precondition to meet reproducible production conditions. The paper discusses three types of substrate pretreatment prior to the actual film deposition: intensive Ar etching, metal ion etching by cathodic arc and HIPIMS technology respectively. Particular attention is paid to ion implantation during metal ion etching and the related epitaxy of the growing film. The resulting enhanced adhesion guarantees successful deposition of very hard and highly stressed e.g. TiAlN based superlattice coatings. The industrial realization of these methods of pretreatment is outlined by verification in a double (twin) cathode, combined cathodic arc/unbalanced magnetron and combined HIPIMS/unbalanced magnetron approaches. Two industrialized applications will be discussed in detail: (1) performance of superhard C-DLC coatings utilizing a five cathode batch type coater and (2) a simultaneous HIPIMS/UBM process depositing multilayer TiAlN/CrN coatingsproduced in a large scale multi cathode equipment.

3:40pm **TS6-1-MoA-7 Applying Thin Film Synthesis and Characterization Methods to Improving Photovoltaics*, Angus Rockett (arockett@mines.edu),*** Colorado School of Mines, USA **INVITED**

Prof. Joe Greene has been an amazing mentor and teacher to me. Without his help and patience, I would never have succeeded as I have. My career is entirely thanks to Joe both during my graduate study and more importantly afterward. This talk briefly reviews how the synthesis and characterization of thin films, particularly by sputter deposition, as I learned from or with the support of Joe, has been applied to the full spectrum of materials applied to photovoltaics. Film materials studied include silicon, binary, and ternary materials and alloys. Novel dielectrics and contact materials have been developed including a metastable alloy of 30% Cu in bcc Mo. Characterization methods include microstructural, microchemical, and optoelectronic approaches. The results have been simulated with continuum elasticity, finite element, Monte Carlo, and density functional methods. The result is a detailed picture of how defects in semiconductors affect the performance of photovoltaics and how they are related to process conditions.

4:20pm **TS6-1-MoA-9 May the Interatomic Forces be with You; Self-Organized Nanostructure Design in Functional Nitride Alloy Films (Virtual Presentation)*, Lars Hultman (lars.hultman@liu.se),*** *G. Greczynski,* Linköping University, Sweden*; I. Petrov, J. Greene,* Linköping University, Sweden; University of Illinois at Urbana-Champaign, USA; National Taiwan University of Science and Technology, Taiwan **INVITED**

During ~40 years our group has developed strategies for thin film formation during physical vapor deposition, spanning epitaxial growth and crystallographic texture control to self-organization of nanostructures. Both primary and secondary phase transformations from the vapor phase and in the as-deposited state, respectively, are explored. Self-organization from surface and bulk diffusion is used to enhance mechanical and electronic properties of functional ceramics by structural design, here exemplified by transition metal and group-III nitride metastable alloy model systems: TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN. Material characterization is performed by XRD, analytical STEM, FIB, and isotopic-substitution APT. Molecular dynamics simulations, *Ab initio* calculations, and phase-field modelling are employed to assess phase stability, diffusion, and decomposition behavior from lattice mismatch and electronic band structure effects. Our concept of age hardening is reviewed, where spinodal decomposition is established for TiAlN by the formation of cubic-phase nm-size domains in a {100}-checker-board pattern of TiN and AlN at temperatures corresponding to cutting tool operation. 2-D-nanolabyrinthine structuring in ZrAlN is obtained from intergrowth of non-isostructural phases *c*-ZrN/*w*-AlN: {110}║{11-20} interfaces. Superhardening in TiN/Si_3N_4 nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN_x tissue layer, which is shown to be vacancy-stabilized cubic-phase SiN_x. A hardness maximum at 34 GPa – short of ultrahard – is observed in TiN/SiN_x(001) superlattices at the epitaxial-to-amorphous thickness-limit for the SiN_x layers. For $In_xAl_{1-x}N$, we report inherently-curved-lattice epitaxial growth of nanospirals with controllable chirality as well as core-shell nanorod formation. The emerging inherently nanolaminate family of so-called MAX phases is briefly reviewed with examples from Ti_2AlN including for non-van-der Waals intercalation of noble metals. More recently, we discovered transmorphic heteroepitaxy between CVD-grown AlN epilayer and SiC(0001) wafer substrates. The atomic configuration transits over two atomic layers from SiC ® $(Al_{1/3}Si_{2/3})_{2/3}N$ with ordered vacancies on 1/3 of the Al and Si positions ® $(Al_{2/3}Si_{1/3})N$ ® AlN. The resulting special epitaxial AlN layer has state-of-the-art low lattice defect density, enabling growth of high-quality thin GaN HEMT heterostructures for superior power electronics.

5:00pm **TS6-1-MoA-11 From Thin Films to Solid Oxide Fuel Cells***, Scott Barnett (s-barnett@northwestern.edu),* Northwestern University, USA **INVITED**

This talk will start with a brief history of how my background in thin films in Joe Greene's group helped lead to a new approach to making practical solid oxide fuel cells (SOFCs). Although thin film vapor deposition techniques have not supplanted conventional ceramic processing of SOFCs, this talk will highlight vapor deposition methods likely to play an increasing role going forward. Recent developments in SOFCs and solid oxide electrolysis cells (SOECs) will be discussed. SOFCs are being increasingly applied for clean efficiency electrical generation, and produce highly concentrated CO_2 exhaust that is nearly sequestration-ready. SOECs have potential for highest efficiency conversion of renewable electricity to hydrogen and other renewable fuels. The devices can also be operated in both SOFC and SOEC modes to allow large-scale electrical energy storage – a key technology needed for enabling increased utilization of renewable wind and solar energy resources. Current research areas will be highlighted including improving device performance via reduced electrolyte thickness and highly-active nano-scale electrodes, and determining the mechanisms that limit device long-term stability.

Coatings for Use at High Temperatures
Room Pacific E - Session A1-3-TuM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling III

Moderators: Gustavo García-Martín, REP-Energy Solutions, Spain, **Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

9:00am **A1-3-TuM-4 Protective Sol-Gel Coatings for Steels Against Corrosion of Molten Carbonates for Concentrated Solar Power Plants**, ***Gustavo García Martín (gusgarci@ucm.es)***, Universidad Complutense de Madrid, Spain; *T. de miguel Gamo,* Universidad Complutense de Madrid , Spain; *I. Lasanta Carrasco, M. Lambrecht, F. Pérez Trujillo, N. Garcia, C. Gómez de Castro,* Universidad Complutense de Madrid, Spain

In the last few years, the interest in renewable energies has suffered a significant increase, representing the Concentrated Solar Power (CSP) technology in the present and the future of the electric energy obtained from the sun on large scale. Commercial CSP plants usually use molten salt mixtures as thermal energy storage mediums. The currently used industrial compound is an alkali-nitrate mixture composed of 60 wt.% NaNO3/40 wt.% KNO3. However, the development of new molten salt mixtures with higher thermal stabilities that allow increasing the working temperature has received great interest in the last few years. In this respect, many authors have recently proposed the replacement of molten nitrate salts by molten carbonate salts, making possible an increase in the operational temperature beyond 700 °C. However, one of the main drawbacks of this medium consists in the severe corrosion problems to which its composition and high temperature lead. Thus, the development of protective coatings for steels could be an interesting alternative, both from a technological and economical point of view, for increasing the lifetime of pipes and tanks in contact with molten carbonates. In both cases, the levelized cost of electricity (LCoE) would suffer a substantial reduction, which is one of the major objectives currently set in CSP technology. Thus, this work aimed at developing zirconia-based sol-gel protective coatings (on stainless steels and monitoring the protective behaviour in contact with a eutectic ternary Li_2CO_3-Na_2CO_3-K_2CO_3. Corrosion tests were performed at 700°C up to 1000 h results were supported by gravimetric and microstructural characterizations. All results were compared to the uncoated steels. Results showed the promising behaviour of the coated substrates. The corrosion monitoring system showed the protective behaviour of the coatings, these improving the behaviour of the uncoated samples, where detachments and high weight variations were observed.

9:20am **A1-3-TuM-5 Experimental Study on Steam Oxidation Resistance at 600ºC of Inconel 625 Coatings Deposited by HVOF and Laser Cladding**, ***Francisco Javier Pérez Trujillo (fjperez@ucm.es)***, *G. García Martín, A. Illana Sánchez, T. De Miguel Gamo,* Universidad Complutense de Madrid, Spain; *F. Gonçalves , M. Sousa,* Tecnologia e Engenharia de Materiais , Portugal

Technological developments around electric generation power plants aim to increase the thermal efficiency of conversion processes in steam turbines, developing materials able to resist ultra-supercritical (USC) conditions (600-620°C and 20-30 MPa). 9-12 %Cr ferritic-martensitic steels, commonly used for that application, tend to develop thick and non-protective iron-rich oxide scales. Therefore, partial or complete spallation of these oxide scales may cause serious consequences for the lifetime and safe operation of the components in contact with the steam and even the own plant. The solution to prolong their service life is to modify their surface, by means of protective coatings that retard interdiffusion mechanisms that take place at that temperature range.

Inconel 625 is used for its high strength, excellent fabricability (including joining), and oxidation resistance up to 982°C, so has been considered as one possible candidate for A-USC power plants (up to 700°C and 35 MPa).

In this research Inconel 625 coatings were deposited by High Velocity Oxy-fuel (HVOF) and laser cladding (LC) processes on a 12%Cr steel to improve its oxidation resistance. A high-temperature oxidation test under isothermal conditions up to 500 h was performed on uncoated and coated steel in a pure steam atmosphere at 600°C. The specimens were weighed monitoring at different times during the testsand characterized before and after oxidation tests by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). The results have shown that the application of Inconel 625 coatings reduces the weight gain of the steel by more than 50%. In addition, after 500 h of oxidation both coatings deposited by HVOF and LC exhibited an excellent oxidation resistance at 600°C in pure steam due to the formation of thin layers of protective Cr_2O_3 and $NiCr_2O_4$ oxides on the external surface of the coatings.

9:40am **A1-3-TuM-6 Oxidation Kinetics of γ-TiAl Based Coating Materials**, ***Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at)***, *S. Kagerer, O. Hudak,* TU Wien, Austria; *M. Schloffer,* MTU Aero Engines, Muenchen, Germany; *H. Riedl,* TU Wien, Austria

The reduction of carbon emissions as well as the improving of fuel efficiencies tied to modern aerospace and aviation have heavily invested in the development of lighter and more durable high temperatures materials. γ-TiAl bulk materials, with their low density and distinguished creep resistance, fulfill all these tasks till 780°C. Above 780°C, oxidation protection of γ-TiAl based alloys is a challenging task for the aero- and automotive industry. Here, especially thin films rise the possibility to protect these alloys while not affecting other material properties. Typically, ceramic like thin films are applied to defend the bulk materials against oxidation and corrosion attacks. Within this study, we applied a different approach utilizing metallic coating materials deposited by PVD.

Therefore, we grow Al-rich γ-TiAl based coatings onto well-established TNM bulk alloys using a semi-industrial scaled unbalanced magnetron sputtering system. To study the oxide scale formation and its kinetics, also on a long-term view, all coatings were oxidized at 850 °C up to 1000 h in ambient air. The scale formation and accompanying diffusion processes have been investigated methodically by various electron imaging techniques (SEM and HR-TEM) as well as structural and chemical analysis. The prevalent diffusion process was separated in two dominating effects: *(i)* oxygen inward diffusion and outermost scale formation as well as *(ii)* Al interdiffusion between the coating and bulk interface. The so obtained diffusion lengths were used to estimate diffusion coefficients by the parabolic growth rate of the TGO and the oxygen inward diffusion by a logarithmic rate law. In a further step, morphological changes due phase transformation based on Al diffusion processes was investigated in detail. The highly dense, thermally grown oxide (alumina based scale) reaches a thickness up to maximum of 4 µm depending on the coating thickness (> 10 µm) leading to superior protection of the bulk material. In summary, the application of γ-TiAl based coating materials to enhance the oxidation resistance of TNM bulk alloys is an interesting alternative to ceramic like coatings, also on a long-term perspective.

10:00am **A1-3-TuM-7 The Impact of Aluminide Slurry Coatings on the Oxidation and Fatigue Resistance of High-Strength Ni-Based Valve Alloys**, ***Sebastien Dryepondt (dryepondtsn@ornl.gov)***, *R. Pillai , B. Armstrong, M. Lance, G. Muralidharan,* ORNL, USA

Increasing temperature in light and heavy-duty internal combustion engines offers a straightforward solution for increasing engine efficiency and reducing CO_2 emission. Development of new Ni-based high temperature alloys is, however, burdensome due to the need for both high strength and high oxidation resistance. One solution is to apply corrosion-resistant coatings to high strength materials. A slurry aluminide coating was, therefore, deposited on commercial (alloy 31V) and ORNL-developed high strength gamma prime Ni-based superalloys. A significant improvement of the alloy cyclic oxidation resistance at 900°C and 950°C in air + 10%H_2O was observed for both alloys due to coating application. The coated ORNL sample exhibited more rapid oxidation rates than the 31V coated sample due to the higher Ti concentration in the former alloy leading to the formation of Ti-rich nonprotective oxides. High cycle fatigue testing was also conducted on bare and coated specimens to assess the coating impact on the alloy fatigue resistance at 800-900°C. Similar cycles to rupture were measured for the bare and coated samples, confirming that the coated ORNL alloy is a viable option for valve application up to ~900°C. Further optimization of the substrate/coating couple could allow for even higher valve operating temperature.

This research was sponsored by the U.S. Department of Energy, Energy Efficiency & Renewable Energy, Vehicle Technologies Office, Powertrain Materials Core Program.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-3-TuM

Properties and Characterization of Hard Coatings and Surfaces III

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

8:00am **B4-3-TuM-1 Thermal Stability of Nanotwinned Metallic Thin Films (Virtual Presentation)***, **Fan-Yi Ouyang (fyouyang@ess.nthu.edu.tw)**,* National Tsing Hua University, Taiwan **INVITED**

The vertically integrated systems, three-dimensional integrated circuit (3D-IC), are regarded as a solution to the demand of both the trend of miniaturization for electronic devices and the better performance. Metal-to-metal direct bonding technology has been considered as a promising method to connect different chips in 3D-IC packaging. Twinning structure has been regarded as an important strengthening mechanism because of its special properties, including low electrical resistivity, great thermal stability, high strain rate sensitivity, and increased mechanical strength, which is a good candidate for application in electronic application. In this talk, the key deposition parameters to fabricate nanotwinned structure in FCC metallic Ag and Cu thin films by sputtering system is reviewed and we found the substrate bias and deposition temperature are the most critical one. In addition, their corresponding thermal stability are investigated by annealing at 150 to 500 ℃ under ordinary vacuum environment. The results show that the thermal stabilities of the nanotwinned metallic thin films are significantly affected by interlayer and defects in the films. Highly (111) preferred orientation (over 95% surface area) of metallic thin films can be found and they can maintain a columnar structure with high-density nanotwins with twin spacing around 10 nm after annealing at 450 ℃. However, the (200) anisotropic abnormal grain growth can also be found in the highly (111)-oriented nanotwinned metallic thin film after the annealing process at over 250 ℃, and the columnar structures with high-density nanotwins are consumed. The mechanism of abnormal grain growth in highly (111)-oriented nanotwinned metallic thin films will be discussed. This study successfully established the roadmap on the microstructure and properties of nanotwinned metallic thin films for different industrial applications.

8:40am **B4-3-TuM-3 Phase Stability and Mechanical Characteristics of Sputtering (Mo, Hf)N Coatings***, **Shu-Yu Hsu (stuu96753@gmail.com)**, Y. Chang,* National United University, Taiwan*; F. Wu,* Dept. of Materials Science and Engineering, National United University, Taiwan

This work focused on microstructure and mechanical property evolution of (Mo, Hf)N coatings in terms of input power modulation and annealing temperature. The influence of input power and annealing on composition, phase, hardness, modulus, and tribological behavior was discussed. The MoN,HfN, and (Mo, Hf)N films were fabricated through radio frequency reactive magnetron sputtering at a fixed Ar/N_2 inlet gas ratio of 12/8 sccm/sccm. For MoN and HfN films, the input power on Mo and Hf targets were both set at 150W. As for (Mo, Hf)N coatings, the input power modulation was set as 150W and 25 to 200W. The vacuum annealing was performed at 500 and 650^{o}C for 1 hr, followed by the furnace-cooling to room temperature. The structure of MoN film exhibited B1-MoN, γ-Mo_2N, and MoN_2 phases, while the HfN film existed δ-HfN and c-Hf_3N_4 phases. The Hfcontents in(Mo, Hf)N coatings increased linearly from 0 to 12.8 at.% with input power rose. When Hf was below 5.6 at.%, a polycrystalline microstructure with δ-HfN, B1-MoN, β-Mo_2N, γ-Mo_2N and MoN_2 phases were identified. According to nano-indentation, scratch and wear test results, the best combination in mechanical characteristics of (Mo, Hf)N film were observed when input power ratio of Mo/Hf was set as 150/100W. The coating exhibited a highest hardness of 22.5 GPa and presented a least wear damage. The vacuum annealing effect onmultiphase feature and grain recrystallizing was discussed. The dense structure, excellent adhesion and superior tribological behavior of the nitride films owing to multiphase strengthening and solid-solutioning were anticipated.

Keywords: Microstructure; (Mo, Hf)N; Input power; Annealing; tribological behavior

9:00am **B4-3-TuM-4 Evidencing Different Dislocation Types in Magnetron-sputtered Epitaxial TiN Thin Films on MgO***, **Janella Salamania (janella.salamania@liu.se)**, D. Sangiovanni,* Linköping University, IFM, Sweden*; L. Johnson, I. Schramm, K. Calamba,* Sandvik Coromant, Sweden*; T. Hsu,* Linköping University, IFM, Sweden*; B. Bakhit,* Linköping University, IFM, Thin Film Physics Division, Sweden*; R. Boyd, F. Tasnadi, I. Abrikosov, L. Rogström, M. Odén,* Linköping University, IFM, Sweden

Although the growth and microstructure of titanium nitride coatings have been extensively studied, the presence and atomic structures of different dislocation types in TiN films remains overlooked. Here, a series of highly crystalline heteroepitaxial (001)-oriented TiN (B1) films has been grown on high-purity MgO substrates by DC reactive magnetron-sputtering from pure Ti targets at 800°C in a mixed Ar/N_2 atmosphere. Using a combination of high-resolution aberration-corrected scanning transmission electron microscopy (STEM), fast Fourier transform (FFT) filtering, atomic segmentation and localization, we present evidence of different dislocation types, including partials, in as-deposited TiN films. Besides the perfect edge dislocation types, Shockley partials, Frank partials, and Lomer sessile configurations exist. We support our experimental findings by performing classical molecular dynamics (MD) and density functional theory (DFT) calculations of these defect configurations to gain detailed insights about the dislocation core structures and properties. Our results suggest that a variety of dislocations should be considered when interpreting and evaluating the properties of TiN films.

9:20am **B4-3-TuM-5 TiN/$Zr_{0.34}Al_{0.66}$N Multilayer Films: Growth Temperature Dependence on Structure and Mechanical Properties***, **Marcus Lorentzon (marcus.lorentzon@liu.se)**, N. Ghafoor, J. Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

TiN/ZrAlN multilayer are shown to exhibit high hardness and thermal stability when grown as cubic(c)-TiN and high Al containing $Zr_{0.43}Al_{0.57}$N nanocomposite layers with segregated domains of c-ZrN and wurtzite(w)-AlN [1]. We extend these investigations to tune the phase and resulting interface structure of nanocomposite layer as a function of growth temperature and ZrAlN layer thickness.

1µm thick TiN/$Zr_{0.34}Al_{0.66}$N multilayer films were deposited at RT, 200°C, 350°C, 500°C, 800°C and 900°C with equal layer thicknesses of 2-10nm using ion assisted reactive DC magnetron sputtering from elemental Ti and compound $Zr_{0.5}Al_{0.5}$ targets on single crystal MgO(001) and Si(001) substrates with a substrate bias of -30V.

Preliminary analysis shows strong effect of growth temperature on overall texture of the multilayers, driven by change in the morphology of ZrAlN layers and interface structure. Regardless of texture, all multilayers exhibit sharp interfaces, analyzed from appearance of higher order multilayer reflections in X-ray reflectivity profiles. In agreement with previous study [2], $Zr_{0.34}Al_{0.66}$N layers exhibit nanocomposite formation with segregated domains of thermodynamically stable c-ZrN and w-AlN binary compounds. On the other hand, RT grown $Zr_{0.34}Al_{0.66}$N layers exhibit single cubic phase with the lattice match with TiN layers. XRD shows single common peak from the layered structure indicative of TiN/$Zr_{0.34}Al_{0.66}$N superlattice formation. Large residual stress observed in low temperature grown superlattice films also indicates interface coherency strain generated due to superlattice formation. We will present details of superlattice structure at different temperatures and layer thicknesses, as well as stress generations and nanoindentation response of TiN/$Zr_{0.34}Al_{0.66}$N films analyzed by x-ray diffraction, x-ray reflectivity, elastic recoil detection analysis, Rutherford backscattering spectrometry, nanoindentation, and transmission electron microscopy.

[1] K. Yalamanchili, F. Wang, H. Aboulfadl et. al., “Growth and thermal stability of TiN/ZrAlN: Effect of internal interfaces”, Acta Mater 121 (2016) 396-406, https://doi.org/10.1016/j.actamat.2016.07.006

[2] N. Ghafoor, I. Petrov, D. Holec, et. al., “Self-structuring in Zr1-xAlxN films as a function of composition and growth temperature, Sci Rep 8, 16327 (2018). https://doi.org/10.1038/s41598-018-34279-w

9:40am **B4-3-TuM-6 Physicochemical Properties of Single Phased Tantalum Nitride Thin Films***, **Aurélie Achille (aurelie.achille@icmcb.cnrs.fr)**, A. Poulon-Quintin, F. Mauvy, D. Michau, S. Fourcade,* CNRS, Univ. Bordeaux, ICMCB, France*; C. Labrugere,* CNRS, Univ. Bordeaux, PLACAMAT, France*; M. Cavarroc,* SAFRAN Paris-Saclay – SAFRAN Tech, France

Stoichiometric Tantalum Nitrides (TaN) exist as a face-centred cubic phase, which is a metastable high temperature phase and as a stable hexagonal phase. Using reactive RF Magnetron Sputtering and reactive High Power

Impulse Magnetron Sputtering (HiPIMS) both phases are obtained with different microstructures. This talk will be focus on the metastable cubic phase. First, the structural and optical properties are presented. Evolution of the electrical conductivity with the temperature will be presented. Using cyclic voltammetry measurements, the electrochemical properties (corrosion current and potential) will be analysed as a function of the operating temperature up to 120°. All the presented results will be discussed based on the microstructure differences (depending on the sputtering method used).

Coatings for Biomedical and Healthcare Applications
Room Pacific C - Session D2-TuM

Medical Devices: Bio-Tribo-Corrosion, Diagnostics, 3D Printing

Moderators: Steve Bull, Newcastle University, UK, **Hamdy Ibrahim**, University of Tennessee at Chattanooga, USA, **Margaret Stack**, University of Strathclyde, UK

8:00am **D2-TuM-1 Characterization of Hydroxyapatite Coatings Produced by Pulsed-laser Deposition on Ti_6Al_4V Substrates Fabricated by Electron Beam Melting**, ***Octavio Andrés González-Estrada (agonzale@uis.edu.co)***, *R. Ospina, A. Pertuz,* Universidad Industrial de Santander, Colombia

Additive manufacturing is a disruptive technology that has changed the design of bone implants for clinical applications. In this work, the effect of the deposition energy parameter on the mechanical properties and surface microscopy of Ti6Al4V alloy substrates manufactured by electron beam melting (EBM) and coated with hydroxyapatite (HA) deposited by the pulsed laser technique (PLD) was investigated. The average hardness and microhardness values were obtained under microindentation and indentation tests following the standard practice for instrumented indentation ASTM E384-17, as well as, scratch tests for adhesion behavior. The morphology and chemistry of the substrate coating were evaluated using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), resulting in average values of HA particle formation size of the coating. Variables that reflect the incidence of deposition parameters in relation to the mechanical and micrographic properties of the HA coating were assessed.

8:20am **D2-TuM-2 Preclinical in Vitro and in Vivo Assessment of High-Strength and Corrosion-Controlled Magnesium-Based Bone Implants**, *C. Billings,* University of Tennessee Knoxville, USA*; M. Abdalla,* University of Illinois - Chicago, USA*; D. Anderson,* University of Tennessee Knoxville, USA*;* ***Hamdy Ibrahim (HAMDY-IBRAHIM@UTC.EDU)***, University of Tennessee at Chattanooga, USA

Magnesium is a lightweight metal that is naturally present in the human body with a biodegradable nature in aqueous mediums. These properties make magnesium an attractive material for its use in various biomedical applications when the material is not recommended to stay permanently in the body, such as bone implants. Some of the main challenges that hinder the use of magnesium for bone fracture repair are its limited mechanical strength and fast corrosion rates which results in peer biomechanical performance in the body. To this end, we have developed both a biocompatible magnesium alloy (Mg-Zn-Ca-Mn-based alloy) and a fabrication method (heat treatment and coating) that deliver a high-strength and corrosion-tailored material that can provide the needed stability during the healing period for bone implant applications, and subsequently degrade until vanished completely after the healing of tissues. The created coating consists of two layers; a first ceramic layer (10 µm thick) made by using the micro arc oxidation (MAO) process followed by a thinner layer (1-2 µm thick) of Ca/P-based ceramics created by using the sol-gel technique. The sol-gel coating resulted in a significant reduction in corrosion rate, as low as 1.1 µm/year which is 27 times less than that for the MAO-coated alloy alone. In vitro and in vivo assessments of our magnesium alloy and fabrication method showed high levels of biocompatibility in terms of cytotoxicity, degradation rates, and fracture healing. For instance, our animal studies, using New Zealand white rabbit utilizing a lateral femoral condyle model, showed no negative effects on bone formation, and no evidence of a strong or persistent inflammatory reaction. The results of this study show that it is possible to produce biocompatible magnesium-based implants with stronger and more corrosion-controlled properties.

8:40am **D2-TuM-3 Understanding Tribological Contact in Biomedical Applications; The Role of Surface Film Formation and Its Correlation With Friction and Wear**, ***Mark Rainforth (m.rainforth@sheffield.ac.uk)***, The University of Sheffield, UK*; R. Namus, J. Qi, J. Nutter,* University of Sheffield, UK **INVITED**

The impact of tribology (friction and wear) on the economy is a substantial 5-8% of GDP and plays a central role in everyday life, for example, in transport, manufacturing, process engineering and medical devices.The tribological performance of a component is a strong function of the interaction between the component surface and the operating environment, and how the surface changes in response to the contact stresses. In many cases, the tribo environment activates electrochemical reactions, which is particularly true in orthopaedic components. It is these dynamic changes that determine the success or failure of the component. In many cases, distinct surface structures are generated by the sliding contact. Of these, the formation of tribofilms is perhaps the most important. Evidence is mounting that tribofilms play a crucial role in the success of components, particularly in the articulating surfaces in orthopaedic components. The conditions under which tribofilms form is still far from clear. In this work a detailed analysis of the tribocorrosion behaviour of Ti-6Al-4V and CoCrMo alloys was undertaken under a range of electrochemical and load conditions in order to determine the conditions under which a tribofilm forms and the role that the tribofilm plays. The structure of the tribofilm is considered in detail, down to the atomic scale. High resolution transmission(scanning) electron microscopy and electron energy loss spectroscopy have been used to characterise the structure and chemical composition of the tribofilm. A detailed, quantitative, analysis of surface deformation was also undertaken, in particular, the geometrically necessary dislocation (GND) density was quantified using precession electron diffraction (PET). For the first time, graphitic and onion-like carbon structures were found. It has been clearly shown that the presence of carbon nanostructures in the tribocorrosion process and the formation of the tribofilm leads to an improved tribocorrosion behaviour of the system, in particular a reduction in wear and friction. A clear correlation between applied potential and tribofilm formation has been established, with tribofilms forming on a passive surface, but not on a metal surface where an oxide is not present. Interestingly, there appears to be a correlation between the extent of surface deformation with the presence of a tribofilm and the surface potential; anodic conditions result in much greater surface deformation than cathodic conditions. However, there was no correlation between the surface deformation and the wear rate. The implications for these observations on the wear performance of these materials is discussed.

9:20am **D2-TuM-5 Corrosion Resistance of Cerium Oxynitride Thin Films for Use in Implants and Prothesis**, *G. Numpaque Rojas,* ***Brian Felipe Mendez Bazurto (bfmendezb@unal.edu.co)***, *G. Cubillos Gonzalez,* Universidad Nacional de Colombia

Due to its chemical properties and high corrosion resistance, the cerium oxide has been widely used in aeronautical and naval industry as coating of aluminium alloys [1, 2]. The CeO is deposited mainly by suspended techniques, clean high vacuum techniques deposit of cerium oxide has not been studied since being a pyrophoric solid, and the films obtained are porous and easily delaminated. In this work, we determine the conditions of pressure, temperature and nitrogen flow to deposit homogeneous films on stainless steel AISI 316L surgical grade and corrosion resistance cerium oxynitride was evaluated. CeOxNy/ZrOxNy coatings were obtained from a 4 in. ×1/4 in. Zr-Ce (99.9%) target (Stanford Advanced Materials). RF reactive sputtering technique, in atmosphere of N2/O2, with a flow ratio ΦN2/ΦO2 of 20 was used. The structural analysis carried out through X-ray diffraction (XRD) showed that the CeOxNy/ZrOxNy coatings had a cubic polycrystalline structures preferencial growth for CeOxNy, while ZrOxNy is amorphous. The SEM analysis evidenced that the films grew with homogeneous morphology and exhibited a columnar growth. Corrosion resistance evaluated from the potentiodynamic polarization curves in Hank's solution [3], showed that the coating increases the corrosion resistance of steel by two orders of magnitude. CeOxNy/ZrOxNy coatings deposited on surgical grade stainless steel could be a promising candidate to be used in osteosynthesis processes.

9:40am **D2-TuM-6 Porous Ti Under Tribocorrosion Solicitations: Some Positive Feedback and Some Scientific Benefits***, A. Gomes Costa,* CMEMS-Minho University, Portugal*; F. Viana,* FEUP, Portugal*; L. Rocha,* DTX, Portugal*; F. Toptan,* DMSE, İYTE, Turkey*; **Jean Geringer (geringer@emse.fr)**,* Mines Saint-Etienne, France

About biomaterials dedicated to bone substitutes, some candidates are promising like Hydroxyapatites, cell growth boosters, etc. One candidate is titanium foam for two reasons: promoting vascularization thanks to 3D structure and bone cells attachments and growth. Some concerns are on tribocorrosion resistance. This work is dealing with titanium foam (void 50% approx.) under tribocorrosion solicitations in physiological environment, i.e. bovine serum. The consequences of the micro-displacements (+- 40 µm sinusoidal displacement) under normal loads from 22.5N till 200N were analyzed through the materials integrity. Moreover the tribological analysis was investigated and the Master curve, A (dissipated energy over the total dissipated energy) vs. 1st OCP (Open Circuit Potential) drop was used to manage the influence with normal load and displacement amplitude. The results are in accordance with stick/slip phenomenon. A fretting map was illustrated and the fretting regimes were highlighted. The A-1st OCP curve is in accordance with the type of degradations, i.e. macroscopic wear.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E3-TuM
Coatings for Automotive and Aerospace Applications

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Rainer Cremer**, KCS Europe GmbH, Germany, **Philipp Grützmacher**, Institute of Engineering Design and Product Development , Austria

8:40am **E3-TuM-3 Thermomechanical Stability of Hard DLC Coatings Produced by HiPIMS-DOMS***, **João Carlos Oliveira (joao.oliveira@dem.uc.pt)**,* University of Coimbra, Portugal*; A. Vahidi,* University of Coimbra, Iran (Islamic Republic of)*; F. Ferreira, R. Serra, A. Cavaleiro,* University of Coimbra, Portugal

DLC films are very resistant to abrasive and adhesive wear making them suitable for applications that experience extreme contact pressure. For this reason, they are one of the most promising solutions for application in piston´s rings of internal combustion engine (ICE). However, recent trends in the automotive industry, such as reduced engine sizes and turbocharging, require higher operating temperatures and loads, which the classical DLC films deposited by magnetron sputtering cannot withstand. High Power Impulse Magnetron Sputtering (HiPIMS) has been actively investigated for hard DLC deposition. In HiPIMS, a large fraction of sputtered atoms is ionized, thanks to 2–3 orders of magnitude higher plasma densities than in classical magnetron sputtering. However, in the standard HiPIMS process based on Ar, the ionized fraction of C is very low (few percent), due to the low carbon ionization cross section by electron impact.

In previous work, the authors have shown that adding Ne to the plasma up to 50 % results in the deposition of denser and smoother DLC films, with improved tribological properties and increased hardness. In this work, the thermal stability of DLC films deposited in Ar-Ne discharge gas by Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS, was investigated. In a first step, the thermal stability of the films by annealing up to 700 ºC in a protective atmosphere. The structure of the DLC films deposited without Ne in the discharge gas was stable up to 500 ºC, while clear signs of graphitization were detected at higher temperatures by Raman spectroscopy. The stability of the film up to 500 ºC was confirm by pin-on-disk tests and nanoindentation at room temperature after annealing. The structure of the DLC films deposited with Ne in the discharge gas was stable up to annealing at 700 ºC as shown by Raman spectroscopy. However, the hardness of the films decreases from 25 to 20 GPa upon annealing at 700ºC, while the specific wear rate increases from 0.5 to 1.25 x 10^{-16} m^3/Nm. The thermal stability of the DLC films was also characterized by pin-on-disk tests at high temperature. The coatings were tested up to 400 ºC in ambient atmosphere. Adding Ne to the deposition plasma resulted in an increased thermal stability by 50 ºC for the film deposited with a mixed Ne + Ar discharge gas.

9:00am **E3-TuM-4 Static and Dynamic Friction Assessment Using Novel High Temperature Tribometer***, **Marwan Azzi (marwan.azzi@polymtl.ca)**,* Polytechnique Montreal, Canada*; E. Bitar-Nehme,* Tricomat inc, Canada*; J. Sapieha,* Polytechnique Montreal, Canada*; l. Martinu,* Polytechnique Montréal, Canada

Tribology in extreme environments has recently gained significant interest in the aerospace and energy generation communities, largely due to the increased demand for development of durable and more efficient engineering components with an increased performance beyond the current limits. For instance, the next generation gas turbine engines are required to reduce fuel consumption and pollution emission by significant amount which requires a step change in the design and operating environment of the mechanical systems (e.g. higher temperature and contact pressure).

In the present work, a novel experimental test rig has been developed to rigorously investigate the evolution of the static and dynamic friction as well as the wear resistance of a tribological contact exposed to high temperatures (HT) for long period of time. Pin-on-Flat configuration has been adopted in the design with the flat sample being mounted in a furnace that heats up to 800oC. Here, we present an approach to assess static and dynamic friction, and we illustrate it by the results obtained on several materials including stainless steel and Inconel substrates with TiN- and CrN-based vacuum coatings deposited by magnetron sputtering. The measurements showed that a number of sliding cycles is necessary to reach a stable static and dynamic coefficient of friction (CoF). These sliding cycles could be performed uni-directionally or bi-directionally with no effect on the steady-state value of CoF. In addition, it was found that the HT exposure time with closed and stationary tribological contact increases significantly the static CoF which might be related to processes such as diffusion that take place at the interface. The HT tribological testing combined with detailed microstructural characterization of the wear scar (SEM, EDS and Raman spectroscopy) allowed to determine the friction and wear mechanisms. The oxide layer formed at HT was found to play a crucial role in the evolution of HT static friction.

9:20am **E3-TuM-5 Study of the a-C:H Coating Wear Behaviour in Boundary Lubricated Tribological Contacts Using Raman-Based Profilometry (Virtual Presentation)***, **Ardian Morina (A.Morina@leeds.ac.uk)**,* University of Leeds, UK*; N. Xu,* University of Leeds, UK , UK **INVITED**

While for ferrous boundary lubricated tribological systems, it is relatively well established that the tribofilms formed from lubricant additives determine friction and wear performance, the effect of lubricant additives on DLC coating wear performance and mechanisms is still not clear. The ability to quantify coating thickness as a function of testing time has the potential to provide new insights on the correlation between tribofilm formation and coating wear, enabling improved lubricant and coating designs.

In this paper, the development of a novel method for measuring coating thickness at the nanoscale level, with the potential to be used for in-situ wear measurement during the test, will be reported.The method is based on using a Raman-active coating underlayer as a sensor of the coating thickness.In this approach, the a-C:H coating is considered a light attenuating layer of the silicon underlayer. The method has been used to study the a-C:H coating wear rate from dry and a boundary lubricated system using molybdenum dialkyldithiocarbamate (MoDTC) additive. A two-stage wear progression mechanism has been proposed for the first time to clarify the detrimental effect of MoDTC-derived tribofilm on a-C:H wear by combining detailed structure and composition analysis. The results have also been supported by post-test Raman spectroscopy, optical profilometer, EELS and TEM analysis.

Keywords: wear measurement, coating, additives, Raman, solid-liquid lubricating

10:00am **E3-TuM-7 Erosion Resistance of TiAlN Coatings for Aerospace Applications***, **Zeliha Idil Kara (e194125@metu.edu.tr)**, S. Ozerinc,* Middle East Technical University, Turkey

Aircraft engine components are subjected to extreme conditions of stress and temperature, resulting in challenging materials requirements. An additional issue is erosion taking place in the air intake since the stochastic nature of the erosion makes the surface susceptible to the formation of micro-cracks, which can cause premature failure that can be catastrophic for the whole aircraft. An effective route to increase the resistance of the components against these harsh environments is the application of wear-resistant coatings. TiN & TiAlN-based coatings produced by physical vapor deposition are commonly preferred due to their low thickness, the ability to effectively coat complex shapes, and the additional advantage of providing resistance to corrosive environments. This study evaluated the characteristics and the performance of TiAlN PVD thin film coatings with an emphasis on erosion performance. Microstructural and mechanical characterization combined with erosion and corrosion testing provided insight into the performance of these coatings under the above explained harsh conditions. Single-layer (≈10 µm thick) TiAlN coatings were applied on the titanium substrates by the cathodic arc deposition method. The microstructure of the coatings was investigated by SEM and X-ray diffraction. The mechanical properties were determined by nanoindentation testing. The adhesion of the coating was examined by scratch tests performed according to EN ISO 20502 in a 10 to 50 N loading range. Solid particle erosion tests were performed according to ASTM G76 by using two different angles of particle impingement of the TiAlN thin film coating. Lastly, salt spray tests were performed according to ASTM B117 to quantify the corrosion resistance of the coatings. The results show that the TiAlN coatings have a high density and exhibit a cubic crystal structure with nanograins. The hardness and elastic modulus of the coatings were in agreement with the previously reported literature values. The erosion tests showed that the coatings dramatically reduce the erosion rate compared to uncoated specimens. The uncoated specimens showed severe surface roughness and crack formation whereas the coated surfaces were intact. Overall, the results demonstrate the effectiveness of the TiAlN coatings in reducing erosion and corrosion, making them suitable for aircraft engine applications. Future studies will focus on the further optimization of the coating composition and morphology for superior mechanical performance.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F2-1-TuM

High Entropy and Other Multi-principal-element Materials I

Moderator: Erik Lewin, Uppsala University, Sweden

8:20am **F2-1-TuM-2 Elaboration and Characterization of High Entropy Nitride Al-Ti-Zr-Ta-Hf (-N) Deposited by Reactive Magnetron Sputtering for High Temperature Applications***, **Djallel Eddine TOUAIBIA (djallel_eddine.touaibia@utt.fr)**, M. ELGARAH, S. ACHACHE,* LASMIS, France*; A. MICHAU, F. Schuster,* Commissariat à l'Energie Atomique et aux énergies alternatives (CEA) Saclay, France*; F. SANCHETTE,* University of Technology Troyes (UTT), France

AlTiTaZrHf(-N) high entropy nitrides films were deposited in various argon-nitrogen gas mixtures on glass and silicon substrates. X-ray diffraction analyses reveal a transition from amorphous to an FCC single phase by increasing the nitrogen content.

Films morphology is not influenced by nitrogen content, all films have a compact morphology. Energy dispersive spectroscopy analysis shows an increasing of the film nitrogen content when the flow rates ratio RN2=N2/Ar+N2 varies between 0 and 15% and stabilizes above. Evolution of hardness and Young's modulus are discussed and the maximum values are obtained for a flow rates ratio RN2 of 10% at 27.67 GPa and 205.56 GPa respectively. Chemical bonds and tribological performances will be discussed and high temperatures stability is investigated.

8:40am **F2-1-TuM-3 Strain-Stabilized Al-Containing High-Entropy Sublattice Nitrides***, **Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at)**[1], B. Hajas,* TU Wien, Institute of Materials Science and Technology, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; K. Yalamanchili, H. Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; M. Hans, J. Schneider,* RWTH Aachen University, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The impact of configurational entropy, enthalpy, and strain energy on the phase stability of high-entropy materials has not yet been investigated quantitatively. We used ab-initio calculations to predict the driving force for decomposition of 126 equimolar Al-containing high-entropy sublattice nitrides (HESN), which are all metastable with respect to all corresponding equimolar lower-entropy nitride phases. The entropy stabilization of ≈-0.06 eV/at at 1073 K is overruled by the 0.10-0.27 eV/at enthalpy-governed driving force for decomposition. Stabilization is however predicted for 22 compositions due to the -0.01 to -0.28 eV/at strain energy contribution caused by large differences in equilibrium volume between the HESN and their decomposition products. The predicted stabilities were validated with diffraction and tomography data of 9 annealed nitride systems. Hence, it is evident that only strain enables the stabilization of the here studied Al-containing HESN, while the entropic contribution is overruled by endothermic mixing.

[1] **Graduate Student Award Finalist**

9:00am **F2-1-TuM-4 Structural and Mechanical Properties Investigation of a New TiTaZrHfW(-N) Refractory High Entropy Films Deposited by Reactive Magnetron Sputtering***, **Abdelhakim Bouissil (abdelhakim.bouissil@utt.fr)**, S. Achache, F. Sanchette, M. El Garah,* LASMIS, Antenne de Nogent, Université de Technologie de Troyes, France

In the last decade, refractory high entropy thin films have attracted more attention due their superior proprieties at high temperatures [1]. Besides the thermal stability, these new materials present a good resistant to oxidation and can also keep good mechanical properties, high hardness and elastic modulus etc, at temperature up to 1600 °C, which is interesting compare to conventional alloys [2][3]. TiTaZrHfW(-N) films are synthesized by reactive magnetron sputtering in various argon plus nitrogen atmospheres. The microstructure, mechanical and thermal properties are investigated. Optical emission spectroscopy is performed to analyze the target nitriding conditions and to optimize the deposition parameters. The nitrogen flow rate ratio $R_{N2}=\Phi_{N2}/(\Phi_{N2}+\Phi_{Ar})$ is varied from 0 to 30%. XRD analyses show a transition from an amorphous structure to FCC single phased films once the nitrogen is added (5%). By increasing the nitrogen flow rate, preferential orientation from {111} to {200} is observed. The morphology of the films changes from compact to columnar when the nitrogen ratio exceeds 5%. The hardness and Young's modulus are also studied and the maximum values, 29 GPa and 257 GPa respectively, are obtained at R_{N2}= 9%. All nitrides show a good thermal stability under vacuum at 800 °C for three hours compared to metallic film, for which phase transition occurs.

[1] O. N. Senkov, D. B. Miracle, K. J. Chaput, et J.-P. Couzinie, « Development and exploration of refractory high entropy alloys—A review », *J Mater Res*, vol. 33, nº 19, p. 37, 2018.

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[3] O. N. Senkov, G. B. Wilks, J. M. Scott, et D. B. Miracle, « Mechanical properties of Nb25Mo25Ta25W25 and V20Nb20Mo20Ta20W20 refractory high entropy alloys », *Intermetallics*, vol. 19, nº 5, p. 698–706, mai 2011, doi: 10.1016/j.intermet.2011.01.004.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country C - Session G1-TuM

Advances in Application Driven Research: New Methods, Materials, and Equipment for PVD, CVD, and PECVD Processes

Moderators: Satish Dixit, Plasma Technology Inc., USA, **Martin Engels**, IonBond Inc., USA

9:40am **G1-TuM-6 Photons meet Plasma – Adding Value to your Al, Mg and Ti Components***, **Anna Buling (buling@ceranod.de)**, ELB Eloxalwerk Ludwigsburg GmbH, Germany; J. Zerrer,* ELB Eloxalwerk Ludwigsburg, Germany

PEO, plasma-electrolytical oxidation, remains as an unknown or at least niche surface technology, giving lightweight metals a hard and robust protection shell. Expiring an increasing interest in the research society in the last decade, it is supposed to be promising for increasing lightweight potential but being not ready for wide industrial applications, due to high costs or being applicable only on small series. In this talk we will refute these reservations by unveil high demand applications of our clients, who use our surfaces on their components under harsh conditions. The CERANOD® surfaces can withstand high vibration loadings providing a high corrosion and wear protection for alloys of Al or Mg. One of our automotive clients is using our technology on highly loaded components in the power train, whereas the second generation of a lager-volume production ist starting now, providing to the world's biggest OEMs. This illustrates that PEO is neither too expensive when hitting the demands nor a niche technology for very particular fields. In a further application case a Mg component modified by our ceramic atomic bonded surface found its way in large production series last year after being tested world-wide for several years in an innovative ICE application.

We will show application possibilities and different fields of our surface modification used industrial in tribological, corrosive and high temperature applications, whereas, e.g., maintenance-free power units can be realized.

Being convinced that facing the incessantly growing demands on sustainability, efficiently and endurance in automotive, aerospace and machinery applications, is only possible by lightweight, including multi-material mix, accompanied by the right solutions for the surfaces, we enhance our technologies. Most recently, we found that especially in the case of Aluminum casting alloys an adopted PEO process leads to positive tribological behavior in combination with novel low-viscosity oils. The utilization of Direct Interference Laser structuring and hybridizing with a solid lubricating polymer manifold the positive effect. A 1000-h wear test just being finished prior this submission proves a very promising solution with low friction and almost no wear.

We will report on wear and corrosion test results accompanied by SEM and EDS findings for different CERANOD® solutions. These findings will be compared and correlated with different application cases of our clients, who utilize our solutions on their end products to enable the usage of lightweight metals under harsh tribological, vibrating and /or corrosive environments, and, thus, saving a lot of energy and resources.

10:00am **G1-TuM-7 The Effect of Coating Conditions on the Life of PVD Coated Steel Rods Immersed in a Molten Aluminum Die Casting Alloy***, **Stephen Midson (smidson@mines.edu)**, N. Delfino de Campos Neto, W. May, A. Korenyi-Both, M. Kaufman,* Colorado School of Mines, USA

Die casting is a high-volume casting processes, where liquid metals (primarily alloys of aluminum, zinc or magnesium) are injected at extremely high speeds and pressures into re-usable, hardened steel dies. In commercial die casting operations, PVD coatings are applied to aluminum die casting dies to reduce the erosion of the steel die by the liquid metal, and to minimize soldering (sticking) of the solidifying aluminum to the die.While these types of PVD coatings are becoming relatively widely used, there is little rigorous data to identify the best coating conditions to maximize life of the coatings.This presentation will report on a laboratory study that examined the effect of coating conditions on coating life.Three conditions have been studied, coating thickness, substrate roughness, and the impact of nitriding the steel surface prior to the PVD coating.Using an accelerated test, 11 mm diameter rods of H13 steel PVD coated with CrN were rotated at 540 rpm in a crucible of molten aluminum A380 alloy held at 700°C.The rods were periodically removed from the melt (typically every 1-2 hours) to observe their condition, and it was found that the coatings would fail either close to the melt line or at the end of the rod, and once the coated failed the underlying steel was rapidly dissolved.The results of the testing will be reported in this presentation, along with metallography characterizing the conditions and failures of the coatings.

10:20am **G1-TuM-8 Carbon-Based Surface Solutions for High Performance Forming Tools - A Journey from Material Research to Industrial Solutions***, **Vishal Khetan (vishal.khetan@oerlikon.com)**,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, Switzerland **INVITED**

With rapid increase in use of non-ferrous materials especially aluminium in automotive industry, manufacturing challenges occurring from galling have become significant. Along with increase the service life of forming tools used for processing these materials, decreasing maintenance downtime and end product quality are key for good production reliability. Multiple strategies have been investigated both in academia and industry to mitigate these challenges. Some of them are reduction of surface roughness (Polishing of tools), Nitriding or Nitro carbonizing of tools (diffusion treatment) and more recently use of Carbon based coatings. Different carbon based coatings deposited by physical vapor deposition (PVD) or chemical vapor deposition (CVD) have been used for these applications. With appropriate pre and post treatment - They have helped significantly reducing galling in industry. The preferred choice of technique to deposit these coatings depends on the requirement of the application namely type and dimension of material being processed, surface roughness requirements and challenges involved in the technique to coat the tools to avoid adhesion challenges of the coatings owing to the geometry of the tools.

Owing to multiple factors involved in mitigating galling in non-ferrous materials forming - decision making to select an appropriate surface solution (a combination of coating and pre/post treatment before and after coating) needs significant trial in the form of Design of experiments or trial and error method which is time consuming and often makes decision making difficult for the OEM to select an appropriate solution in a cost effective way.

This presentation will focus on usage of a laboratory based tribological test which results in effectively evaluating adhesive wear in the system and provides appropriate insights into effectiveness of a total surface solution in an industrial application in short duration and being cost effective. The test rig presented is known as the load scanner rig which can effectively simulate the tendency of Aluminum sticking on to different substrate and suggest the effectiveness of the tooling system to provide an indication towards its effectiveness to a given application in Aluminium forming. They save time and resources needed for expensive production tests. Furthermore the tests also help the OEM or tool maker take correct decision on the type of carbon coating he needs to use for their specific alloy and tooling system. Hence, providing a pathway to maximize the cost benefit for their investment on a surface solution in a scientific way.

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-1-TuM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderators: James Gibson, RWTH Aachen University, Germany, **Olivier Pierron**, Georgia Institute of Technology, USA

8:00am **H2-1-TuM-1 Reflectance Anisotropy Spectroscopy and Microscopy for the Investigation of Ultrathin Films With Micron Resolution***, **Ralph Spolenak (spolenak@mat.ethz.ch)**,* ETH Zurich, Switzerland **INVITED**

Raman microscopy is the lab-scale gold standard for resolving stress distributions at the micron length scale. Unfortunately, the Raman effect is limited to polarizable materials, which typically excludes metals, an important materials class for both optical and plasmonic applications. Reflectance anisotropy spectroscopy (RAS) is, as our group recently demonstrated, sensitive to the effect of elastic distortion on the band structure of metals and thus allows for the determination of elastic strain.

While this is already valuable as an averaging technique further insight in both the plastic and brittle behavior of metals can only be gained on the local scale. Consequently, this contribution focuses on the development of a broad band RAS microscope, with the challenges of the broadening of the incidence angle as well as the accessible wave length range.

Our group is proud to present first results on pattering induced strain fields in gold thin films, the analysis of strain-engineered semiconductor devices and the observation of single plasmonic dipoles.

8:40am **H2-1-TuM-3 Combinatorial Mechanical Microscopy Using Correlated Nanoindentation Mapping and EDX***, **Jeffrey M. Wheeler (jeff.wheeler@femtotools.com)**,* FemtoTools AG, Switzerland

Mechanical microscopy is an emerging technique using high-speed nanoindentation to map the mechanical behavior and extract phase-level properties from complex microstructures with micron-scale lateral resolution. As such, it is a powerful technique for combinatorial materials science investigations on samples with compositional gradients, such as diffusion couples. In this work, correlated high-speed nanoindentation and energy-dispersive spectroscopy (EDX) were applied to investigate the Ni—Ta system. All seven phases in the system were clearly resolved in the resulting maps, and the mechanical properties and composition ranges for each phase were determined. Good agreement with *ab initio* calculations was generally observed with some exceptions, most notably $NiTa_2$. This was achieved using a simple correlation method utilizing directly overlaid data matrices to allow compositional labeling of mechanical data. This allowed easy data segmentation without requiring complicated statistical deconvolution methods. Without this correlative method, phase deconvolution of the Ni—Ta system would have been challenging due to several phases possessing adjacent compositions and mechanical properties. This demonstrates the potential of this new correlative approach for future investigations, particularly those involving complex microstructures and/or compositional variation.

9:00am **H2-1-TuM-4 Progress in the Development of High Strain Rate Nanoindentation Experiments***, **Warren Oliver (warren.oliver@kla.com)**,* KLA Corporation, USA*; C. Walker, B. Hackett,* Texas A&M University, Department of Materials Science & Engineering, USA*; P. Sudharshan,* International Advanced Research Centre for Powder Metallurgy & New Materials (ARCI) , India*; G. Pharr,* Texas A&M University, USA

High strain rate mechanical testing using instrumented indentation has recently received considerable attention. High strain rates as high as 10^4 are achievable at reasonable indenter velocities (on the order of 0.5 m/s) because the sample size is small. An instrument capable of displacement measurements at rates as high as 1.25 Mhz with sub nanometer resolution and a time constant of 10 microseconds has been constructed. The system also incorporates mechanics that allow the load frame to have a stiffness as high as 90 MN/m making the associated correction very small. While the system directly measures the displacement signal needed accurately, measuring the loads exerted on the sample in sub millisecond experiments can be challenging. In some cases, the time constant of the loading system must be considered. In addition, the load can be dominated by inertial effects. Dynamic models used to describe the system will be considered. A number of approaches for calculating or measuring the loads exerted on the sample will be discussed. Preliminary data for fused silica and Aluminum will be presented.

9:20am **H2-1-TuM-5 Testing the Adhesion of a Sintered Ag Film on a Cu Substrate Using Laser Shocks***, **Xavier Milhet (xavier.milhet@ensma.fr)**,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; T. de Resseguier,* institut pprime - CNRS - ENSMA - Université de Poitiers, France*; A. Sghuri,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; L. Signor,* institut pprime - CNRS - ENSMA - Université de Poitiers, France

Silver (Ag) paste sintering, is now used for die bonding in the latest generation of power electronic modules. Since the processing conditions require low temperature, low stress and short time, the Ag joints exhibit a porous structure that evolves significantly when exposed to the operating temperatures (between 250C and 300C) [1,2]. In order to model the behavior and properties evolution, there is a need for a fine characterization of the joint itself as well as those of the interface, especially during aging. While the first point has now been relatively widely investigated [3-5], the information on the interface properties is still scarce. In this study, we have explored an alternative route to test the adhesion of the Ag film on a copper (Cu) substrate using laser driven shocks: a laser pulse is calibrated to induce tensile loading near the interface between the substrate and the film, and time-resolved velocity measurements complemented by post-recovery observations provide quantitative information on the adhesive strength. Although such highly dynamic load is somewhat far from the practical application, this method presents the advantage over other techniques to really focus on the interface properties. The results are used to explore the relationship between adhesion, aging and the underlying microstructure.

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9:40am **H2-1-TuM-6 Transfer Learning in Characterization of Nanoindentation Induced Acoustic Events***, **Antanas Daugela (antanas_daugela@hotmail.com)**,* Nanometronix LLC, USA*; J. Daugela,* Johns Hopkins University, USA

A passive monitoring of acoustic waves during nanoindentation has been attracting the attention of material scientists since the inception of nanomechanical test instruments. The conventional acoustic wave signal treatment via RMS or integrated energy values proved that quantitative acoustic wave properties correlate well with the local contact materials' phenomena such as yield point initiation for W(100) [1, 2], Sapphire [3], phase transformations on SMA, and differentiating of thin film fracture modes.A nanofatigue phenomenon can be observed on thin films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves and post test imaging, which helps in identifying the materials' phenomena [4].However, the true potential of the acoustic characterization method is unleashed in the synergy between wavelet based acoustic signal decomposition and machine learning [5].

The Transfer Learning is a subclass of machine learning which utilizes existing Deep Learning Neural Networks [5].In this work, a Transfer Learning based signal classification of nanoindentation induced passive and active acoustic events is explored.Both passive and active acoustic monitoring can be conducted during nanoindentation with the integrated utrasonic tip.The proposed Transfer Learning technique yields a reliable classification of acoustic signatures on submicron thick coatings.

References:

1. A. Daugela et al, *Zeitschrift fur Metallkunde*, **92(9)**, p.1052-1056 (2001)

2. N. I. Tymiak et al, *Journal of Materials Research*, **18(4)** , p.1–13 (2003)

3. N.I. Tymiak et al, *Acta Materiallia*, **52** p.553-563 (2004)

4H. Kutomi et al, *Tribology International*, **36**, p.255-259 (2003)

5. A. Daugela et al, *Materials Science & Engineering A*, **800** 140273 (2021)

10:00am **H2-1-TuM-7 Nanoindentation Testing to Measure Surface Free Energy in Thin Films and Engineered Surfaces***, M. Sebastiani,* Università degli studi Roma Tre, Italy*; P. Phani,* International Advanced Research Centre for Powder Metallurgy & New Materials (ARCI), India*; **Edoardo M. Rossi (edoardo.rossi@uniroma3.it)**,* Università degli studi Roma Tre, Italy*; R. Guillemet,* Thales Research & Technology, France*; W. Oliver,* Nanomechanics Inc., KLA Corporation, USA

The ability to engineer and control the Surface Free Energy (SFE) of functional materials is critical for a multitude of applications as this property represents a relevant design parameter for producing components with precisely controlled interfacial performances. The non-destructive measurement of SFE in nanopatterned superhydrophobic hard surfaces is a challenge in both research and industry since, in most cases, time-consuming contact angle measurements (CAMs) are not feasible. Nanoindentation testing can offer a possible contact-mechanics methodology that allows measurement of intrinsic surface properties [1]. In this sense, a novel method has been developed for the assessment of the adhesive interactions by carefully controlling environmental and instrumentation issues. A commercially available nanoindenter has been specifically modified to enable accurate measurement of the pull-off forces raising between the tip and the sample surface. A novel testing protocol implementing adhesion-accounting contact mechanics models [2] has been developed to leverage the new hardware capabilities.

A set of reference surfaces was selected for testing and validation: (i) highly energetic, new, and atomically flat surfaces from cleavage of the silicate sheet-based structure of muscovite mica; (ii) DSP germanium <100> crystals. The latter yielded the pristine substrates for the development of superhydrophobic surfaces, via both patterning and fluorinate silane coating. Those processes performances were independently studied and, ultimately, their interplayed role was investigated on both nanopatterned and silanized substrates. CAMs were performed on all the surfaces investigated to provide comparative results. The method is found to measure SFE over five orders of magnitude, covering hydrophilic to super-hydrophobic surfaces.

[1] F. M. Borodich et al. Proc. R. Soc. A. 464, 2759–2776 (2008).

[2] K. L. Johnson et al. J. Colloid Interface Sci. 192, 326–333 (1997).

Topical Symposia
Room Town & Country A - Session TS6-2-TuM

A Session to Acknowledge the Contributions of Joe Greene to the ASED, ICMCTF, AVS, and IUVSTA II

Moderator: Scott Barnett, Northwestern University, USA

8:00am **TS6-2-TuM-1 Metal-Ion-Controlled Thin Film Growth: What Have We Learnt During the Last Decade?***, **Grzegorz (Greg) Greczynski (grzegorz.greczynski@liu.se)**,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; I. Petrov, J. Greene,* University of Illinois at Urbana Champaign, USA*; L. Hultman,* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

Ion irradiation is a key tool for controlling the nanostructure, phase content, and physical properties of refractory ceramic thin films grown by magnetron sputtering. Up until recently, gas ion irradiation was used to enhance adatom mobility in the surface region. Development of high power pulsed magnetron sputtering (HiPIMS), which provides metal-ion plasmas with tunable degree of ionization, enabled systematic studies of the effects of metal-ion irradiation on properties of refractory ceramic thin films. The original motivation for the use of metal-ions stems from the fact that they are film constituents, hence they can provide the benefits of ion-mixing (film densification at low film-growth temperatures) without causing the high compressive stresses associated with trapping of gas ions in interstitial sites. Since 2012 we have explored several pseudobinary TM nitride model systems including TiAlN, TiSiN, VAlN, TiTaN, TiAlTaN, and TiAlWN.[1] Experiments were carried out in a hybrid HiPIMS/DCMS configuration.[2]A substrate bias V_s was synchronized with the metal-ion-rich portion of the HiPIMS pulses to allow for a control of metal-ion energy, based on the input from time-resolved mass spectrometry analyses. This enabled us to suppress the role of gas ion irradiation and allowed us to study the influence of intense M_1^+ andM_2^+ metal-ion fluxes on film growth kinetics, microstructure, and physical properties over a wide range of M_1M_2N alloy compositions. We established that the effects of metal-ion irradiation depend on the mass of incident ion with respect to that of film constituents.Irradiation with lower-mass metal-ions (e.g. Al^+ or Si^+) results in the near-surface trapping with the depth controlled by the V_s amplitude. This enabled unprecedented control over the phase content of metastable ternary nitrides and the growth of NaCl-structure M_1M_2N solid solutions far above the M_1N concentration range achieved with DCMS.[3] At the other extreme, bombardment of the growing film surface with pulsed high-mass metal ion fluxes (e.g., W^+ or Ta^+) during HiPIMS/DCMS deposition of $Ti_{1-x}Ta_xN$, $Ti_{1-x-y}Al_xTa_yN$, and $Ti_{1-x-y}Al_xW_yN$ alloys provides fully-dense, low stress, films without intentional substrate heating. The high metal-ion mass irradiation leads to effective low-energy recoil generation that provide sufficient adatom mobility, necessary to obtain high-quality fully-dense films, in the absence of conventionally used resistive heating. Thus, the process energy consumption is greatly reduced, while the new possibilities open up for coating temperature-sensitive substrates.

8:40am **TS6-2-TuM-3 Predictive Kinetics-based Epitaxial Film Growth Modeling for the SiGe, Si:B and SiGe:B Systems**, ***Glenn Glass (glenn.glass@intel.com)***, Intel Corporation, USA **INVITED**

CVD growth of Si-based epitaxial thin films continues to hold relevance in industrial applications as well as a model system for scientific discovery. Observation of thin film growth rate trends from hydride precursors combined with quantitative temperature-dependent surface measurements of dangling bond reaction-site densities are combined as input parameters. We demonstrate a model with no fitting parameters that predicts film growth rates across a wide range of temperature, gas flow and flow ratios. The combination of surface bond density measurements (activation energy and frequency factor in the Polanyi–Wigner formalism) and growth rates provides insight into surface segregation behavior that can drive significant second-order effects including roughening and relaxation.

9:20am **TS6-2-TuM-5 Growth Kinetics of Spontaneous Superlattices, and Single Wall Carbon Nanotubes Using Gas Phase Precursors**, ***Yonglim Foo (Yonglim.Foo@SingaporeTech.edu.sg)***, Singapore Institute of Technology, Singapore **INVITED**

The segregation of C during $Si_{1-y}C_y$/Si(001) growth during gas-source molecular beam epitaxy, using Si_2H_6 and CH_3SiH_3 has a strong influence on the growth kinetics. During growth of the initial Si-rich layer, strain-driven C segregation to the subsurface results in charge transfer from surface Si atom dangling bonds to C backbonds. This decreases the Si_2H_6 sticking probability, and, hence, the instantaneous deposition rate, thereby enhancing C segregation. This results in an interesting observation, where alloy superlattice structures consisting of alternating Si-rich and C-rich layers form spontaneously during constant Si_2H_6 and CH_3SiH_3 precursor fluxes at Ts = 725–750 C. The Si-rich layer continues until a critical C coverage is reached allowing nucleation of a C-rich layer which grows until the excess subsurface C is depleted. The process then repeats with periods tunable through the choice of Ts and $y_{avg.}$

The second section of the talk will be on the early career research work by author, which is heavily influenced by Professor Joe Greene's attention to growth kinetics. The growth dynamics of a single-walled carbon nanotube (SWNT) was observed in real-time using an in situ ultrahigh vacuum transmission electron microscope at 650 °C. SWNTs preferentially grow on smaller sized catalyst particles (diameter ≤ 6 nm) with three distinct growth regimes (incubation, growth, and passivation). All of the observed SWNTs grow via a base-growth mechanism with C diffusion on active Ni catalyst sites. Under the same experimental conditions, formation of carbon nanocages was observed on larger Ni catalyst particles. The evolution of SWNTs or nanocages is dependent on catalyst size, and this can be rationalized from both energetics and kinetics considerations.

10:00am **TS6-2-TuM-7 Engineering of Soft Materials for Stretchable Electronics**, ***Nae-Eung Lee (nelee@skku.edu)***, Sungkyunkwan University, Korea (Republic of) **INVITED**

Stretchable electronics is promising for wearable sensor applications. In particular, wearable sensor devices with a form factor of skin-attachable patch which can sense skin strains, monitor vital signs and detect biomarkers from collected body fluids for disease diagnostics, and can be also used to detect the hazardous environmental factors around human have been extensively investigated. For successful implementation of various components into such stretchable skin-attachable sensor patches, engineering of soft substrates and functional materials is of great importance for skin-conformality, durability, stability, and minimal strain-induced signal interference. In this presentation, structural engineering of conventional elastomeric substrates and synthesis of intrinsically stretchable materials for application to stretchable electronics will be discussed. Firstly, structurally engineered substrates of mogul-patterned, trench-patterned, or skin-mimicking elastomers which can mitigate the stress level on the functional layers on them have been designed and developed. The applications of the structurally engineered elastomeric substrates to stretchable physical sensors (strain, pressure, and temperature), chemical sensors (gases) and biosensors (protein, enzyme) by employing low-dimensional nanoscale materials (0D, 1D and 2D), nanocomposites and their hierarchical nanohybrids onto them will be highlighted. Secondly, I will present the synthesis of intrinsically stretchable, transparent, and tough copolymer substrate with excellent temperature and chemical resistance applied to stretchable substrate and microfluidics. In addition, other forms of intrinsically stretchable functional materials such as stretchable solid or hollow microfibers with biodegradability or conductivity will be also demonstrated for electrode materials or microfluidic channel materials for stretchable bioelectronics.

Exhibitors Keynote Lecture
Room Town & Country A - Session EX-TuM

Exhibition Keynote Lecture
Moderator: Grzegorz (Greg) Greczynski, Linköping University, Sweden

11:00am **EX-TuM-1 Fabrication and Characterization of Industrially Important Films and Coatings**, ***Vincent S. Smentkowski (smentkow@ge.com)***, GE Research, USA **INVITED**

General Electric – Research (GE-R) has been the center of innovation for the GE businesses and strategic partners for more than a century. Our mission is to see, move, and create a brighter future through innovation. In 2018,GE-Research made a strategic decision to expand our collaboration with external partners to develop advanced and differentiating technologies in the areas of materials development, characterization, and analytics. I will highlight novel capabilities for film/coating deposition and how advanced characterization provided solutions and solved a problem that enabled important industrial-technological breakthroughs and ultimately the development of new/improved products. The presentation will focus on the characterization of both surface and sub-surface layers.

Coatings for Use at High Temperatures
Room Town & Country D - Session A2-1-TuA

Thermal and Environmental Barrier Coatings I

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Pantcho Stoyanov**, Concordia University, Canada

1:40pm **A2-1-TuA-1 Mechanisms of CMAS Attack on Aero-Engine Components***, Elisa Zaleski (elisa.zaleski@pw.utc.com),* Pratt & Whitney, USA **INVITED**

Gas turbine engines operating in hot, sandy environments ingest siliceous debris termed CMAS for calcium magnesium aluminosilicate (CMAS). This siliceous material deposits on the surface of hot section components leading to premature degradation of these materials. As engine temperatures rise, CMAS-induced failures accelerate, leading to the need for more robust, capable mitigation strategies. This talk will focus on the aspects and mechanisms of CMAS attack most relevant to gas turbine engines.

2:20pm **A2-1-TuA-3 A New Approach to Protect Thermal Barrier Coatings (TBCs) Using Air Plasma Spray (APS)/High-Velocity Oxygen Fuel (HVOF) Coating of Si_3N_4***, Said Bakkar (sbakkar@udallas.edu), E. Zucha, J. Moldenhauer, E. Steinmiller,* University of Dallas, USA*; T. Hossain,* Ceriumlab , USA*; W. Flanagan,* University of Dallas, USA

Gas Turbine Engines (GTEs) operate at high temperatures, submersed in a high-density gas. Thermal barrier coatings (TBCs) are widely used to protect the engine superalloys from oxidation and other degradation. TBC is a compound of Yttrium stabilized zirconia (YSZ). These TBCs are vulnerable to Calcium–Magnesium–Alumino–Silicate (CMAS) deposits and volcanic ash penetration. A new approach of protecting the topcoat of the TBC from the infiltration of molten CMAS was explored using various thicknesses of silicon nitride Si_3N_4 to work as a sacrificial/Impermeable layer. The High-Velocity Oxygen Fuel (HVOF) and Air Plasma Spray (APS) coating techniques were used and the CMAS test was performed using torch and furnace techniques at 1250 °C. The blocked CMAS infiltration in this approach was investigated using XRD, SEM, TEM techniques.

2:40pm **A2-1-TuA-4 Development of a Low Power Plasma Reactor for the Local Deposition of YSZ Thermal Barrier Coatings at Atmospheric Pressure***, Sandra Segondy (sandra.segondy@chimieparistech.psl.eu),* Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), France*; C. Rio, S. Landais,* ONERA, DMAS, Université Paris-Saclay, France*; C. Guyon, F. Rousseau,* Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), France

Repair methods are of great interest for the aeronautic industry, especially for gas turbines. Deposition techniques that can quickly and easily repair small and localized damaged areas of Thermal Barrier Coatings (TBCs) located on combustion chambers could be economically interesting. In a first approach, a Low-Power Plasma Reactor (LPPR) working at low pressure (< 1000 Pa, 240 W) and using solution precursors was tested to locally deposit performant Yttria Stabilized Zirconia (YSZ) as TBC. Highly porous TBCs exhibiting low thermal conductivity were deposited, however, vacuum conditions were difficult to implement at an industrial scale. For this reason, a new version of LPPR working at atmospheric pressure with solution precursors was investigated.

The plasma torch (AcXys Plasma Technologies) based on a non-thermal rotating arc technology was mounted on a 3-axis motorized table (**Fig. 1**). The plasma discharge was generated in the reactor by AC electrical power with a frequency of 80 kHz. Operating power ranged between 600 – 1000 W using air as the discharge gas (gas flow rate: 35 slpm). The precursors were composed of zirconium and yttrium salts in aqueous solution. The liquid precursors were injected (solution feed rate: 1 mL/min) in the plasma afterglow to be sprayed and deposited onto superalloy substrates (with or without a MCrAlY bond coat) to form a TBC. Because the afterglow temperature was colder than in the case of thermal spray processes (T < 1000 °C), the spray distance was lower than 10 mm. Therefore, the YSZ deposition could be done locally in hard-to-reach regions through this low power plasma.

FTIR analysis was used to evaluate the ratio of produced oxides over the remaining precursors. The coating microstructural characteristics and the porosity were assessed by SEM observations. The composition and crystalline structure were determined by EDX and XRD respectively. The YSZ coatings exhibited the expected stoichiometry, a precursor conversion of 98 mol%, a tetragonal structure (**Fig. 2**), a good adherence to the substrate and a porosity evaluated around 30 vol%. In addition, the thickness of the YSZ coating could be higher than 100 µm in less than 1 hour (**Fig. 3**). The coating morphology seemed to exhibit two different microstructures depending on the deposition conditions: a more porous morphology closer to a columnar structure and a denser and granular microstructure (**Fig. 4**). The impact of the coating deposition conditions explaining these two different microstructures is currently under investigation.

3:00pm **A2-1-TuA-5 Oxidation Behaviour and Mechanical Properties of Sputter-Deposited $TMSi_2$ Coatings (TM = Mo, Nb, Ta)***, Ahmed Bahr (ahmed.bahr@tuwien.ac.at),* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; S. Richter, T. Glechner, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; J. Ramm,* Oerlikon Surface Solutions AG, Liechtenstein*; O. Hunold,* Oerlikon Surface Solutions AG , Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

High temperature environments not only involve materials with excellent creep properties, but also highest oxidation resistance and chemical inertness. Transition-metal disilicides ($TMSi_2$) based thin films are suggested as promising candidates for novel protective coating materials used in various high temperature applications. $TMSi_2$ exhibit an attractive mix of highest phase stability, reasonable mechanical properties and outstanding oxidation resistance.

In this study, we investigated the role of Si on the phase formation and oxidation kinetics of sputter-deposited $TMSi_2$ (TM = Mo, Ta, Nb) films. The coatings were analyzed in terms of chemical composition, phase constitution, and mechanical properties (i.e. H and K_{IC}) using diverse high-resolution characterization techniques. Moreover, the oxidation kinetics were systematically studied for all three systems at different temperature regimes up to 1400 °C. These analyses were supported by a detailed structural and morphological characterization of oxide scales formed.

4:00pm **A2-1-TuA-8 New Hydrogen Barrier Coatings***, Akram ALHUSSEIN (akram.alhussein@utt.fr), I. LAKDHAR,* University of Technology of Troyes , France*; J. CREUS,* La Rochelle University , France

The interaction of hydrogen with different metallic materials was reported and discussed in the literature. It has been found that hydrogen affects significantly the mechanical properties. This smallest chemical element penetrates into the metallic structure and reduces its ductility and loading capacity [1].

Coatings present a great solution to protect a material and give it multifunctional properties. Coatings are widely considered as a good solution to design hydrogen barriers in order to trap the adsorbed hydrogen and avoid its diffusion towards the substrate through the interface.

The objective of our work is the development of new generation of hydrogen barrier coatings to protect metallic components used in hydrogen atmosphere. After three years of working on this research project, we successfully developed a new AlTiW thin film deposited by magnetron sputtering technique [2]. The deposition rate was controlled to obtain 4 µm as an uniform film thickness.

The functional properties of coating such as corrosion properties and thermal stability as well as its protective performance for steels in a hydrogen environment were investigated. The influence of tungsten content on the microstructure, thermal stability, mechanical properties, corrosion resistance and hydrogen permeation inhibition of the coating was analyzed.

XRD, DSC and TEM analyses were carried out to check the amorphous state of the coating and to determine the glass transition and crystallization temperatures. These later were increased with the increase of W concentration up to 17 at%. On the other side, the corrosion resistance in a saline solution was decreased. The addition of W led to increase the coating mechanical properties (hardness and Young's modulus).

Chemical and electrochemical hydrogen charging methods were carried out to expose coated steels to hydrogen. The tungsten incorporation in the binary AlTi coatings highly improved their resistance to hydrogen absorption. The results obtained confirm that the $Al_{45}Ti_{38}W_{17}$ coating presents the best hydrogen barrier behavior.

In the near future, we will focus on the enhancement of the coating efficiency and the development of other nanostructured coatings for using in different real conditions.

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4:20pm **A2-1-TuA-9 Dual–Layer PVD Coating System With Integrated Diffusion Barrier for Oxidation Protection of γ–Tial Based Alloys***, **Peter-Philipp Bauer (peter-philipp.bauer@dlr.de)**,* German Aerospace Center, Germany*; R. Swadźba,* Łukasiewicz Research Network - Institute for Ferrous Metallurgy, Poland*; L. Klamann, N. Laska,* German Aerospace Center, Germany

Titanium aluminides are used as structural materials for turbine blades in jet engines due to their low density and the resulting weight reduction. However, their application is limited to service temperatures below 800 °C due to insufficient oxidation resistance. A feasible way to increase the service temperature is the application of Al-rich oxidation protective coatings to ensure the formation of a thermally grown alumina layer. Nevertheless, interdiffusion processes, especially of Al, between the intermetallic coatings and the TiAl-based substrate materials have detrimental effects on the coating as well as on the substrate alloy. Therefore, the interdiffusion processes should be suppressed or at least reduced.

In the present work, the properties of a 1 µm thick layer of the Ti_5Si_3 phase as a potential diffusion barrier for an afterwards applied oxidation resistant Al–Ti coating was investigated. For this purpose, DC magnetron sputtering was used to deposit a coating of partially crystalline Ti_5Si_3 phase prior to the deposition of an Al_2O_3 forming Al-30Ti (in at.%) top layer. The deposition was performed as a one-batch process in an industrial scale multisource sputter coater. This allowed depositing the Ti_5Si_3 interlayer from pure Ti and Si targets. Afterwards, the Al-30Ti top layer was deposited in the same sputter process by changing the substrate position and using Ti and Al targets.

Cyclic oxidation tests at 900 °C for 1000 cycles (1 h each) combined with thermogravimetric analysis were performed in laboratory air in order to study the oxidation behavior of the coating systems. The morphologies of the coating systems and the microstructural development during the oxidation tests were investigated by scanning electron microscopy and high-resolution transmission electron microscopy. The intermetallic phases and the phase evolution were monitored by in–situ high temperature x-ray diffraction as well as standard x–ray diffraction.

The results show that the Ti_5Si_3 phase could effectively slow down the Al depletion in the Al-30Ti at.% coating due to minor Al inwards diffusion into the γ–TiAl substrates. As a result, the dual–layer coating system provided a high oxidation resistance due to the long-term stable formation of thermally grown alumina on the surface. The stability of the interlayer of the Ti_5Si_3 phase was excellent and it was still present even after 1000 1-h-cycles of oxidation at 900 °C without any changes in thickness. In contrast, the single layer coating of Al-30Ti suffered from breakaway oxidation after already 800 cycles of exposure to 900°C in air.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-4-TuA

Properties and Characterization of Hard Coatings and Surfaces IV

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

4:40pm **B4-4-TuA-10 Synthesis by CVD and Properties of Polycrystalline Silicon Coatings for Structural Applications***, **Axel Le Doze (ledoze@lcts.u-bordeaux.fr)**, G. Couégnat, J. Danet, F. Rebillat, G. Chollon,* LCTS, CNRS, Univ. Bordeaux, CEA, SAFRAN CERAMICS, France

Environmental barrier coatings (EBCs) are used to limit the oxidation/corrosion of ceramic matrix composites. The silicon bond coat (BC) is a key component of the EBC system. In use, the silicon BC oxidizes to form a silica layer (TGO) at the EBC/BC interface. For high temperature applications, excessive creep may lead to unacceptable deformation of the system and impede its use as coating for rotating parts with high centrifugal loads. It is therefore crucial to control the creep behavior of the BC. Currently developed by plasma spraying, the silicon BC is composed of micrometric grains. Tailoring the silicon microstructure could be an efficient way to adjust the creep behavior of the BC. Chemical vapor deposition (CVD) is a process that allows the coating microstructure to be varied.

In this work, the CVD of polycrystalline silicon from $SiHCl_3/H_2$ was explored in details and a selection of coatings were prepared on various substrates for testing. A microbalance and FTIR spectrometer were coupled to the reactor to monitor deposition kinetics and the composition of the exhaust gas. The morphology and microstructure of the deposits were investigated by SEM (grain size, surface roughness) and EBSD (grain size and orientation, texture), and the creep properties by high temperature flexural tests (3-point bending). The oxidation/corrosion kinetics of the deposits were also evaluated *post mortem* after annealing in a corrosion furnace at controlled H_2O pressure and gas flow.

Several microstructures were obtained by varying the CVD conditions (temperature, pressure, total gas flow, $H_2/SiHCl_3$ ratio) and thermal annealing. Distinctive responses of the silicon coatings to mechanical stresses have been measured, illustrating different deformation mechanisms (intra-granular dislocations, diffusion at grain boundaries). This work confirms that the creep behavior of polycrystalline silicon is strongly dependent on the microstructure (grain size/orientation, nature and proportion of grain boundaries). The oxidation/corrosion tests show that oxidation kinetics are relatively independent of the microstructure.

In conclusion, a wide variety of microstructures can be obtained by CVD and thermal annealing. They result in creep behavior that can vary considerably, but similar corrosion rate. The thermomechanical properties of CVD Si can be readily modulated without compromising its corrosion resistance.

5:00pm **B4-4-TuA-11 Erosion Resistance of Thin Films Under Solid Particle Flows and Temperature***, **Kai Treutler (treutler@isaf.tu-clausthal.de)**, J. Hamje,* Clausthal University of Technology, Germany*; T. Bick,* Clausthal University of Technology, Clausthal, Germany*; V. Wesling,* Clausthal University of Technology, Germany

Components such as turbine blades are often provided with protective coatings to protect them from wear. These are usually ceramic or metallic coatings that can be applied using the PVD process, for example. While hard ceramic coatings are very effective for sliding wear, soft coatings with a metallic character are better for impact wear. The aim of the investigations presented is the characterization of metallic-ceramic coatings under particle jet wear at elevated temperatures. The presented coatings offer the advantage that they can be converted to a ceramic state with the aid of heat treatment. If the heat treatment is carried out by means of a laser beam, the coating properties can be influenced locally and adapted according to the stress. The wear behaviour of f.e. Ti-Si-C and Ti-Si-B coating systems will be presented below at angles of incidence of 30°, 45° and 60° and an abrasive mass flow rate of 9 g/min. For this purpose, the surfaces were irradiated at room temperature and 200°C with a mixture of clay dust and quartz powder, and the abrasion was determined gravimetrically.

Coatings for Biomedical and Healthcare Applications
Room Pacific D - Session D3-TuA

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

Moderator: Danieli B.C. Rodrigues, University of Texas at Dallas, USA

1:40pm **D3-TuA-1 Enhanced Mechanical Properties and Microbiological Behavior of a Ag-C:H Coating Produced by Reactive pDCMS***, N. Fukumasu, **Pâmella Esteves (pamellaesteves@usp.br)**, V. Malaquias,* University of São Paulo, Brazil*; E. Prados,* Federal University of ABC, Brazil*; M. Hirata, A. Tschiptschin, I. Machado, R. Souza,* University of São Paulo, Brazil

Surfaces presenting antimicrobial activity became more relevant during the COVID-19 outbreak, in which restricting the spread of virus and bacteria agents become important in crowded places, such as hospitals and public transportation. Literature reports the use of metallic coatings, such as silver and/or copper, promote excellent antimicrobial activity but present lower adhesion and mechanical properties, mainly when compliant substrates are used. Nanocomposite coatings based on silver and carbon may be applied to improve such characteristics, preserving the antimicrobial activity. The deposition of carbon coatings, using physical vapor deposition techniques, may require high substrate temperature (>200ºC) for long periods of deposition time (>1h), which is not suitable for overall polymer substrates. In this work, the pulsed direct current magnetron sputtering (pDCMS) technique was applied to produce Ag-C coatings on PMMA-based substrates. High purity silver and carbon targets were used to produce Ag and Ag-C coatings using Ar as plasma gas. In addition, a mixture of Ar+H allowed the production of Ag-C:H coatings. The mixture of Ar+H was applied only during the carbon deposition phase to enhance the coating growth rate and promote additional features, including a higher degree of sp_3 carbon bonds, which improves mechanical properties. All coatings were analyzed using Raman spectroscopy, XPS, instrumented indentation, scratch test, SEM+EDS and microbiological tests (*E. Coli* and Sars-CoV-2). Results indicate that Ag-C coatings presented an increase in hardness and substrate adhesion, but lower antiviral and bactericidal activity when compared with pure Ag coating with similar thickness. Nevertheless, the use of Ar+H mixture, in which H_2 acted as a reactive gas during the deposition of the amorphous carbon, resulted in an Ag-C:H coating with higher mechanical properties while presenting improved antiviral and bactericidal effects than pure Ag coating.

2:00pm **D3-TuA-2 Coating of Titanium Surfaces with Silver-Chitosan using Silane Linkers***, **Emily Coleman (cclman22@memphis.edu)**, E. Abuhussein, M. Edwards, J. Bumgardner, J. Jennings,* University of Memphis, USA

Titanium implants and instruments are widespread in the field of orthopedics due to the material's strength, resistance to corrosion, and bone-like mechanical properties. Silver ions have broad spectrum antimicrobial properties against bacteria and fungi and thus are advantageous as an implant coating in combination with chitosan biopolymer. Previous titanium coating attempts with chitosan-silver solutions gave weak adherence to the substrate and removal of the coating after contact with saline. In the current study, methods were demonstrated for attaching chitosan-silver conjugates to titanium using silane linkers to increase stability and adherence of the coating. Titanium coupons were polished and sonicated in soapy water to remove oil and residue, then in acetone and ethanol. The coupons were covered in sodium hydroxide (5 M) for 24 hours at 60°C to allow the titanium surface to accumulate hydroxide reactive groups. After rinsing with deionized (DI) water, the coupons were immersed in a 95% (v/v) ethanol solution (pH = 4.5). Using a nitrogen environment glove box, the silanization agent was added to create a 2% (v/v) silane solution in ethanol. Non-adhered silane was removed with ethanol, and coupons were dried at 110°C for 10 minutes before addition of chitosan silver (Chitozan Health, LLC). After drying overnight, coupons were immersed in phosphate buffer for 1 hour before rinsing with DI water and drying fully. To evaluate the bonding strength between the titanium coupons and the chitosan coating, Instron mechanical testing with a custom fixture was performed on coupons that were glued to pegs using GorillaWeld Steel Bond Epoxy Two Part Adhesive. Electron dispersive spectroscopy (EDS) was used to evaluate the success of the coating process by determining the presence of silver after 24-hour aqueous exposure. The mechanical testing suggested that the coating process was successful, and coating-adhesive strength exceed the adhesive strength of the glue-peg interface. EDS results indicated that the amount of silver on the surface of silanated coupons (10-15%) was significantly greater than non-silanated coupons (<1%), and the silver was homogenously distributed on the silanated coupon surface (**Figures 1 and 2**). Overall, results suggest that the silanation procedure for coating titanium surfaces promotes retention of silver on the titanium surface. Further studies are planned to assess the antimicrobial efficiency over time and human cell compatibility of the coatings. Coating strategies could be implemented with many application methods including dip coating, solution casting, electrospraying, and electroplating.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E1-1-TuA

Friction, Wear, Lubrication Effects, and Modeling I

Moderators: Noora Manninen, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, **Andreas Rosenkranz**, Andreas Rosenkranz, Universidad de Chile

1:40pm **E1-1-TuA-1 2D Transition Metal Carbide MXenes: Their Synthesis, Tunable Compositions and Mechanical Properties***, **Babak Anasori (banasori@iupui.edu)**,* Indiana University-Purdue University , USA*; B. Wyatt,* Indiana University-Purdue University, USA **INVITED**

Two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides, known as MXenes, have evolved as competitive materials and fillers for developing composites and hybrids for different applications. MXenes are denoted by a chemical formula of $M_{n+1}X_nT_x$ (n = 1 to 4), where M represents n+1 layers of early transition metals (groups 3 – 6 of the periodic table) which are interleaved by n layers of X, where X represents carbon or nitrogen. In addition, T_x represents surface terminations bonded to the outer M layers of MXenes, where T are generally a mixture of –O, –F, –(OH), or –Cl surface groups. MXenes are synthesized via a top-down topochemical etching of their precursor carbides and nitrides, such as MAX phases. MXene flakes have strong mechanical properties (330 ± 30 GPa and 386 ± 13 GPa for $Ti_3C_2T_x$ and $Nb_4C_3T_x$, respectively), which make MXenes the stiffest solution-processable 2D nanomaterials to date. The current forty synthesized MXene compositions paired within-depth ability to control their composition and structure makes MXenes a unique family of 2D materials with unlimited number of compositions and tunable properties. In this talk, we provide an overview of different MXenes compositions, their synthesis, and MXenes' mechanical properties and discuss the effects of MXenes' compositions, synthesis, and processing steps on their mechanical properties.

Keywords: MXenes, 2D materials, carbides, mechanical properties, composites.

2:20pm **E1-1-TuA-3 Grain Boundary Sliding and Low Friction in BCC Metals***, **Michael Chandross (mechand@sandia.gov)**,* Sandia National Laboratories, USA*; A. Hinkle,* CCDC & CBC, Aberdeen Proving Ground, USA*; M. Jones, P. Lu,* Sandia National Laboratories, USA*; N. Argibay,* Ames Laboratory, USA **INVITED**

We show evidence of low friction in BCC metals through molecular dynamics simulations and ultra-high vacuum experiments. This is shown to be correlated with grain boundary sliding (GBS) as the primary mechanism of deformation. Specifically, when grain sizes at the sliding interface are smaller than a critical, material-dependent value (on the order of 10-30 nm), a crossover occurs from dislocation mediated plasticity and Hall-Petch strengthening to GBS and interfacial softening. Results from simulations and experiments are quantitatively compared to a new predictive model of shear strength.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the US Department of Energy's National Nuclear Security Administration under Con- tract No. DE-NA0003525. This work was funded by the Laboratory Directed Research and Development (LDRD) program. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the US Department of Energy or the United States Government.

3:00pm **E1-1-TuA-5 Evaluation of Tribocoatings in Low Viscosity Fuels***, **Maddox Dockins (maddoxdockins@gmail.com)**, A. Ayyagari, S. Srivilliputhur,* University of North Texas, USA*; S. Berkebile,* US DEVCOM Army Research Laboratory, USA*; D. Berman, A. Voevodin, S. Aouadi,* University of North Texas, USA

M. Dockins[1], A. Ayyagari[1], S. Srilliviputhur[1], S.P. Berkebile[2], D. Berman[1], A.A. Voevodin[1], S.M. Aouadi[1]

[1]Department of Materials Science and Engineering, University of North Texas, Denton, TX 76203, USA

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Degradation of sliding surfaces creates a significant problem for mechanical assemblies. In the case of next generation fuel delivery systems, steel on steel contacts in low viscosity fuel environments have been shown to experience scuffing failure after extended operation under rough conditions, as well as poor general tribological performance. To prevent this scuffing-induced failure, various surface modification techniques were implemented, such as the application of carbide- and nitride-based protective coatings via PVD and plasma spray methods. These surface modification techniques were evaluated in various fuel environments and counterbody compositions using a high frequency reciprocating rig tribometer in a sliding velocity range of 0.2 to 0.6 m/s and contact pressures ranging from 500 to 1200 MPa. Their relative performance was evaluated according to their wear rates, average coefficient of friction, and oxidation as determined via SEM/EDS. These results were explained theoretically through density functional theory calculations that quantify the effect of surface interactions with the fluid.

4:00pm **E1-1-TuA-8 Phototribology: Control of Friction by Light***, B. Perotti,* UCS, Brazil*; A. Cammarata,* Czech Technical University in Prague, Czech Republic*; F. Cemin,* Université Paris-Saclay and UNICAMP, Brazil*; S. Sales de Mello,* UCS and UNICAMP, Brazil*; L. Leidens,* UCS, Brazil*; F. Echeverrigaray,* UCS and UNICAMP, Brazil*; T. Minea,* Université Paris-Saclay, France*; F. Alvarez,* UNICAMP, Brazil*; A. Michels,* UCS, Brazil*; T. Polcar,* University of Southampton and Czech Technical University , UK*; **Carlos Figueroa (cafiguer@ucs.br)**,* UCS, Brazil

Friction phenomenon is a complex manifestation of nature originated in energy dissipation events owing to the mechanical lost work of non-conservative forces. It is a property influenced by contact area, normal force, surface chemistry, mechanical properties, among others. There are several ways of tuning friction, all of them nonreversible processes. Thus, the active control of friction though external sources is a challenge in tribology. In this study, we report active control of friction forces at the nanoscale in TiO_2 thin films (anatase) obtained by HiPIMS as a function of the presence or absence of UV radiation (λ = 365 nm and nominal power of 5 mW) by friction force microscopy (FFM). According to the effects, this phenomenon of light-matter interaction is reversible, stable, and can be tuned/controlled by UV light. The radiation incidence modifies the physicochemical interactions at the sliding interface in TiO_2 thin films bringing on a dramatic reduction of frictional force of up to 61%. To understand the energy dissipation process, the characteristic frequencies of the system were analyzed; to this aim, atomic force microscopy signals were measured by wavelet analysis. The results show that the surface activation by UV light reduces the dissipated energy. *Ab initio* simulations were used to corroborate that the electron excitation augments the electronic density on the material surface. According to these results one can conclude that the reduction in friction is a result of the lower atomic orbital overlapping on the surface. These findings contribute to a new conceptual framework in tribology where light may be defined as a fourth body and the integration of tribology with photonics and optoelectronics providing a promising direction for applications in micro- and nano-opto-electromechanical systems.

4:20pm **E1-1-TuA-9 Development and Evaluation of Self-Lubricating Nanocomposite Coatings for Metal Forming Dies***, **Jianliang Lin (jlin@swri.org)**,* Southwest Research Institute, San Antonio Texas, USA

Die failure in metal forming industry results in substantial losses of time and money. Conventional lubricants are widely used for die release as well as for cooling assistance on the die surface. However, lubrication is difficult at high temperatures. Oxidation and scaling occur on the work pieces that lead to poor surface finish and possible warping of the material during cooling. The aim of the research is to develop a self-lubricating nanocomposite coating system for metal forming die components and investigate the self-lubricating behavior and thermal stability of the coatings at elevated temperatures. The designed coating systems consist of a nanocomposite matrix doped with solid lubricant phases, e.g. noble metals and amorphous carbon. The composite structure offers multifunctionality, including high wear resistance, good oxidation resistance, crack resistance, and self-lubricating properties at elevated temperatures. In this study, different nanocomposite coating matrixes, e.g. TiSiCN and CrAlN, were doped with different levels of Ag. The coatings were deposited by high power impulse pulse magnetron sputtering (HiPIMS) assisted by hot filaments. The elemental composition, phase structure, microstructure, adhesion, and mechanical properties of the coatings were studied by different means. The tribological properties and self-lubricating behavior of the coatings were evaluated using a high temperature tribometer at 700 °C. The thermal stability and thermal shock resistance of the coatings were evaluated using thermal cyclic test by cycling the coatings from RT to 700 °C with a testing cycle up to 1200 cycles. The results showed that the density and adhesion of all coating systems decreased as the Ag content increased in the coatings. The lowest COF of 0.1 was achieved in the coatings at 700 °C. Excellent thermal stability and thermal shock resistance, and high temperature lubricity were observed in the coatings with an optimal Ag content.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F2-2-TuA

High Entropy and Other Multi-principal-element Materials II

Moderator: Erik Lewin, Uppsala University, Sweden

2:00pm **F2-2-TuA-2 Structure and Properties of Refractory MoNbTaW+X (X = Ti,V,Cr,Mn,Hf) High Entropy Alloy Thin Films Deposited by HiPIMS***, G. Gruber,* Montanuniversität Leoben, Austria*; A. Lassnig, S. Zak, C. Gammer, M. Cordill,* Austrian Academy of Sciences, Austria*; **Robert Franz (robert.franz@unileoben.ac.at)**,* Montanuniversität Leoben, Austria

Refractory high entropy alloys (HEAs) represent a new class of materials that show promising properties, such as high hardness, good thermal stability and sluggish diffusion, which makes them suitable for various potential applications. Within this study a series of refractory HEAs was deposited using high power impulse magnetron sputtering keeping the base alloy MoNbTaW constant and adding a fifth element: Ti, V, Cr, Mn or Hf. The targets used for the synthesis of each alloy contained all five elements in an equimolar concentration. As analysed by X-ray diffraction and transmission electron microscopy, all films showed a bcc solid solution phase structure in as-deposited state. Further, the thermal stability of the films was analysed by annealing in vacuum up to 1200 °C revealing that the bcc phase is stable to a temperature of at least 1000 °C. Changes in the residual stress state and mechanical properties due to annealing were studied by the wafer curvature method and nanoindentation, respectively. The performed work is intended to contribute to a comprehensive understanding about phase and thermal stability of refractory HEA thin films.

2:20pm **F2-2-TuA-3 Effect of Rare-earth yttrium Addition on Microstructure and Thermal Stability of Refractory TiTaZrHfW High Entropy Film***, **Mohamed EL GARAH (mohamed.el_garah@utt.fr)**,* University of Technology of Troyes , France*; L. PATOUT, A. CHARAI,* Aix Marseille University , France*; F. SANCHETTE,* University of Technology of Troyes , France

High entropy alloys (HEAs) are of considerable interest due to their superior properties. Since 2004, they are defined as quasi- or equimolar alloys and they consist, at least, of five elementary elements with an atomic percentage ranging from 5 to 35 at.% [1-3]. High Entropy Films (HEFs) have been also reported to have excellent properties such as good wear [4] and corrosion resistance [5] and excellent thermal stability [6]. Rare earths have excellent physical and chemical properties. They play an interesting role to improve the performance of the coatings. The effect of the addition of yttrium Y as a rare earth element, on the microstructure, the mechanical properties and on the thermal stability of TiTaZrHfW refractory film is studied. A series of $(TiTaZrHfW)_{100-x}Y_x$ films were synthesized using magnetron sputtering technique. Y content is varied by changing the discharge current applied to Y target. No change of the films microstructure is observed when Y is added with small amount, however with high Y content new phases are formed. The phase evolution is evaluated by calculating the thermodynamic criteria ΔHmix, ΔSmix, Ω and δ and the result are compared to the experimental analysis. Nanoindentation measurements indicate a degrading of mechanical properties when the film is doped with Y element. The highest values of hardness and Young's modulus are obtained for TiTaZrHfW film at 9.69 GPa and 111.63 GPa respectively. Moreover, thermally stability of TiTaZrHfW film without and with Y element is investigated.

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2:40pm **F2-2-TuA-4 Investigation of Strain Stabilization in Aluminum-Based High Entropy Sublattice Nitride Films**,
***Balint Hajas (balint.hajas@tuwien.ac.at)**, A. Kretschmer, A. Kirnbauer, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien University, Vienna, Austria

Hard protective coatings allow for increased lifespan of machining tools and more versatile fields of application. Less than two decades ago the world of material science was introduced to the so called “high entropy alloys” (HEAs), a field that has since seen enormous growth in popularity. Applying the concept of metallic HEAs, which typically consist of a solid solution of at least five primary elements in near equiatomic composition, we developed various nitride and oxy-nitride coatings, where at least five different metals (in near equiatomic composition) share the same metal-sublattice. Hence, essentially their metal-sublattice is high entropic, however, for simplicity these will be named high entropy nitrides respectively oxynitrides.

Based on Density Functional Theory calculations, several Al-based single-phase high entropy nitride systems were selected for further experimental investigations. The selection criterion was basically their ability to delay the wurtzite AlN phase formation (essentially through strain stabilization) upon exposure to elevated temperatures. In addition to these high entropy nitrides, also their oxynitrides and Si-alloyed nitrides were developed, all of which by reactive magnetron sputtering.

The primary investigation focused on how the mechanical properties such as hardness and fracture toughness of the nitride coatings changed due to vacuum annealing up to 50 hours, and how the oxynitrides related to those results, and whether the formation of the wurtzite phase could be detected. The secondary investigation was aimed towards the oxidation resistance of the coatings, and if the additional silicon could delay the oxidation process. Their characterization includes X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, nanoindentation and cube-corner indentation.

4:00pm **F2-2-TuA-8 Magnetron Sputtering of Hard and Strong Multicomponent (HfNbTiVZr)C Thin Films**,
***Barbara Osinger (barbara.osinger@kemi.uu.se)**, S. Fritze, L. Riekehr, E. Lewin, U. Jansson,* Uppsala University, Angstrom Laboratory, Sweden

Thin films of the high entropy alloy HfNbTiVZr have shown promising mechanical properties and interesting charge transfer effects, reducing atomic size mismatch and in turn the lattice distortion δ. Being able to tune the electronic structure is especially interesting for the design of multicomponent carbides, as their desirable properties are a result of their bond character. This, along with general properties of group 4-6 carbides, like ceramic hardness, high wear resistance and ultra-high temperature strength, motivates the investigation of the (HfNbTiVZr)C system.

This study focused primarily on multicomponent carbide (HfNbTiVZr)C thin films with varying carbon concentrations (0–44 at.%), synthesised by non-reactive DC magnetron sputtering. All carbide films exhibit a single solid solution phase with NaCl-type structure and a lattice parameter of approximately 4.53 Å. The hardness increases to 34 GPa compared to 10 GPa for the metallic films. Additionally, phase stability based on films deposited at elevated temperatures (300-700°C), compared with predictions made by CALPHAD methods, will be discussed.

4:20pm **F2-2-TuA-9 Comparative Study of Reactively and Non-Reactively Sputtered High-Entropy Metal-Sublattice Carbides**,
***Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)**, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany

High-entropy alloys (HEAs) and high-entropy metal-sublattice ceramics (HESCs) have recently gained particular attraction in the field of materials research due to their promising properties, such as high hardness, high strength, and thermal stability. Within this work, we report on the phase formation and thermal stability of high entropy metal-sublattice carbides to provide a further insight to a more extensive understanding of the high-entropy effect, according to which, based on the Gibbs-free energy, such materials should be stabilised in the high-temperature regime. Therefore, (Hf,Ta,Ti,V,Zr)C coatings were reactively and non-reactively sputtered from a single powder-metallurgically produced composite target (either metallic or consisting of the respective binary carbides). Reactively sputtered coatings were synthesised using an C_2H_2 – Ar mixture with different $C_2H_2/(C_2H_2+Ar)$ ratios (f_{C2H2}). After deposition, the coatings were investigated in as-deposited state and after vacuum annealing between 800 and 1200°C. The structure and morphology, the chemical composition, the mechanical properties, and the thermal stability of the coatings were investigated by scanning electron microscopy, X-ray diffraction, and nanoindentation.

The non-reactively sputtered as well as reactively sputtered coatings with f_{C2H2}= 20 % show a single-phased face-centred cubic (fcc) structure. The hardness for the non-reactively sputtered HESCs is with ~41 GPa higher than that of the reactively sputtered one which exhibits a hardness of 35 GPa. This indicates that due to the use of C_2H_2 also regions of amorphous carbon form, which slightly weaken the coating already in the as-deposited state. After vacuum annealing up to 1200 °C the non-reactively sputtered coatings maintain a hardness of ~40 GPa indicating retarded softening mechanisms due to sluggish diffusion. Additionally, powdered free-standing coating material was investigated by XRD in as deposited state and after vacuum annealing up to 1300 °C. The results of these investigations show, independent of the synthesis route, no phase transformation within the investigated temperature range. This behaviour was also observed in previous studies on different material classes such as nitrides, borides, and oxides indicating a stabilisation due to the high-entropy metal sublattice.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific E - Session G3-TuA

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications
Moderators: Stepan Kyrsta, Oerlikon Luxembourg, **Christoph Schiffers**, CemeCon AG, Germany

1:40pm **G3-TuA-1 A New Tool in Coating Design: Managing Intrinsic Stresses in HiPIMS**,
***Christoph Schiffers (christoph.schiffers@cemecon.de)**, T. Leyendecker, W. Kölker, S. Bolz, B. Mesic,* CemeCon AG, Germany

Until now, the residual stresses of a coating could not be adjusted independently of other properties. The classical work around was adding layers of soft materials such as CrN to the film design. Such a multilayer is not ideal when high oxidation resistance and high hardness is needed for the application.

The unique feature of HiPIMS is the ability to actively design the intrinsic stresses in a coating material. In-depth plasma analysis shows that the short HiPIMS pulses consist of several phases. Synchronizing the HiPIMS pulses on the cathodes with a pulsed Bias is the technique for attracting the ionized target species and forming the coating out of them while suppressing unwanted contributions such as gas ions.

Having control over the intrinsic stresses of a coating material by the timing of the HiPIMS synchronisation adds a fully new option to the coating designer’s toolbox: stress management of the material. This triggers a paradigm shift: hardness by the composition of the material and a dense, low stress coating morphology by the HiPIMS process.

Managing intrinsic stresses in HiPIMS gives new coating options such as 12 µm thick films for heavy duty insert milling applications as well as precisely defined stresses for making TiAlSiN coatings on micro-tools even more wear resistant. Managing stresses in HiPIMS is about mastering stress and strain for the coating’s application.

2:00pm **G3-TuA-2 Self-lubricating CrAlMoN High Performance Tool Coatings for Machining of TiAl6V4***, K. Bobzin, C. Kalscheuer, M. Carlet,* ***Nina Stachowski (stachowski@iot.rwth-aachen.de)****,* Surface Engineering Institute - RWTH Aachen University, Germany*; W. Hintze, C. Möller, P. Ploog,* Institute of Production Management and Technology - Hamburg University of Technology (TUHH), Germany

Titanium alloys such as TiAl6V4 enable a significant performance improvement in different industry sectors. However, machining of titanium alloys presents a considerable challenge due to the low thermal conductivity of λ = 5.8 W/mK, Young's modulus of 110 GPa ≤ E ≤ 140 GPa as well as the strong adhesion tendency. This leads to high thermal and mechanical loads on the cutting edge resulting in early tool failure. Currently uncoated cemented carbide tools are commonly used for turning of TiAl6V4. However, self-lubricating physical vapor deposition (PVD) coatings like CrAlVN and CrAlMoN provide a promising approach to increase tool life. For this purpose, the coating ability to form lubricating oxide phases is essential. Self-lubricating oxide phases form under tribological loads, e.g. during machining processes due to the oxidation of specific transition metals such as vanadium or molybdenum. These oxide phases contribute to a decrease of thermal and mechanical loads in the contact between cutting edge and workpiece which may lead to an increased tool performance in TiAl6V4 cutting. In the present study, self-lubricating CrAlVN and CrAlMoN coatings were investigated on cemented carbide tools. The coatings were deposited by hybrid direct current magnetron sputtering / high power pulsed magnetron sputtering processes. Coating morphology, thickness, chemical composition, indentation hardness, indentation modulus as well as oxide phase composition were analyzed. Moreover, friction and wear behavior of the coated cutting tools were determined using a pin on disc (PoD) tribometer at ϑ = 20 °C, ϑ = 600 °C and ϑ = 800 °C against a TiAl6V4 counterpart. Additionally tool life and deformation behavior of the coated cutting inserts was analyzed after turning of TiAl6V4. The CrAlVN and CrAlMoN coatings possessed a dense morphology and a smooth surface topography. Both coating variants exhibited a good adhesion to the cemented carbide tools. For increased test temperatures, the tribological analyses showed a reduction in the coefficient of friction. In case of the CrAlVN coated samples, a friction reduction was observed at ϑ = 800 °C. In contrast thereto, a friction reduction was already found at ϑ = 600 °C for CrAlMoN. As compared to the uncoated reference and to the CrAlVN coated cutting inserts an increase in tool life for CrAlMoN coated cutting inserts was achieved for turning of TiAl6V4.

2:20pm **G3-TuA-3 Coating Design for Components for Extreme Applications***,* ***Ricardo Alexandre (ricardo@teandm.pt)****,* TEandM, Portugal **INVITED**

Coating design plays a paramount role in coating performance enabling performance increases in industrial components and tools. Thru the decades, coating design development has evolved from simple single layer coatings to more and more complex designs, starting from bilayers to current advanced nanostructures. When we look at extreme applications are these coatings able to protect and functionalize the surface successfully? At what extend production processes can be impacted? What about complying with demanding and restrictive product specifications? The application, at industrial scale, of sophisticated coating designs poses limitations? What kind? These are questions challenging, not only, coating developers, but also job coaters in direct contact with the market applications, where clients bring about complex and demanding surface treatment challenges driven by productivity focused production processes and sophisticated products. In order to bring some light into these questions four case studies will be presented. These case studies combine extreme working conditions (wear, corrosion, temperature, etc.) with product/process demanding specifications. Coating designs, its performance impact and industrial scale coating challenges and limitations will be discussed.

3:00pm **G3-TuA-5 The Use of Coatings to Minimize Soldering in Aluminum High Pressure Die Casting***,* ***Nelson Delfino de Campos Neto (ndelfino@mines.edu)****, A. L. Korenyi-Both,* Colorado School of Mines, USA*; C. Vian,* Stellantis, USA*; S. P. Midson, M. J. Kaufman,* Colorado School of Mines, USA

In the aluminum high pressure die casting (HPDC) process, the molten aluminum alloy is injected into reusable steel dies at high speeds (gate speeds of between 25 and 45 m/sec) and high pressures of 70 to 100 MPa or higher. To try to prevent the liquid metal from soldering (sticking) to the steel die, lubricants (parting agents) are sprayed into the die surface prior to each shot, but some level of soldering often still occurs. In addition, the rapid cooling of the die surface by the lubricant spray can promote heat checking, thereby dramatically shortening the life of the die. During aluminum HPDC, core pins located near the gate experience extreme conditions, such as higher temperatures and greater soldering and abrasion/erosion due to interactions with the flowing liquid metal. One possible solution for minimizing soldering and to address the extreme conditions adjacent to the gate is the application of hard coatings to these more vulnerable regions of the die. However, the decision-making process for selecting appropriate coatings for application to dies is often still very subjective. Several researchers have attempted to use laboratory tests for evaluating the effectiveness of various coating materials, but these laboratory tests typically lack the high gate speeds and pressures that are inherent to the die casting process. While more complex and realistic tests have been performed using laboratory-based or production die casting machines, only a limited number of die coatings have been examined, mostly produced by the PVD process. In the study reported here, a commercial die used to produce large automotive die castings was examined, as it incorporated two core pins located directly in front of the gate. A range of PVD, PACVD and diffusion coatings were applied to the core pins, and both qualitative and quantitative measurements were used to identify the amount of aluminum soldered to each coated pin. Characterization of the soldered interfaces was performed to understand coating failure, and to indicate best die coatings for aluminum HPDC applications.

4:00pm **G3-TuA-8 Bringing Together Research, Job Coating and Market Needs***,* ***Carles Colominas (carles.colominas@iqs.url.edu)****,* Flubetech, Spain **INVITED**

Job coating must be carried out through high tech but well-known technologies, to minimize technical and economic risks. A combination of high degree of specialization, customer orientation and a deep understanding of plasma technology allows PVD job coating companies to provide a proper coating service for a wide variety of applications, ranging from cutting tools to plastic or aluminum injection or biomedical implants. However, today's highly demanding and increasing market needs (local and global) push job coating companies to adapt to new circumstances to take advantage of new opportunities and finding new niches, like electric mobility or additive manufactured parts. Research projects must be essentially applied and focused and strategically and rigorously selected to provide benefits in the short and medium-term.

In this talk, several projects developed by our SME job coating company on cutting tools, metal forming, plastic injection, energy and biomedical fields will be presented. Developments include doped amorphous carbon films and multi-layered ceramic coating systems deposited by regular magnetron sputtering, high power impulse magnetron sputtering (HiPIMS) and duplex coatings by cathodic arc deposition. In all cases, coatings were developed using industrial PVD machines. Different aspects will be discussed, including the substrate influence, adhesion to the substrate, coating microstructure control, deposition temperature, tribological properties and chemical inertness (oxidation and wettability by liquid aluminum).

4:40pm **G3-TuA-10 CrON-based Coatings for Plastic Processing Applications***,* ***Anders O. Eriksson (anders.o.eriksson@oerlikon.com)****, T. Vermland, D. Fopp-Spori, J. Tischhauser,* Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein

Polymeric materials are used in a wide range of applications including packaging, bottle caps, furniture, window frames, as well as automotive parts and high-end components. The manufacturing process often includes injection molding or extrusion processes. To achieve long lifetime, performance, and stability in high volume manufacturing processes, coatings are applied on the parts of the tooling that are in contact with the polymer melt. Increasing requirement for high-strength light-weight materials, for example driven by E-mobility, promote the use of polymers with high percentage of glass-fiber or carbon-fiber reinforcement. The use of biopolymers is also increasing. Consequently, the conditions for tools and components are becoming harsher and typically involve a combination of abrasive wear, corrosion, and plastic adhesion. To allow performance enhancements in the contemporary plastics processing industry, we describe the development of a coating solution based on CrON. The selection of coating materials, tuning of coating architecture, and coating properties will be discussed and correlated with application requirements and performance.

Preferred for Session G3

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H3-TuA

Characterization of Coatings and Small Volumes in Harsh Environments

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, **Peter Hosemann**, University of California, Berkeley, USA

2:20pm **H3-TuA-3 Stabilized Nanocrystalline Thin Films for Enhanced Thermal, Radiation, and Mechanical Performance***, **Brad Boyce (blboyce@sandia.gov)**,* Sandia National Laboratories, USA **INVITED**

Nanocrystalline thin films can be alloyed to promote thermal stability via solute segregation to grain boundaries.The segregation can impede boundary migration kinetically via solute drag or Zener pinning, or thermodynamically by reducing the boundary's energetic cost.In this study we examine a Pt-Au alloy where the Au has been shown to promote boundary stability upon annealing.Going beyond the thermal contribution, we explore the Pt-Au alloys performance under monotonic tension, fatigue loading, wear loading, and ion irradiation.In each of these cases, the presence of solute can provide synergistic benefits on material properties.However, there are cases where the solute is also detrimental; for example, an over abundance of Au at the grain boundaries can lead to an overall embrittlement and reduced ductility.Through a series of in-situ TEM, in-situ SEM, and ex-situ experiments, we explore the complex role of solute segregation on the thermal, mechanical, and radiation properties.Finally, we propose a chemical pathway to achieve gradient nanostructured metals via compositional tailoring.Unlike the existing plastic deformation methods, like surface mechanical attrition, the compositional tailoring can lead to a heterogeneous grain structure that is 'antifragile': naturally stabilized against further evolution.

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3:00pm **H3-TuA-5 Explaining How *H/E* Influences Coating System Wear Under Harsh Conditions - Insights from Elevated Temperature Nanoindentation, Scratch and Impact Tests***, **Ben Beake (ben@micromaterials.co.uk)**,* Micro Materials Ltd, UK

The ratio of hardness to elastic modulus (H/E) of coating systems and their wear resistance under harsh conditions has been explored. Small-scale tribo-testing at room and elevated temperature (to 600C) has been used to simplify the wear conditions, allowing the role of contact severity, length scale and damage tolerance to be studied to determine why coating optimisation strategies are effective and why they can fail.

Results show the importance of relatively low elastic modulus in reducing tensile stresses in sliding/abrasive contact. This is a key factor in why coating design for optimised H/E and resistance to plastic deformation, H3/E2, can be more effective than aiming for extremely high hardness.

The influence of substrate ductility and load support on the damage tolerance of the coating system in impact tests has been investigated by testing at different contact size (nano/micro/macro). The combination of a coating with moderate hardness, high plasticity index and a tough (i.e. damage tolerant) substrate can improve impact resistance.

The results of the small scale tests show that mechanical and microstructural factors should not be considered in isolation. The role of coating microstructural design in optimising the high temperature mechanical properties of coating systems and their performance in tribologically severe contact conditions such as high speed machining is highlighted.

4:00pm **H3-TuA-8 *In-Sem* Micromechanical Testing Up to 1000 °C of High Entropy Transition Metal Nitride Thin Films Alloyed With Al***, A. Pshyk,* Linköping University, IFM, Sweden*; **Thomas Edwards (thomas.edwards@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; B. Bakhit,* Linköping University, IFM, Sweden*; M. Jain,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Küttel,* Alemnis AG, Switzerland*; G. Greczynski, L. Hultmann,* Linköping University, IFM, Sweden*; J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Transition metal nitride (TMN) based thin films have a hugely diverse range of applications due to their unique properties including high hardness, thermal stability, high-temperature oxidation resistance and low coefficient of friction. Recently, high entropy transition metal nitrides (HENs) have proven to be among the most promising ways to advance TMN-based thin films. HENs have gained considerable interest in the scientific community, demonstrating a blend of properties often highly enhanced in comparison to their conventional TMN counterparts. Although the outstanding properties of HENs have been well demonstrated at room temperature, their thermal stability and related high temperature mechanical properties are rarely investigated: the question of their potential as high temperature structural materials remains open.

Here, we investigated the mechanical properties of different HENs at temperatures up to 1000 °C by micromechanical testing. Equimolar (TiHfNbVZr)N and (TiHfNbVZrTa)N thin films alloyed with different Al content were deposited using a novel hybrid method combining high-power impulse magnetron sputtering (HiPIMS) from an Al target with DC magnetron sputtering (DCMS) from high entropy alloy targets, i.e. equiatomic TiHfNbVZr and TiHfNbVZrTa targets, in which a negative substrate bias is synchronized with the Al-rich portion of the HiPIMS pulse. The elevated temperature performance of the HENs was evaluated using a state-of-the-art high-temperature micromechanical testing system to carry out micropillar compression. The tests were performed *in situ* in an SEM at 25, 500, 700, 800, 900 and 1000 °C under vacuum, allowing observation of the deformation mechanism changes at elevated temperature, and avoiding oxidation. This direct measurement of mechanical properties (strength, plasticity limit, stress-strain behaviour, brittle-to-ductile transition) of HENs at elevated temperatures was interpreted in relation to the microstructure, phase composition, lattice distortion and valance electron concentration of the HENs, as well as phase changes upon annealing, e.g. spinodal decomposition. Further high temperature notched microcantilever fracture toughness measurements are currently underway.

Experimental details such as indenter material selection and chemical reactivity are also discussed.

4:20pm **H3-TuA-9 Custom Cryo-Nanoindenter for in-Situ Investigations of the Brittle-to-Ductile Transition in a Scanning Electron Microscope***, **Hendrik Holz (Hendrik.Holz@fau.de)**, S. Gabel, B. Merle,* University Erlangen-Nuernberg, Germany

Hydrogen is a promising energy carrier, which however needs to be transported and stored at cryogenic temperatures. A more thorough understanding of the mechanical behaviour of structural materials and coatings at those low temperatures is crucial to ensure safe operations. While nanomechanical testing of materials at elevated temperatures has gained traction over the past few years, only a handful of nanoindentation systems are yet commercially available for operation below room temperature. In this work, we present a novel custom-built cryo-cooled in-situ nanoindenter, which is operated inside a scanning electron microscope. This nanoindenter is based on a commercial system from Femtotools, where we have added low-vibration gas flow cooling and temperature control. In this presentation, we will show first applications to the brittle-to-ductile transition of chromium. Chromium is commonly used as a coating on top of steel and is therefore a natural candidate material for liquid hydrogen tanks. Its suitability for cryogenic application is paramount.

4:40pm **H3-TuA-10 Development of a Novel High Strain Rate Nanoindenter for Small-Scale Mechanical Characterization Over a Wide Strain Rate Range***, **Stefan Zeiler (stefan.sz.zeiler@fau.de)**, H. Holz, B. Merle,* University Erlangen-Nuernberg, Germany

Understanding the changes in mechanical behavior at high deformation speeds and the influence of the microstructure are crucial steps to increase the damage tolerance of components that are exposed to impacts during their lifetime, e.g. safety-relevant components in cars and airplanes. Currently, there is a deficit in experimental techniques for probing the mechanical behavior of coatings and small volumes at high strain rates. In this presentation, we will introduce a nanoindenter with enhanced electronic components, which was used to overcome the indentation strain rate limitation of conventional nanoindentation (ca. 0.1 s^{-1}). An intrinsically displacement-controlled piezo-actuator is operated in combination with a piezo-based load cell and a 1 MHz data acquisition system. Novel testing methods allow measurements with constant indentation strain rates up to ca. 10^4 s^{-1}. This presentation will focus on challenges with the experimental procedures and show first applications to superplastic alloys over several orders of magnitude of indentation strain rate.

Topical Symposia
Room Pacific C - Session TS2-1-TuA

Thin Films on Polymer Substrates: Flexible Electronics and Beyond

Moderators: Oleksandr Glushko, Erich Schmid Institute of Materials Science, Austria, **Barbara Putz**, Montanuniversität Leoben, Leoben, Austria

1:40pm **TS2-1-TuA-1 in Situ Observation of Strain Transfer and Crack Formation in Evaporated and Printed Thin Films and Devices on Compliant Substrates***, Patric A. Gruber (patric.gruber@kit.edu), N. Misra, T. Haas , S. Yi, B. Kim,* Karlsruhe Institute of Technology (KIT), Germany **INVITED**

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.

2:20pm **TS2-1-TuA-3 Electrical Resistance During Cyclic Loading of Conductive Coatings – What Information is Hidden in the Data?***, **David Gebhart (david.gebhart@oeaw.ac.at)**, M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

An increase in electrical resistance during cyclic loading of metallic films on polymer substrates is mainly a function of crack density in the film, mean crack length (and its distribution), and mean crack depth. Those factors cannot be separated in a single data point but an ensemble of datapoints may show trends that can be attributed to single factors. With a material system of a 150 nm Au coating on polyimide (Upilex-S; 50 µm), with and without a 30 nm Cr interlayer, a thorough analysis was done on information contained within electrical data obtained during cyclic tensile straining. With strain-controlled sinusoidal loading, twenty 4-wire resistance data points were recorded per cycle. By analyzing peak shape evolution, i.e. full width at half maximum values, cycle amplitudes, and curves fitted to minima and maxima points of each cycle, various damage initiation and propagation events could be identified and a distinction could be made between through-thickness cracking and surface necking. The findings are validated with imaging and characterization methods. Easy to implement and easily automated methods are presented, which can be used retroactively on acquired data, to make an argument for the effectiveness of deep analysis of electrical resistance data in fatigue investigations of conductive coatings.

2:40pm **TS2-1-TuA-4 Plasma Surface Activation of Epoxy Painted Polymer Composites to Enhance Adhesion of PVD Coatings***, **Nicolas Ranger (nicolas.ranger@oerlikon.com)**,* Oerlikon Balzers/IRCER, France*; C. Jaoul, P. Tristant,* IRCER, France*; T. Maerten,* Oerlikon Balzers, France*; S. Belveze,* Oerlikon Balzers , France*; S. Guimond,* Oerlikon Balzers, Liechtenstein*; M. Cavarroc,* Safran Tech, France

Polymer-based composites materials are increasingly employed in aircraft industry as replacement of metallic components due to their excellent specific properties (strength- and stiffness-to-density ratios). But aircraft surfaces are subject to harsh environmental conditions (rain, sand, gas, etc.) detrimental to polymer composites lifetime. As a result, deposition of hard ceramic films is required to protect them. PVD coating are envisioned but adhesion of such films is known to be low on these substrates [1].

Surface pre-treatments are therefore critical to improve the adhesion of coatings on polymer composite. Nowadays, it is commonly accepted that the enhancement of the adhesion of a coating is related to the density of nucleation sites at the polymer surface [2-3]. One simple way to quantify the increase of nucleation sites is by measuring surface energy.

The aim of the present study is to evaluate the effect of low pressure Ar, N_2 and O_2 plasmas on epoxy painted carbon fiber reinforced composite surface as adhesion-promoting treatment. Various plasma conditions are tested by changing parameters like gas mixture, bias voltage and duration. The surface energy is measured by contact angle measurements. These measurements are complemented by chemical analysis (XPS) and surface morphology observations (Profilometer, SEM, confocal microscopy) to understand the surface modification mechanisms.

Finally, the most promising plasma conditions as adhesion-promoting treatment are applied prior to the deposition of a titanium film deposited by magnetron sputtering. The adhesion is, then, evaluated using conventional methods (scratch and pull-off tests) to quantify the benefit of the pre-treatment.

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3:00pm **TS2-1-TuA-5 MOKE-XRD Experiment for the Study of Magnetomechanical Properties of Thin Films Deposited on Stretchable Substrates***, H. Mahmoud,* Université Sorbonne Paris, Université de Poitiers—CNRS, France*; **Damien Faurie (faurie@univ-paris13.fr)**,* Université Sorbonne Paris, France*; P. Godard,* Université de Poitiers—CNRS, France*; D. Thiaudière,* Soleil Synchrotron, France*; P. Renault,* Université de Poitiers—CNRS, France*; F. Zighem,* Université Sorbonne Paris, France

Stretchable/flexible electronics has been a rapidly growing field for several years. In particular, magnetic systems realized on stretchable/flexible substrates are of increasing interest for their potential applications [1-2]. These will be subjected to large strains during their use. It is therefore important to understand the different phenomena involved at very large strains in order to estimate the durability of their functional properties, through the study of elementary magnetomechanical phenomena [3].

In this context, we have developed an original experiment coupling *in situ* Magneto-Optical Kerr Effect (MOKE) magnetometry, biaxial traction, digital image correlation on the DiffAbs beamline of the SOLEIL synchrotron, in order to follow the evolution of the magnetic quantities at different mechanical regimes (elastic domain, plasticity, multicracking) (figure 1 (a), supplementary material). This device has been used to study model thin films of Cobalt (20 to 100 nm) deposited on Kapton (polymide) substrate. The evolution of the magnetization curves as a function of the applied strain was analyzed in order to estimate the evolution of the coercive field, the remanent magnetization and the saturation field. This analysis has been correlated to the different deformation micromechanisms estimated thanks to the monitoring of the elastic strains by X-ray diffraction (figure 1 (b), supplementary material).

Through this presentation, we will show the instrumental development of the device (biaxial tensile machine coupled to the magnetometer) as well as the mechanisms underlying the measured properties according to the type of loading (equibiaxial or complex). The perspectives of these first studies will also be discussed (understanding of the physical mechanisms, effects of lateral nanostructuring, ...).

[1] D. Makarov, M. Melzer, D. Karnaushenko, O.G. Schmidt, Applied Physics Reviews 3 (1), 011101 (2016)

[2] F. Zighem, D. Faurie, Journal of Physics: Condensed Matter 33 (23), 233002 (2021)

[3] S. Merabtine, F. Zighem, D. Faurie, A. Garcia-Sanchez, P. Lupo, A. Adeyeye, NanoLetters 18, 3199 (2018)

4:00pm **TS2-1-TuA-8 Nanoscale Deformation Mechanisms in Thin Film Metallic Glasses Explored by in-Situ SEM With Digital Image Correlation***,* ***Oleksandr Glushko (oleksandr.glushko@unileoben.ac.at)****, C. Mitterer, J. Eckert,* Montanuniversität Leoben, Austria

Digital image correlation (DIC) is a powerful technique allowing detailed mapping of local strain distributions from the images of deformed surface. Spatial resolution of DIC is restricted only by the pixel size of the image and quality of random speckle pattern on the surface. Here we demonstrate the capabilities of DIC to capture propagation of shear bands in thin film metallic glasses with spatial resolutions down to few tens of nanometers.

PdSi metallic glass films were sputter deposited on polyimide substrate and then covered with randomly distributed nano-sized Indium islands. Additionally, the films were pre-structured with specific FIB-milled patterns in a way that the formation of cracks is locally prohibited but in-plane shear bands can freely propagate. Straining experiments were performed in-situ in SEM and GOM Correlate software was employed for DIC analysis. Shear bands propagating within the film plane do not necessarily lead to appearence of surface traces and thus cannot be detected on the SEM images with a naked eye. With DIC analysis shear bands are clearly visualized as bands of extremely localized strains, significantly exceeding the strains in the rest of the film. Local strains before and after generation of shear bands were carefully measured and an analogue of von Mises yielding criterion is formulated. Additionally, provided analysis proved that shear bands are “cold” during operation, i. e the temperature on the surface stays far below the glass transition temperature. Demonstrated technique of combining pre-patterned polymer-supported films with in-situ SEM straining and DIC is shown to be extremely effective to capture microplasticity phenomena with nanoscale resolution.

Topical Symposia
Room Town & Country A - Session TS6-3-TuA
A Session to Acknowledge the Contributions of Joe Greene to the ASED, ICMCTF, AVS, and IUVSTA III

Moderators: Ivan G. Petrov, University of Illinois at Urbana-Champaign, USA, **Angus Rockett**, University of Illinois at Urbana-Champaign, USA

1:40pm **TS6-3-TuA-1 Perspective on Thin-Film Metallic Glasses: Road to Industrial Production (Virtual Presentation)***,* ***Jinn P. Chu (jpchu@mail.ntust.edu.tw)****,* National Taiwan University of Science and Technology, Taiwan **INVITED**

This presentation provides brief overviews on the recent application-oriented researches on thin film metallic glasses (TFMGs) in various fields such as biomedical, biosensors, and nanotube arrays. For instance, TFMGs have been shown to improve the mechanical properties and the surface properties (such as non-stick characteristics) of the underlying substrates. The surface topography of TFMGs has also been revealed to affect chemical activity, cell-adhesion, and wetting-related properties of surfaces. In addition, the first-ever metallic-glass nanotube array on Si has been successfully fabricated by a widely-used lithography and sputter deposition process for very large-scale integration. These research works actually suggest that thin film is the most suitable approach to answer many unrevealed questions on its bulk metallic glass counterpart. Nevertheless, the remaining question is where the researches on TFMGs are headed. This article also highlights future challenges and opportunities associated with the further development of TFMG for the industrial production.

2:20pm **TS6-3-TuA-3 Hollow Cathode Discharges: The Influence of the Electrode Material and Cathode Geometry***,* ***Stephen Muhl (muhl@unam.mx)****,* IIM UNAM, CDMX, Mexico*; R. Sangines,* CNyN (CONACYT) UNAM, Ensenada, BC, Mexico*; J. Cruz,* CNyN UNAM, Ensenada, BC, Mexico **INVITED**

I first meet Joe Greene in 1999 in a Mexican Vacuum Society meeting, and in 2011 he invited me to submit a review article on my hollow cathode work to Thin Solid Films. That task greatly increased my knowledge of hollow cathodes, but also showed me that I did not really understand how they worked.

Traditionally, in a low-pressure gas discharge, electrons emitted from the cathode are accelerated by the cathode sheath. They produce light emission in the cathode glow, then stop producing it in the cathode dark space until they get to the edge of the negative glow. The secondary electrons and ions are accelerated by the sheath producing additional ionization and this avalanche maintains the discharge. However, recent work has shown that this is wrong in that the cathode glow is not generate by electrons, and that the basic description has many problems.

Hollow cathodes include almost any cathode with a cavity-like geometry, cylindrical, planar or spherical. In 1916, F. Paschen showed that such a system can produce a high electron flux and plasma density, in part, by reducing the loss of electrons in the similar way as in a magnetron. In general, there are three types of hollow cathode discharge, at low power and/or low gas pressures, it is a typical low-current high-voltage plasma. For certain combinations of gas pressures and hollow cathode diameters, with high applied powers, the negative glow of the plasma almost completely fills the interior the cathode and the plasma current, and density can be orders of magnitude greater than that of a typical discharge. Finally, if the cathode material is not cooled the discharge can transform into a dispersed arc, the hot electrode produces thermal-field electron emission as an additional source of electrons, and this even further increases the plasma density and current.

The conventional explanation for the hollow cathode effect involves high-energy “pendulum” electrons which are reflected between the opposing sheaths on either side of the inside of the cathode; the long trajectory of these electron is considered to produce an increased number of secondary electrons, with this resulting in the higher plasma density and current. Here we describe some problems associated with this well-accepted model and present an alternative explanation based on doubly charged ions. Finally, we report the results of recent studies of the dependence of the I-V characteristics of an argon discharge on the geometry of a cylindrical cathode, the metal used to make the cathode, spatially resolved optical emission spectroscopy of the hollow cathode and measurements of the ion flux as a function of the experimental conditions.

4:00pm **TS6-3-TuA-8 Ti-Nb Based Alloy Coatings Produced by Magnetron Co-sputtering***,* *D. Gonzalez,* Universidade Federal de Sao Carlos, Brazil*; V. Amigo-Borras,* Universitat Politècnica de València UPV, Spain*; V. Mastelaro,* Universidade de Sao Paulo, Brazil*;* ***Pedro Nascente (nascente@ufscar.br)****,* Universidade Federal de Sao Carlos, Brazil **INVITED**

The AISI 316L stainless steel (SS) has been widely used as implant material due to its adequate biomechanical and biocompatibility properties. Its advantages compared to other used metallic materials, such as the CoCr alloys and titanium and its alloys, are its formability, weldability, and affordability. One of its main disadvantages is the release of harmful corrosion products in the human body. This limitation can be overcome by the coating of the SS with an alloy that has a higher corrosion resistance and a better biocompatibility. Ti, Nb, and Zr are non-toxic and non-allergenic elements that exhibit excellent biocompatibilityand low cytotoxicity; in addition to these qualities, they have total solubility among themselves. We report on binary Ti-Nb and ternary Ti-Nb-Zr alloy coatings deposited on AISI 316L SS by magnetron co-sputtering. The composition, phase formation, structure, morphology, texture, film growth, and mechanical and tribological properties of the $Ti_{80}Nb_{20}$, $Ti_{75}Nb_{20}Zr_5$, $Ti_{60}Nb_{20}Zr_{20}$, $Ti_{50}Nb_{20}Zr_{30}$, and $Ti_{40}Nb_{20}Zr_{20}$ (at.%) coatings are investigated. For low Zr content, two phases are detected: Predominantly the β phase and, in a lesser degree, a nanoscale metastable ω phase. For Zr amounts equal or higher than 20 at.%, only the β phase is detected. The coating with higher Zr content presents lower elastic modulus and hardness values. The coating morphology is affected by the increasing addition of Zr, from a growth characteristic of the zone I to a growth characteristic of the zone T of the structure zone diagram (SZD). The texture also is influenced by the Zr amount, going from {111} to {101} for the direction of the film growth, due to the increase in the strain energy and the total mass of the species in the plasma. The Ti-Nb-Zr coatings exhibit high ductility and high adhesion,, which are characteristics of a high combined plastic deformation on the coating/substrate system, and no delamination is observed. These findings indicate that the Ti-Nb-Zr coatings are promising candidates for biomedical applications.

4:40pm **TS6-3-TuA-10 Bill Sproul Award and Honorary ICMCTF Lecture: Modelling Reactive Sputtering: Back to the Future***, **Diederik Depla (Diederik.Depla@ugent.be)*** [1] *, J. Van Bever, K. Strijckmans,* Ghent University, Belgium **INVITED**

When looking back on our endeavor in the field of reactive magnetron sputtering, the authors may conclude that the technique is conceptual simple. This simplicity however conceals the underlying complex relationships between the simultaneously occurring processes. Hence, experimental results are often surprising or unexpected. Modelling of reactive magnetron sputtering is therefore indispensable to unravel this complexity. This conclusion was also drawn by others in the early days when this technique was first applied. Though less complete as compared to the historical research by J. Greene, a short historical overview of modelling attempts will be presented. However, it will provide a framework to discuss some essential and common features of the models, including the Reactive Sputter Deposition (RSD) model developed by our team. For the latter model the implemented processes will be reviewed. Some important results, such as the double hysteresis behavior and the presence of non-reacted oxygen atoms will be discussed. If these results are confronted with experiments, the general trends can be explained. If it either comes to the details, it is clear that new developments will be needed in the future. In this way our endeavor in modelling is luckily not finished.

[1] **Bill Sproul Awardee**

Special Interest Talks
Room Town & Country A - Session SIT2-TuSIT

Special Interest Session II
Moderator: Samir Aouadi, University of North Texas, USA

7:00pm **SIT2-TuSIT-1 Evaluating Electro-Mechanical Reliability using In-Situ Methods***, Megan J. Cordill (megan.cordill@oeaw.ac.at),* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria **INVITED**

Electrical, mechanical and interfacial properties of thin metal films on compliant polymer substrates are important to understand in order to design reliable flexible electronic devices. Thin films of Cu, Au, and Al on polyimide (PI) substrates were examined for their use as interconnects in flexible electronic devices. Using in-situ tensile straining with atomic force microscopy (AFM), X-ray diffraction (XRD), and confocal laser scanning microscopy (CLSM) mechanical and interfacial behavior can be examined. AFM and CLSM can provide information about crack spacing and film delamination, while XRD experiments are utilized to determine the lattice strains and stresses present in the films. If these in-situ techniques are combined with in-situ 4-point-probe (4PP) resistance measurements, the influence of the mechanical damage on the electrical properties can be correlated. This combination of multiple in-situ investigations are particularly useful when studying the electro-mechanical behavior under cyclic loading conditions where some materials can have an improvement of the electrical conductivity after a few hundred cycles. Mechanisms behind these phenomena as well as methods to measure the adhesion of metal-polymer interfaces found in flexible electronic devices will be discussed.

Coatings for Use at High Temperatures
Room Pacific E - Session A2-2-WeM

Thermal and Environmental Barrier Coatings II

Moderators: Sabine Faulhaber, University of California, San Diego, USA, **Kang Lee**, NASA Glenn Research Center, USA

8:00am **A2-2-WeM-1 Design of Multi-Component Rare Earth Silicate EBCs for Property Optimization***, M. Ridley, C. Miller, R. Webster, H. Olson, A. Salanova, K. Tomko, J. Tomko, J. Ihlefeld,* University of Virginia, USA*; C. Toher,* Duke University, USA*; P. Hopkins,* ***Elizabeth Opila (ejo4n@virginia.edu)****,* University of Virginia, USA **INVITED**

Environmental barrier coatings (EBCs) are required for application of SiC-based ceramic matrix composites in hot section turbine engine applications. State of the art EBCs are composed of ytterbium silicates. Multicomponent rare earth (RE) silicates offer the opportunity to simultaneously optimize a multitude of coating properties, including thermal conductivity, steam resistance, calcium magnesium aluminosilicate (CMAS) resistance, and thermal expansion coefficient. Design criteria for RE cation selection in multicomponent RE silicates can be formulated. Thermal conductivity of the EBCs can be reduced via phonon scattering mechanisms attributed to a wide range of RE mass and size. Large RE cations favor formation of an apatite barrier layer limiting further CMAS reactions. Small RE cations favor the beta-phase disilicate and X2 monosilicate with more favorable steam resistance and thermal expansion coefficients. Preliminary results for multicomponent rare earth silicate EBC thermal and thermochemical property optimization will be presented.

8:40am **A2-2-WeM-3 Cyclic Steam Oxidation of Single Layer Ytterbium Disilicate-Based Environmental Barrier Coatings Deposited onto Enhanced Roughness Silicon Carbide***, K. Kane,* Oak Ridge National Laboratory, USA*; E. Garcia,* Center for Thermal Spray Research, Stony Brook University, USA*; C. Parker, M. Lance, B. Pint,* ***Mackenzie Ridley (ridleymj@ornl.gov)****,* Oak Ridge National Laboratory, USA **INVITED**

Environmental barrier coatings (EBCs) are used to protect SiC-based structural components from water vapor induced recession in gas-turbine environments. The current generation of EBCs are typically comprised of a ytterbium disilicate (YbDS) top coat deposited onto a Si bond coat with atmospheric plasma spray. While having already achieved commercial success in the aviation sector, these EBCs are inherently temperature limited by the melting temperature of Si, 1414°C. Increasing EBC application temperatures therefore necessitates the removal of the Si bond coat. In this study, single layer ytterbium disilicate/monosilicate EBCs were deposited directly onto SiC manufactured with enhanced roughness to increase single layer adhesion. 1-h cyclic steam testing was conducted at 1350° and 1425°C, and several variations of ytterbium disilicate based EBCs were tested on several variations of enhanced roughness to investigate the relationship between EBC composition and underlying SiC geometry on both thermally grown oxide formation and coating spallation. This research was funded by the Advanced Turbine Program, Office of Fossil Energy, Department of Energy.

9:20am **A2-2-WeM-5 Raman Spectroscopic Identification of Ytterbium Silicate and Thermally Grown Oxide Silica Phases in Environmental Barrier Coatings***,* ***Michael Lance (lancem@ornl.gov)****, K. Kance, B. Pint,* Oak Ridge National Laboratory, USA

To accurately model the long-term durability of multilayered (bond coat/ top coat) environmental barrier coatings (EBCs), a more complete understanding of the phase composition and transformations of the silica thermally grown oxide (TGO) is desired.For the top coating, mixed Y/Yb silicate EBCs have been proposed as a dual-function thermal/environmental barrier coating that may also offer several other advantages over solely Yb-silicate EBCs. For the TGO formed during thermal cycling in steam, cristobalite formation and subsequent ß- to α-cristobalite transformation has been identified as a potentially life limiting parameter. In this study, Raman micro-spectroscopy was used to both compare top coating phase evolution of mixed Y/Yb- and Yb-silicate EBCs, and to quantify cristobalite formation on a thermally sprayed Si bond coating. This research was funded by the Advanced Turbine Program, Office of Fossil Energy, Department of Energy.

9:40am **A2-2-WeM-6 The Behavior Of Suspension Plasma Sprayed 8YSZ Thermal Barrier Coating With Laser Microtextured Bond Coat Under High Temperature Testing***,* ***Pawel Sokolowski (pawel.sokolowski@pwr.edu.pl)****, T. Kielczawa, M. Nowakowska,* Wroclaw University of Science and Technology, Poland*; R. Musalek, T. Tesar,* Institute of Plasma Physics of the Czech Academy of Sciences, Czechia

Despite intensive development, the Thermal Barrier Coating technology still relies on the idea of oxidation resistant metallic bond coat and thermally insulating ceramic top coat. The interface between these two layers plays a crucial role in how the structure of the TBC system behaves during high-temperature operation. In this work, laser microtexturing is proposed as a method for controlling that interface.

The 80 to 100 µm thick NiCrAlY layer was deposited by Atmospheric Plasma Spraying over the nickel-based super alloy substrate. Then, the infrared fiber nanosecond laser was used for shaping the topography of the bond coat prior to the top coat deposition. The surface geometry was controlled by the laser set-up operational conditions, mainly: (i) laser power, (ii) frequency, (iii) scanning velocity, and (iv) inter-pass spacing. The two groove-based patterns were finally selected for further work together with one as-sprayed bond coat, as a reference. The 8 wt.% yttria stabilized zirconia (8YSZ) was deposited by means of Suspension Plasma Spraying over all three types of bond coats. The samples were then subjected to isothermal oxidation and thermal cyclic fatigue testing to study the influence of bond coat topography on the overall behavior of coatings under high-temperature conditions. Microstructural studies revealed that the tailored bond coat topography may promote the obtaining of a homogeneous, columnar-like top coat. On the other hand, the grooves seem to promote locally the oxidation of the bond coat and the substrate. This means that the microtexture depth plays a crucial role and should be very precisely controlled in order to prolong the TBC lifetime.

11:00am **A2-2-WeM-10 Oxidation and Failure in Environmental Barrier Coatings***,* ***Bryan Harder (bryan.harder@nasa.gov)****, K. Lee, M. Presby,* NASA Glenn Research Center, USA*; J. Setlock,* University of Toledo, USA **INVITED**

The use of silicon carbide (SiC) ceramic matrix composites (CMCs) in turbine engines enables increased operating temperatures and reduced cooling demands, which can reduce cost, increase efficiency, and lower emissions.However, due to reactions with the turbine environment that can cause rapid oxidation and recession of components, SiC/SiC CMCs require a protective barrier called an environmental barrier coating (EBC).Although the EBC provides protection from recession via the gas stream, oxidation of the bond coat or substrate occurs with prolonged exposure during operation.The thermally grown oxide (TGO) layer that forms between the EBC and the bond coat or the substrate is a weak interface that can cause failure of the coating system.In this work, we evaluate the influence of the TGO on coating failure in state-of-the-art and advanced EBC systems.The change in the bond strength with a growing TGO layer is discussed as well as the effect of calcium-magnesium-aluminosilicate (CMAS) glass exposure on TGO kinetics and coating adhesion.

11:40am **A2-2-WeM-12 Impact of Surface Degradation on the Radiative Heat Transfer in Thermal Barrier Coatings***,* ***Francis Blanchard (francis.blanchard@polymtl.ca)****, B. Baloukas, M. Azzi, M. Kadi, J. Sapieha, L. Martinu,* Polytechnique Montreal, Canada

As aircraft engine operating temperatures increase, so must the thermal insulation capabilities of the thermal barrier coatings (TBCs) used to shield metallic components in the combustion chamber and high-temperature turbine areas. Heat transfer from the hot gases to the engine components occurs through two main mechanisms: conduction and radiation. Considerable efforts have been deployed over the years to ensure TBCs have low thermal conductivity, thanks to a porous microstructure generally achieved by thermal spray or EB-PVD techniques. The radiative component of heat transfer, however, has been comparatively largely ignored in TBC design. This issue is compounded by the exponential increase in radiative heat for higher gas temperature.While TBCs are naturally reflective to radiative heat due to scattering, this property is vulnerable to degradation, even more so than their low thermal conductivity.

The two main degradation phenomena threatening TBCs over their lifetime are (1) morphological changes due to high heat exposure (sintering, phase transition, etc…) and (2) chemical attack by CMAS (Calcium-Magnesium-Alumino-Silicate). Fundamental understanding of these two mechanisms is an important aspect in the design and development of high performance TBCs. In this work, the effects of high temperature cycling and CMAS infiltration on the optical performance of Yttria-stabilized zirconia (YSZ) coatings prepared by APS were systematically investigated. Absorption and scattering coefficients have been extracted from spectrophotometry measurements in a novel way via the inverse adding-doubling (IAD) method. The microstructure was analysed using scanning electron microscopy (SEM) and mercury infiltration porosimetry (MIP) in an attempt to establish a relationship between the evolving microstructure and the optical properties. Both were found to have a significant impact on performance, with CMAS infiltration having the biggest impact. A finite-difference time-domain (FDTD) model was developed in order to predict the optical performance of TBCs before and after degradation with good agreement with experimental data. This model could be used to investigate ways to mitigate the effect of this degradation.

12:00pm **A2-2-WeM-13 Development and Characterization of an Environmental Barrier Coating System for Novel Mo-Si-Ti Alloys Using Magnetron Sputtering***, **Ronja Anton (ronja.anton@dlr.de)**, N. Laska, U. Schulz,* German Aerospace Center (DLR), Germany

Mo-Si-Ti-based alloys are promising candidates for future high temperature applications beyond-Ni-based superalloys in turbine engines. Mo-Si-Ti-based alloys have a density of about 7.7 g/cm^3 to 7.0 g/cm^3 depending on the Ti content, which makes them lighter than Ni-based superalloys. Moreover, a better creep resistance at high temperature favors the application. Unfortunately, due to their insufficient oxidation and corrosion behavior especially at intermediate (pest oxidation) and partially at high temperature, the necessity of a protective coating becomes inevitable to perform in an oxidizing and water vapor containing atmosphere. In the present work, a multisource sputter coater was used for the deposition of a four-layer EBC system. The oxidation protection was provided by a dual layer coating system, containing a graded Mo-Si interlayer in order to compensate differences in the coefficient of thermal expansion (CTE) and a top layer of pure Si for the development of the desired thermally grown oxide layer of SiO_2. Coatings were applied by DC magnetron sputtering using pure elemental targets of Mo and Si. Regarding a sufficient water vapor resistance, ytterbium monosilicate (YbMS) is well-known and provides a CTE close to the Mo-based substrate alloys. Consequently, to reinsure the thermodynamic equilibrium between the oxidation protective Si layer and the YbMS, a further intermediate layer of ytterbium disilicate (YbDS) was deposited. The manufacturing of the Yb-based silicate coatings was done by reactive magnetron sputtering using oxygen and pure elemental targets of Yb and Si. Since the Yb target is highly reactive and leans towards poisoning, a parameter study with varying pressures, O_2 flows and target currents was performed to find the optimal operating point and the most stable process window to ensure the required coating composition. Finally, the entire EBC system consists of four different layers.

In this study, the multilayer coating system has been applied by magnetron sputtering on two novel Mo-Si-Ti alloys with a chemical composition of Mo21Si34Ti0.5B and Mo12.5Si8.5B27.5Ti2Fe (in at.%). The produced EBC system on the different alloys was tested at 800 °C and 1200 °C in laboratory air as well as in a streaming water vapor test rig. The emphasis was put on the chemical reactions and diffusion processes within the interfaces of the coating system and that were analyzed by scanning and transmission electron microscopy equipped with EDS respectively. In addition, the phase formation was evaluated using high temperature X-ray diffraction techniques.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B5-1-WeM

Hard and Multifunctional Nanostructured Coatings I
Moderator: Tomas Kozak, University of West Bohemia, Czechia

8:20am **B5-1-WeM-2 Enhanced Thermal Stability of (Ti,Al)N Coatings by Oxygen Incorporation***, **Damian M. Holzapfel (holzapfel@mch.rwth-aachen.de)**[1],* RWTH Aachen University, Germany*; D. Music,* Malmö University, Sweden*; M. Hans,* RWTH Aachen University, Germany*; S. Wolff-Goodrich,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; D. Bogdanovski,* RWTH Aachen University, Germany*; M. Arndt,* Oerlikon Balzers Coating Germany GmbH, Germany*; A. Eriksson, K. Yalamanchili,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; D. Primetzhofer,* Uppsala University, Sweden*; C. Liebscher,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; J. Schneider,* RWTH Aachen University, Germany

Thermal stability of protective coatings is one of the performance-defining properties for advanced cutting and forming applications as well as for energy conversion. To investigate the effect of oxygen incorporation on the high-temperature behavior of (Ti,Al)N, metastable cubic (Ti,Al)N and (Ti,Al)(O_xN_{1-x}) coatings are synthesized using reactive arc evaporation. X-ray diffraction of (Ti,Al)N and (Ti,Al)(O_xN_{1-x}) coatings reveals that spinodal decomposition is initiated at approximately 800°C, while the subsequent formation of wurtzite solid solution is clearly delayed from 1000°C to 1300°C for (Ti,Al)(O_xN_{1-x}) compared to (Ti,Al)N. This thermal stability enhancement can be rationalized based on calculated vacancy formation energies in combination with spatially-resolved composition analysis and calorimetric data: Energy dispersive X-ray spectroscopy and atom probe tomography data indicate a lower O solubility in wurtzite solid solution compared to cubic (Ti,Al)(O,N). Hence, it is evident that for the growth of the wurtzite, AlN-rich phase in (Ti,Al)N, only mobility of Ti and Al is required, while for (Ti,Al)(O,N), in addition to mobile metal atoms, also non-metal mobility is required. Prerequisite for mobility on the non-metal sublattice is the formation of non-metal vacancies which require larger temperatures than for the metal sublattice due to significantly larger magnitudes of formation energies for the non-metal vacancies compared to the metal vacancies. This notion is consistent with calorimetry data which indicate that the combined energy necessary to form and grow the wurtzite phase is larger by a factor of approximately two in (Ti,Al)(O,N) than in (Ti,Al)N, causing the here reported thermal stability increase.

8:40am **B5-1-WeM-3 Metastable Single- or Dual-Phase Structures in Magnetron Sputtered W-Zr Thin-Film Alloys: Properties and Thermal Behavior***, M. Cervena, S. Haviar, R. Cerstvy, J. Rezek,* ***Petr Zeman (zemanp@kfy.zcu.cz),*** University of West Bohemia, Czechia

Metastable solid materials such as amorphous or nanocrystalline alloys, supersaturated solid solutions, high-temperature or high-pressure phases persisting at normal conditions, have been of great interest due to a possibility to explore novel structures with unknown properties. These materials are kinetically determined and can be therefore synthesize only by non-equilibrium processes. Magnetron sputtering is thus a suitable technique for their preparation as thin films.

The present study focuses on preparation of thin-film alloys from the W-Zr system by non-reactive magnetron sputtering and systematic investigation of their structure, properties, and thermal behavior at elevated temperature. The films were sputter-deposited in argon gas using two unbalanced magnetrons equipped with a W and Zr target, respectively. The elemental composition of the films was controlled in a very wide composition range (0-100 at.% Zr), by varying the deposition rate from the individual targets.

Using magnetron sputtering, we were able to prepare W-Zr thin-film alloys with several metastable structures in respect to the equilibrium phase diagram [1]. Up to 24 at.% Zr, the structure of W-rich films is characterized by a supersaturated bcc α-W(Zr) solid solution with a highly oriented structure, columnar dense microstructure, enhanced hardness and very low residual stress. In a wide range between 33 and 83 at.% Zr, an amorphous structure with features indicating metallic glass behavior is observed. These films exhibit a very smooth surface, a moderate compressive stress, and a constant electrical resistivity. Above 83 at.% Zr, high-temperature bcc β-Zr(W) and high-pressure hcp ω-Zr(W) phases with an enhanced hardness are prepared in Zr-rich films. Moreover, a very interesting dual-phase structure with crystalline columnar submicrometer-

[1] **Graduate Student Award Finalist**

sized conical domains surrounded by a metallic glass is spontaneously formed at 28 at.% Zr [2].

Preliminary results on the thermal behavior indicate that the stability of the metastable α-W(Zr) solid solution in the W-rich films reaches at least 1000°C and its oxidation resistance is improved by an Zr addition. The stability of the amorphous of W-Zr films with metallic glass behavior depends on their elemental composition and can be as high as 1400°C. Moreover, the oxidation of these films to 600°C leads to a homogenously oxidized amorphous structure with twice higher hardness than in the as-deposited state.

[1] M. Červená, R. Čerstvý, T. Dvořák, J. Rezek, P. Zeman, J. Alloy. Compd. 888 (2021) 161558.

[2] P. Zeman, S. Haviar, M. Červená, Vacuum 187 (2021) 110099.

9:00am **B5-1-WeM-4 A Conformable SiAlN/Mo Thermal Barrier Layer for Titanium Alloys Deposited by Magnetron Sputtering**, *Z. Gao,* The University of Manchester, UK*;* ***Justyna Kulczyk-Malecka (j.kulczyk-malecka@mmu.ac.uk)****,* *P. Kelly,* Manchester Metropolitan University, UK*; P. Xiao,* The University of Manchester, UK

Titanium and its alloys are widely used in the aeronautical and automotive industries, as well as in bio-medical implants due to their low density, high specific strength, and excellent corrosion resistance at lower temperature ranges. Nevertheless, at temperatures above 500ºC Ti alloys exhibit a rapid oxidation, which leads to the formation of a less protective brittle oxide scale that limits its application. To mitigate the formation of a detrimental oxide scale, a protective bilayer coating consisting of an amorphous SiAlN top layer and a Mo interlayer were deposited onto Ti alloys using pulsed DC reactive magnetron sputtering. Coated Ti samples were then exposed to oxidative corrosion in air at 800°C for up to 200 hr and the degradation and thermal barrier ability of the bilayer nitride coatings were studied and correlated with the coating thickness and the presence of the Mo interlayer.

It was found that the thermal barrier nature of the bilayer coating stack is attributed to the interfacial reaction between the Ti substrate and the Mo interlayer and the formation of mechanical twinning within the interfacial reaction product, i.e. a $TiN_{0.26}$ conformable interlayer, which accommodates the thermal mismatch strain between the coating and the substrate upon thermal cycling. The degradation mechanism of SiAlN/Mo coatings is determined by the depletion of the coating induced by interfacial diffusion and reaction between the elements composing the coating and the Ti substrate. The morphology of as-deposited and oxidised samples was characterised using imaging techniques, such as SEM and TEM, the physiochemical properties of the coating were investigated using XPS and EDS and residual stresses in the SiAlN coatings were obtained using a FIB milling-stress driven buckling method. This work, therefore, provides a new coating stack design for aeronautical applications displaying exceptional environmental protection for Ti at high temperatures through the interfacial reaction mechanism, which controls the coating degradation.

9:20am **B5-1-WeM-5 Thermal Decomposition of Hard Coatings - Insights from Nanometer-Scale Characterization***,* ***Marcus Hans (hans@mch.rwth-aachen.de)****,* RWTH Aachen University, Germany*; Z. Czigány,* Centre for Energy Research, Hungary*; D. Neuß, J. Sälker, H. Rueß, J. Krause, P. Ondračka,* RWTH Aachen University, Germany*; D. Music,* Malmö University, Sweden*; S. Evertz, D. Holzapfel,* RWTH Aachen University, Germany*; G. Nayak, D. Holec,* Montanuniversität Leoben, Austria*; D. Primetzhofer,* Uppsala University, Sweden*; J. Schneider,* RWTH Aachen University, Germany **INVITED**

Three-dimensional atom probe tomography is a powerful technique to characterize the local chemical composition of materials. Since the spatial resolution at the nanometer scale is ideally suited to identify decomposition-relevant mechanisms, the thermal stability of (V,Al)N hard coatings is the focus of this talk.

Based on thermodynamic considerations of $d^2\Delta G/dx^2 < 0$, spinodal decomposition is predicted for NaCl-structured $V_{1-x}Al_xN$ with $x \geq 0.35$ by ab initio calculations. Consistent with these predictions, metastable single-phase cubic $(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ thin films exhibit chemical modulations after annealing at 900°C, which implies spinodal decomposition into V- and Al-rich cubic nitride phases. However, the formation of thermodynamically stable wurtzite AlN occurs concurrently and the higher mobility of Al in (V,Al)N in comparison to (Ti,Al)N may be understood by the smaller lattice parameter difference of the cubic VN and AlN phases.

Systematic investigations by post-deposition vacuum annealing revealed the onset of spinodal decomposition after cyclic vacuum annealing at 700°C. Moreover, at this temperature, evidence for Al diffusion to grain boundaries and triple junctions is provided by correlation of transmission electron microscopy and atom probe tomography data. The formation of Al-rich regions can be understood by the more than 25% lower activation energy for bulk diffusion of aluminum compared to vanadium as obtained from ab initio calculations. The significantly larger equilibrium volume of wurtzite AlN compared to the cubic phase explains its initial formation exclusively at triple junctions and grain boundaries. Interestingly, the formation of the wurtzite phase at grain boundaries and triple junctions can be tracked by resistivity measurements, while X-ray diffraction and nanoindentation data do not support an unambiguous wurtzite phase formation claim for annealing temperatures < 900°C.

Hence, it is evident that previously reported formation temperatures of wurzite AlN in transition metal aluminum nitrides, determined by other characterization techniques than chemical and structural characterization at the nanometer scale and/or resistivity measurements, are overestimated.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B6-1-WeM

Coating Design and Architectures I

Moderator: Paul Heinz Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria

11:00am **B6-1-WeM-10 Thermally Induced Phase Formation in Magnetron Sputtered Ru/Al Multilayers - Impact of Modulation Period on Transition Temperatures and Phase Sequence***,* ***Vincent Ott (vincent.ott@kit.edu)****,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; C. Schaefer,* Saarland University, Chair of Functional Materials, Germany*; T. Weingaertner, S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; C. Pauly,* Saarland University, Chair of Functional Materials, Germany*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Intermetallic phases in the CsCl B2 structure like NiAl are in focus since long as engineering materials for high temperature applications. Besides good thermal conductivity, they offer high melting points and good oxidation resistance. A major disadvantage is its brittleness, which limits not only its processing at room temperature but also its potential applications. A promising candidate material with improved mechanical properties is the B2 RuAl phase.

Nanoscale multilayer coatings, which can exhibit self-propagating reactions, are a promising approach to synthesize coatings with a targeted microstructure that allows to tailor the material properties. We will show that the synthesis of B2 structured RuAl thin films is also possible by thermal activation close to equilibrium conditions without ignition of the exothermic self-propagating reaction by utilizing a imprinted nanoscale thin film architecture.It will be demonstrated for magnetron-sputtered Ru/Al multilayer thin films, that a specific phase formation sequenceis dependent of the modulation length and microstructure of the bilayers.Thus, by controlling the phase formation sequence, the microstructure of the resulting single-phase AlRu layer can be tuned. For a specific nanoscale layer design, the final phase AlRu can be formed directly from the deposited multilayer state via this approach, without the formation of intermediate intermetallic phases. This statement will be supported by in-situ HT-XRD, TEM, AES mapping and further analyses.

11:20am **B6-1-WeM-11 Structural Design of Diboride Thin Films (Virtual Presentation)**, ***Marian Mikula (mikula@fmph.uniba.sk)****, T. Fiantok,* Comenius University in Bratislava, Slovakia*; N. Koutná,* Linkoping University, Sweden*; V. Šroba,* Comenius University in Bratislava, Slovakia*; D. Sangiovanni,* Linkoping University, Sweden **INVITED**

Transition metal diborides from the group IIIB to VIIB (TMB_2) represent promising candidates for hard and protective films applicable in extreme temperature conditions and under high mechanical loads. This idea is motivated by the knowledge of their bulk equivalents which exhibit excellent mechanical properties, chemical inertness, high temperature stability and good oxidation resistance. Physical vapor deposition (PVD) techniques allow the growth of TMB_2 films with a specific nanocomposite character often formed by (sub)stoichiometric crystalline α-TMB_2/ω-TMB_2 nanofilaments embedded in an amorphous matrix. Although, these films are extremely hard, unfortunately, they are also inherently brittle, and the presence of an amorphous matrix provides an easy pathway for undesired oxidation at relatively low temperatures. For this reason, their application potential is currently very limited and suitable improvements to their weaknesses are intensively sought: (i) from a technological view, it is the use of progressive technologies (HiPPMS, HiTUS) and understanding the relationship between deposition parameters and specific diboride growth; (ii) from a structural point of view, it is the concept of alloying and multilayer architecture where a certain "tuning" of the films could lead to an improvement of the high-temperature behavior and a more ductile response to the mechanical load. Transport of Ions in Matter simulations and Time-resolved Mass Spectroscopy of deposition processes are very useful tools where we can better understand the growth of diboride films. Here, different angular distribution, ionization of target species, influence of Ar neutrals play an important role. Furthermore, using Density Functional Theory calculations we can predict the structural evolution of diboride systems, and their mechanical properties based on thermodynamic assumptions and valence electron concentrations. As we will show, the simplistic models used in DFT calculations at 0 kelvin are unable to predict formation of nanocomposite structures in diboride films, which are more complex in comparison to, e.g., single phase TM nitride films. In this lecture, several case studies of diboride films will be discussed, with the main focus on improving their mechanical and physical properties using a combination of theoretical predictions and experimental approaches.

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Functional Thin Films and Surfaces
Room Pacific C - Session C1-WeM

Optical Materials and Thin Films

Moderator: Nikolas Podraza, University of Toledo, USA

8:00am **C1-WeM-1 Engineering Ultra-thin Films for Extreme Optics and Photonics***, **Jeremy Munday (jnmunday@ucdavis.edu)**,* University of California at Davis, USA **INVITED**

Ultra-thin optical coatings have a variety of applications from antireflection coatings to optical sensors. The simplicity of using a single optical film makes it an excellent candidate for large scale applications; however, this simplicity also results in design space constraints and limitations. In this talk, I will discuss how we are able to circumvent a number of these issues using specially designed ultra-thin films in unique ways. I will discuss how ultra-thin metal films can convert a visible silicon detector into a near-infrared detector, how hydrogen can be optically detected in ultra-thin metal films, how materials with epsilon-near-zero (ENZ) optical properties can enhance these effects, and how high-melting-point materials can be used to create custom thermal emitters and their application to thermophotovoltaics. I will conclude with an outlook on these technologies and future applications.

8:40am **C1-WeM-3 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov (tatyana.bendikov@weizmann.ac.il)**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University, USA*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects. HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (AMX_3). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$(MA = $CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

9:00am **C1-WeM-4 Tuning the Optical Properties of PVD Deposited SiC Coatings by a Design of Experiments Approach***, **Vincent Tabouret (vincent.tabouret@grenoble-inp.Fr)**, A. Crisci, M. Morais, G. Berthomé, E. Garel, G. Renou, D. CHaussende,* CNRS, France

Silicon carbide (SiC) is a wide bandgap semiconductor that is currently driving a profound evolution in power electronics, thanks to a unique combination of outstanding physical properties. In addition, SiC also exhibits very promising optical properties, making it very suited for applications in photonics, such as waveguides and frequency combs. For this purpose, amorphous SiC (a-SiC) thin films are deposited at very low temperature with the main challenges being the control of bulk properties and the formation of perfects interfaces. Today, the relationships between the deposition conditions and the optical properties of the films is still not clear. This paper aims to provide a comprehensive picture of these relationships and finally to give some hints for further optimization.

Coatings of a-SiC were deposited by Physical Vapor Deposition (PVD) on different types of substrates, such as sapphire and silica on silicon wafers, and using a polycrystalline SiC target as source material.A design of experiments (DOE) methodology was implemented to identify and weight the main deposition parameters with respect to the optimization of the refractive index and attenuation coefficient of the films, measured by spectroscopic ellipsometry. In parallel, a systematic investigation of the chemical and structural properties of the films was carried out, using a combination of XRD, FTIR, XPS and TEM.

9:20am **C1-WeM-5 Submicron Structures Obtained by Laser Dewetting of Metallic Thin Film Stacks***, **Bruno Felipe Leitao Almeida (bruno.almeida2@saint-gobain.com)**, L. Gallais,* Institut Fresnel, France*; J. Fonné, D. Guimard,* Saint-Gobain Research Paris, France

Patterned thin films can have interesting applications in functional glazing provided by their optical and electrical properties. Some examples are: Plasmonic effects of the dewetted structures, anisotropic electrical properties (polarizers) and high resistivity and good transparency, that could be used as transparent electrodes. In this context, dewetting is an interesting way of patterning thin films, including metallic ones.

Although most of the literature work on the laser induced dewetting is on uncapped metallic films (substrate / metallic film) using pulsed laser, the laser induced dewetting can also take place in metallic thin films encapsulated by dielectrics using a continuous wave laser. An example is the stack of Glass / Si_3N_4 / Ag / Si_3N_4 deposited on soda-lime glass by magnetron sputtering, depicting morphologies of lines and islands after laser annealing. According to the temperatures achieved during laser treatment, different mechanisms can take place in continuous wave laser dewetting (solid-state or liquid-state dewetting).

In this stack configuration, our work was interested in studying the different structures that could be obtained. The structuration substantially changed the optical properties of the films. A set of *ex-situ* characterizations has been done on the stack before and after structuration. The techniques used were: ellipsometry, spectrophotometry, Fourier-transform infrared spectroscopy, SEM, AFM and XRD.

In order to obtain more information on the mechanisms responsible for these structures in our systems, a set of *in-situ* techniques (fast microscopy and thermal measurements) has been developed and used to obtain the thermal and temporal dependency of the phenomena. *In-situ* thermal measurements were afterwards confronted to results obtained through numerical simulation. These results showed good accordance for temperatures below the structuration threshold regarding the temporal evolution and the spatial distribution of temperature. For temperatures above the structuration threshold, this is no longer the case. From this point on, the film presented changes in the morphology that affects the optical properties (emissivity and absorption).

We shall present in more details these unique structures and their characterizations, the strategies used to take these changes in account to obtain a better correlation measurement/simulation in elevated temperatures and our interpretation of the mechanisms responsible for its structuration.

11:00am **C1-WeM-10 Design of High-Performance VO_2-Based Thermochromic Coatings, and Pathway for Their Industry-Friendly Preparation**, ***Jiri Houska (jhouska@kfy.zcu.cz)***, *D. Kolenaty, T. Barta, J. Rezek, J. Vlcek,* University of West Bohemia, Czechia **INVITED**

The contribution reports our latest results [1-5] concerning energy-saving thermochromic multilayered VO_2-based coatings for smart window applications prepared by reactive magnetron sputtering. First, we show that and how reactive high-power impulse magnetron sputtering with a pulsed O_2 flow control allows reproducible preparation of crystalline VO_2 of the correct stoichiometry under exceptionally industry-friendly deposition conditions: on soda-lime glass substrates without any substrate bias or post-deposition annealing at a low temperature of around 300 °C. Second, doping of VO_2 by W is employed in order to shift the thermochromic transition temperature (68 °C for bulk, 57 °C for our thin film VO_2) toward the room temperature (40 °C for $V_{0.988}W_{0.012}O_2$, 20 °C for $V_{0.982}W_{0.018}O_2$), without concessions in terms of transmittance and its modulation. Third, we employ ZrO_2 antireflection layers both below and above the thermochromic $V_{1-x}W_xO_2$ layer, and explain an optimum design of the resulting $ZrO_2/V_{1-x}W_xO_2/ZrO_2$ coatings. While utilizing a first-order interference on ZrO_2 leads to a tradeoff between the luminous transmittance (T_{lum}) and the modulation of the solar energy transmittance (ΔT_{sol}), utilizing a second-order interference allows one to optimize both T_{lum} and ΔT_{sol} in parallel. Fourth, we discuss multilayered designs leading, without any further doping, to thermochromic coatings of optimized color (chromaticity as close to white as possible). The state-of-the-art T_{lum} and ΔT_{sol} values achieved under the aforementioned industry-friendly deposition conditions and at lowered transition temperature are in agreement with those predicted during the coating design.

[1] J. Vlcek et al., J. Phys. D Appl. Phys. 50, 38LT01 (2017), 10.1088/1361-6463/aa8356

[2] J. Houska et al., Sol. Energy Mater. Sol. Cells 191, 365 (2019), 10.1016/j.solmat.2018.12.004

[3] D. Kolenaty et al., Sci. Rep. 10, 11107 (2020), doi.org/s41598 020 68002-5

[4] J. Houska, Sol. Energy Mater. Sol. Cells 230, 111210 (2021). 10.1016/j.solmat.2021.111210

[5] J. Houska et al., Design and reactive magnetron sputtering of thermochromic coatings (invited perspective paper), J. Appl. Phys., submitted (2022)

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room Town & Country B - Session E1-2-WeM

Friction, Wear, Lubrication Effects, and Modeling II

Moderators: Noora Manninen, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, **Andreas Rosenkranz**, Andreas Rosenkranz, Universidad de Chile

8:00am **E1-2-WeM-1 MXenes: A Model Material for Solid Lubricants**, ***Philipp Grützmacher (philipp.gruetzmacher@tuwien.ac.at)***, Vienna University of Technology, Austria*; C. Gachot,* TU Wien, Austria*; S. Suarez,* Saarland University, Germany*; A. Rosenkranz,* University of Chile

Typically, liquid lubricants are introduced between rubbing surfaces in machine elements and mechanical systems, thus minimizing friction and wear. Diminishing oil resources, the need for ever lower frictional losses, as well as higher demands on the lubricants in terms of resistance against extreme conditions such as high temperatures or low environmental pressures push liquid lubricants to their limits. Therefore, focus turns to solid lubricants. Two-dimensional materials with graphene-like structure have gained remarkable attention, because they have demonstrated excellent tribological properties, even when applying only one or a few atomic layers of the material to the contact zone. There are even several studies, which reported friction coefficients (COFs) below 0.01 and, therefore, superlubricious performance. However, the mechanisms of friction reduction and the influence of the materials' structural and mechanical properties on the latter are still not well understood. One of the newest members of the class of 2D materials are so-called MXene, which were discovered in 2011. MXenes, which are 2D transition metal carbides, nitrides, and carbonitrides, with layers a few atoms thick and, thus, represent an entire class of 2D materials. Single flakes of MXene can be described by the chemical formula $M_{n+1}X_nT_x$ (n = 1 to 4). MXenes offer an extreme versatility in terms of composition, layer thickness, and surface terminations. This makes them ideal model materials to study the influence of theses parameters on tribological behaviour. Despite a still small number of publications on the tribological prosperities of MXenes the field is rapidly growing. First studies have already shown very promising results in terms of wear resistance and friction reduction, even reaching the superlubric regime.

8:20am **E1-2-WeM-2 Structural and Nanomechanical Properties of Manganese Phosphate Coatings**, ***Esteban Broitman (esteban.daniel.broitman@skf.com)***, *Y. Kadin, P. Andric,* SKF B.V. - Research and Technology Development (RTD), Netherlands*; V. Ott, M. Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Manganese Phosphate (MnPh) coatings are nowadays used in rolling bearings applications due to their advantages such as wear resistance, corrosion resistance, improved fatigue life, and anti-fretting performance.

In this work, MnPh coatings with a thickness of about 5 µm were deposited by a chemical conversion process. AISI 52100 steel substrates were placed in a phosphoric acid bath, where an acid-metal reaction took place locally depleting the hydronium (H_3O^+) ions, raising the pH, and causing a manganese phosphate dissolved salt to fall out of the solution and be precipitated onto the steel surface. Analysis of the surface microstructure and composition of the coatings by X-ray diffraction (XRD), Optical Microscopy (OM), Scanning Electron Microscopy (SEM), and Electron Dispersion Spectroscopy (EDS) has revealed a polycrystalline coating with prismatic-shaped crystals, and about 20% content of Mn. The nanomechanical properties, studied by nanoindentation, exhibit a surface with hardness H_{IT} ~ 1 GPa and Young's modulus E_{IT} ~ 50 GPa. A nanoindentation statistical method was used to obtain H_{IT} and E_{IT} value frequencies over a large area of the coating. We demonstrate that the nanoindentation frequency peaks can be correlated to the coating crystalline orientation revealed by XRD.

8:40am **E1-2-WeM-3 Nanoscale Materials for Macroscale Applications: Zero-Friction and Zero-Wear Carbon Films (Virtual Presentation)**, ***Diana Berman (diana.berman@unt.edu)***, University of North Texas, USA **INVITED**

Friction and wear-related failures remain the greatest problems in today's moving mechanical components, from microelectromechanical devices to automotive assemblies and to biological systems. The critical need to reduce and eliminate the tribological failures constitutes the necessity for continuous search of novel materials and lubrication solutions. In this presentation, we overview recent advances in establishing the fundamental understanding of materials interactions at sliding interfaces and use this knowledge as a guide to developing nanomaterials solutions that enhance reliability and efficiency of tribological systems. We evaluate tribological performance of carbon nanomaterials and demonstrate realization of superlubricity regime at macroscale in carbon-based systems. To extend the lifetime of the tribological materials, we demonstrate tribochemically-driven self-replenishment of carbon-based materials inside the contact interfaces, thus, in addition to the superlubricity, enabling a zero-wear sliding regime.

Overall, the findings have not only allowed us to solve some long-standing puzzles, but could also open a new avenue for the development of new concepts and design strategies for next generation of tribologically efficient materials systems.

9:20am **E1-2-WeM-5 Self Lubricant TiSiN/TiAgN Coatings: Room and High Temperature Tribological Behavior**, *F. Fernandes, A. Al-Rjoub,* University of Coimbra, Portugal*;* ***Albano Cavaleiro (albano.cavaleiro@dem.uc.pt)***, Instituto Pedro Nunes, Portugal

Increasing requirements on high speed and dry cutting applications open up new demands on the quality of cutting tool materials. This is particularly important in the aerospace and automotive industries where easy and premature degradation of the cutting tools is observed during the machining of hard-to-cut materials. Several solutions have been tried to improve the machinability of these alloys, being the application of thin solid films by sputtering techniques the most promising. However, so far, such solution does not yet allow meet the need for high speed machining and green manufacturing required for machining those materials. In this study, novel multilayered TiSiN/Ti(Ag)N with different Ag concentrations were developed with potential to protect the surface of machining tools under the absence of lubrication. In order to estimate their wear resistance at high temperature the coatings were tribologically tested in a pin-on-disc equipment at different temperatures against two different counterparts

(Al2O3 and TiAl6V4 balls). For Al2O3 balls, the hardness and reduced modulus determine the tribological performance of the coatings for tests conducted at room temperature (RT). At 550 ºC, the TiSiN/TiN coating failed, whereas the Ag-containing coating performed better due to the presence of Ag in the contact, which decreased the shear stress and, consequently, the friction. For tests against TiAl6V4 balls, the Ag-containing coating was always better than the TiSiN/TiN one. At 550 C, Ag in the wear track prevented the adhesion of the oxidized Ti-alloy wear debris in the contact, favoring the adhesion of wear debris from the coating to both the coating and counterpart surfaces. No wear could be measured for the 700 ºC tests for both coatings due to different reasons: (i) the presence of oxidized adhered material from the ball to the reference TiSiN/TiN coating surface protected from wear and (ii) the presence of Ag-agglomerated particles decreased the friction and minimized the adhesion wear of the counterpart for the TiSiN/TiN(Ag) coating.

9:40am **E1-2-WeM-6 Design and Tribological Characterization of Self-Lubricating Alloys for Laser Deposition Processes***, H. Torres,* AC2T Research GmbH, Austria*; **Carsten Gachot (carsten.gachot@tuwien.ac.at)**,* TU Wien, Austria*; M. Rodriguez Ripoll,* AC2T Research GmbH, Austria

This work presents the development of self-lubricating metallic alloys for laser deposition processes. Laser deposition processes such as laser metal deposition or direct energy deposition are additive manufacturing techniques that offer a great flexibility and efficiency compared to traditional subtractive manufacturing processes. However, the extreme thermal conditions during deposition and the rapid cooling times pose great challenges in the alloy design. This work illustrates these challenges using metals, such as iron and nickel-base alloys, incorporating lubricious soft metals and metal sulfides.

The microstructure and phase composition of the deposited self-lubricating alloys are characterized using X-ray diffraction, scanning and transmission electron microscopy, showing the importance of having the soft metal as single phase without forming intermetallic compounds or being in solid solution. Additionally, the role on friction of the metal sulfide composition and stoichiometry formed during the laser deposition process is discussed. Afterwards, their friction and wear performance are evaluated using high temperature tribological tests in air and vacuum.

The results reveal that the self-lubricating laser deposited alloys are able to control friction from room temperature to 600 °C in ambient air and at least until 300 °C in vacuum. In ambient air, the friction reduction mechanism is determined by the soft metal and the metal sulfides. At higher temperatures, the contribution of the soft metal diminishes due to oxidation so that the role of metal sulfides to self-lubrication is dominant. In vacuum conditions, the laser deposited self-lubricating alloys can effectively reduce friction down to 0.25 without the aid of an additional lubricant against martensitic stainless steel at 300 °C. This overall tribological performance makes the presented self-lubricating alloys potential candidates for high temperature forming and space applications.

11:00am **E1-2-WeM-10 On the Tribological Performance of Magnetron Sputtered W-S-C Coatings With Conventional and Graded Composition***, **Todor Vuchkov (todor.vuchkov@ipn.pt)**,* Instituto Pedro Nunes, Laboratory for Wear, Testing and Materials, Portugal*; A. Cavaleiro,* University of Coimbra, Portugal

Nanocomposite coatings consisting of an amorphous carbon matrix (a-C) with nanocrystallites of transition metal dichalcogenides (TMDs) embedded in it can provide protection against friction and wear in different operating environments, from vacuum to humid ambient air conditions. Magnetron sputtered W-S-C coatings are part of this group of coatings which shows good adaptive tribological behaviour. One potential issue is the running-in behaviour of these coatings as the formation of lubricious tribofilms is crucial for a good tribological response. These tribofilms are most often rich in WS_2, a lubricious compound that is an exceptional lubricant in inert environments (dry N_2, vacuum). A way to improve the running-in behavior would be to change the chemical composition of the coatings across their thickness. Therefore, we deposited a W-S-C coating with varied carbon content across its thickness. The bottom layers of the film were rich in carbon which improved the hardness and thus the load-bearing capacity. The carbon content was gradually reduced towards the top-most layers and finally, a pure WS_2 layer is deposited. In comparison, coatings with a constant composition of ~30 at. % and 50 at. % of carbon were also deposited. The characterization of the coating included scanning electron microscopy with wavelength dispersive spectroscopy for morphological and a study of the chemical composition. X-ray diffraction for structural analysis. Nanoindentation and scratch testing for hardness and adhesion studies respectively. Finally, tribological studies were performed in ambient conditions, dry N_2 environment and at elevated temperature. The correlation between the tribological results and the physico-chemical properties of the coatings revealed that every coating has an advantageous sliding environment.

11:20am **E1-2-WeM-11 Revising the Role of Oxygen "Impurities" in Tribological and Mechanical Performance of MoS_2 Coatings Under Vacuum and Ambient Air Conditions***, **Andrey Bondarev (bondaan2@fel.cvut.cz)**, T. Polcar,* Czech Technical University in Prague, Czech Republic

The $Mo_{32}S_{66}O_2$, $Mo_{33}S_{58}O_9$, $Mo_{24}S_{38}O_{38}$ and $Mo_{24}S_5O_{71}$ coatings were fabricated by unbalanced magnetron sputtering. The increase of oxygen concentration in the Mo-O-S system from 2 to 38 at.% displace sulfur, and changes the structure from columnar crystalline to dense amorphous Mo-O-S. Hardness and Young modulus rise with an increase of O concentration from 2 to 38 at.%. These changes are accompanied by enhancement of the tribological performance both under vacuum and humid air. The triboactivated formation of the crystalline MoS_2 tribolayer from amorphous Mo-O-S occurs inside the wear track as well as on the counterpart surface. In the case of the low amount of S for MoS_2 formation,the tribofilm is preferentially formed on the counterpart surface. In the case of the $Mo_{24}S_5O_{71}$ coating with low S content, the lubricious MoS_2 tribolayer is not formed and the coatings fail the tribotests both under vacuum and humid air. Under vacuum, the lowest CoF of 0.02 is observed for the $Mo_{33}S_{58}O_9$ coating and associated with interfacial sliding between MoS_2 transfer film and wear track. For the $Mo_{32}S_{66}O_2$ and $Mo_{24}S_{38}O_{38}$ coatings, CoF values of 0.05 and 0.04 are recorded, this slightly higher CoF is associated with mixed interfacial sliding/transfer film shearing mode of friction. In humid air the CoF values of the coatings were 0.27, 0.29, and 0.18 for the $Mo_{32}S_{66}O_2$, $Mo_{33}S_{58}O_9$, and $Mo_{24}S_{38}O_{38}$ coatings,respectively. Probably, the friction is controlled by physisorbed water between the MoS_2 tribolayers that forms hydrogen bonds with S atoms which increases the interlayer binding energy, and CoF, respectively. Wear resistance under vacuum is governed by the ability of the coatings to form continuous and stable MoS_2 tribolayer and their mechanical properties. Wear resistance in humid air is governed by cohesive wear that probably takes a place because of increased interlayer binding energy. Important, that in the case of a moderate concentration of O in the coatings composition ($Mo_{33}S_{58}O_9$) the water physisorption can be suppressed, and that improves wear resistance.

11:40am **E1-2-WeM-12 Understanding Ultra-Low Coefficient of Friction of a-C Coated Surfaces Under High Contact Pressure and Humidity Levels***, **Newton K. Fukumasu (newton.fukumasu@usp.br)**, A. Tschiptschin, I. Machado, R. Souza,* University of São Paulo, Brazil

Carbon-based coatings have attracted significant attention of aerospace, automotive and energy industries, due to low friction and high wear resistance. Usually, these tribological characteristics can be tailored based on different levels of sp^2 to sp^3 carbon bond ratios induced by the presence of hydrogen/dopants or deposition process variables, such as power, substrate bias and sample to target distance. Literature reports that ultra-low friction and superlubricity behavior of carbon-based coatings are influenced by the presence of hydrogen and water molecules at the contact during the tribological test. In this work, experimental and numerical analyses were carried out to understand the conditions of the a-C contacting surfaces that promote ultra-low friction states under high contact pressures. The experimental analyses consisted of ball-on-disk reciprocating tests to evaluate friction and wear of non-hydrogenated amorphous carbon (a-C) coatings, deposited by pulsed-DC magnetron sputtering technique. A polycrystalline graphite target was used to deposit the a-C coating over AISI H13 disks and AISI 52100 balls. Scanning Electron Microscopy (SEM), Raman spectroscopy, optical profilometry and instrumented indentation were applied to characterize tested surfaces. Tribological tests were carried out under dry contact conditions at room temperature, high relative humidity (>60%) and high Hertzian contact pressures (>2 GPa). Results indicated a correlation of the G band peak position (GBPP) with the coefficient of friction. When both surfaces were coated, results showed a stable ultra-low coefficient of friction, stabilized down to 0.03 for the highest GBPP. The digital tribology platform TriboCODE was applied to observe the stress distribution in coated surfaces under tribological applications, in which multiscale numerical simulations suggested a possible whole of water molecules, between carbon surfaces, that induces localized changes on carbon bonds, forming structured tribo-films, promoting both reduction of friction coefficient and improved wear resistance.

New Horizons in Coatings and Thin Films
Room Pacific D - Session F4-1-WeM

New Horizons in Boron-Containing Coatings I

Moderators: Helmut Riedl, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

8:00am **F4-1-WeM-1 Synthesis and Oxidation Behavior of $Ti_{0.35}Al_{0.65}B_y$(y= 1.69- 2.43) Coatings**, *A. Navidi Kashani, S. Mráz, D. Holzapfel, M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; L. Löfler, P. Ondracka,* ***Jochen Schneider (schneider@mch.rwth-aachen.de),*** RWTH Aachen University, Germany

The effect of B concentration on the phase formation and oxidation resistance of $(Ti_{0.35}Al_{0.65})$By with y = 1.69, 2.03, 2.43 coatings was investigated. Elemental B targets in radio frequency (RF) mode and a compound $Ti_{0.4}Al_{0.6}$ target in direct current (DC) mode at floating potential were sputtered. The B concentration was varied systematically by adjusting the applied power to the respective magnetrons while keeping the power supplied to the magnetron with the $Ti_{0.4}Al_{0.6}$ target constant. The oxidation resistance at 700 °C in air for up to 8 hours was compared to a cathodic arc evaporated $(Ti_{0.37}Al_{0.63})_{0.49}N_{0.51}$ coating with an Al/Ti ratio of 1.69 ± 0.19 which is very similar to 1.84 ± 0.42 for the boride coatings. Scanning transmission electron microscopy (STEM) imaging revealed oxide scale thicknesses of 39 ± 7 and 101 ± 25 nm for $(Ti_{0.35}Al_{0.65})B_{2.03}$ and $(Ti_{0.37}Al_{0.63})_{0.49}N_{0.51}$ after 8 hours, respectively. Hence, the close to stoichiometric boride outperforms the nitride coating. This behavior can be understood based on compositional and structural analysis of the oxide scales: While the oxide layer on the diboride is primarily composed of Al and O and protective, the oxide layer on the nitride coating is porous and contains Ti, Al and O.

8:20am **F4-1-WeM-2 Influence of Si Alloying on the High-Temperature Mechanical Properties of CrB_2 Based Thin Films**, ***Lukas Zauner (lukas.zauner@tuwien.ac.at),*** *T. Glechner, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold, J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Among transition-metal diboride based thin films CrB_2 is an exciting prospect due to a unique portfolio of materials properties, especially through offering high fracture resistance [1]. However, this class of PVD coatings suffers from an inherently low oxidation resistance. Therefore, establishing pathways to improve the oxidation resistance and thus maintain the mechanical properties to higher temperatures (*i.e.*, above 1000 °C) for these hard-protective coatings is an integral aspect for future high-performance components in thermo-mechanically demanding environments.

In this work, the influence of Si alloying on the high-temperature mechanical properties and fracture toughness of magnetron sputtered CrB_2 thin films is studied for various concentrations. As indicated by thermogravimetric analysis, adding Si to the hexagonal α-AlB_2 structured coatings improves the onset of oxidation by at least 600 °C in lab-air conditions. This drastic improvement in the formation of a stable oxide scale is further correlated with detailed analysis on the thermal stability and phase formation as obtained by non-ambient X-ray diffraction in both vacuum and lab-air atmospheres. The mechanical properties of the synthesised Cr-Si-$B_{2\pm z}$ thin films – including hardness, Young's modulus and fracture toughness – are obtained by nanoindentation and bending of pre-notched, unstrained micro-cantilever beams in the as-deposited as well as the annealed state. Complementary in-situ characterisation of the aforementioned mechanical properties on coated high temperature bulk materials up to 800 °C allowed for a direct identification of changes in the deformation and fracture mechanisms across the investigated temperature regime [2]. Hence, this study showcases the potential of transition-metal diboride thin films – a class previously deemed unsuitable for high-temperature applications – by utilising Si-alloying to preserve the CrB_2 thin films.

[1] Gu, Xinlei, et al. "Sorting transition-metal diborides: New descriptor for mechanical properties." *Acta Materialia* 207 (2021): 116685.

[2] Buchinger, J., et al. "Fracture properties of thin film TiN at elevated temperatures." *Materials & Design* 194 (2020): 108885.

8:40am **F4-1-WeM-3 Design of Novel Transition Metal Diboride-Based Pvd Thin Films: From Pure Compounds to Alloys, Composites and Multilayers**, ***Michael Stueber (michael.stueber@kit.edu),*** *V. Ott, S. Ulrich,* Karlsruhe Institute of Technology (KIT), Germany*; H. Riedl, P. Mayrhofer,* Technische Universität Wien, Austria **INVITED**

Transition metal diboride hard coatings are attractive material candidates for various high performance applications in engineering. Due to their chemical nature and microstructure these materials exhibit interesting multifunctional properties. Unfortunately, their mechanical properties (i.e. toughness and ductility) and the demand for achieving stoichiometric film composition or appropriate adhesion onto various substrates in physical vapor deposition processes make their utilization often a challenge. Thus, such materials and their deposition experience currently a strong revitalization of research efforts. This presentation will review the recent status of PVD transition metal diboride-based thin films, with a focus on magnetron sputtering techniques. It includes a brief retrospect on pioneering developments in the field, covering fundamental materials science aspects of the diborides as well as advanced coating design concepts such as the various Ti-B-C-N thin films. The major part of the presentation will discuss three design concepts for novel boride-based hard and tough coatings for engineering applications. These are mainly based on the model thin film material TiB_2 which is by far the most detailed characterized PVD transition metal diboride. The first approach describes the alloying of TiB_2 with the intention to design ternary solid solutions, $(Ti,X)B_2$ where X is another metal such as Al, Cr, Zr, V or others. The impact of Al content on phase formation, microstructure and mechanical properties of magnetron-sputtered $(Ti,Al)B_2$ thin films will be described. A second approach refers on the formation of TiB_2-metal composite thin films, which covers the objectives of designing thin film material composed either of a boride matrix with dispersed metal nanoclusters or of a metal matrix with dispersed diboride cluster phase. The metal phase used in this part of the description is the superalloy B2 structured NiAl. Phase formation and microstructure evolution of magnetron co-sputtered TiB_2-NiAl thin films will be covered, both in as-deposited and vacuum annealed state. The third approach deals with the integration of TiB_2 layers into nanoscale multilayers when the second layer constituent is also a metal layer. Focus is again on the combination of TiB_2 with NiAl. Multilayers with variation of the bilayer period and its impact on their structure and properties will be considered. Other relevant diboride thin film design concepts and newest progress achieved by advanced PVD techniques such as HIPIMS or hybrid PVD processes will also be reported.

9:20am **F4-1-WeM-5 Tribological Properties and Thermal Stability of $V_{1-x}Mo_xB_y$ Coatings**, ***Katarína Viskupová (katarina.viskupova@fmph.uniba.sk),*** *B. Grančič, T. Roch, M. Truchlý, M. Mikula, V. Šroba, L. Satrapinskyy, P. Kúš,* Comenius University, Bratislava, Slovakia

Development of space technology encourages research of new materials that are highly performing in extreme conditions. An important category are low wear resistance solid lubricants with stable properties at temperatures above 1000°C and in oxidative environments. Currently widely studied transition metal diborides (TMB_2) offer high temperature stability and excellent mechanical properties, such as high hardness and wear resistance. Vanadium diboride also shows promising tribological properties due to lubrication effect of oxidation products B_2O_3 and V_2O_5 [1]. Our aim is to study effects of alloying of VB_2 coatings with Mo, which may lead to structural decomposition and hence provide good mechanical properties at high temperatures [2]. Moreover, possible formation of MoO_3 during oxidation may influence the tribological properties of the coatings [3]. In our work, we use physical vapour deposition for preparation of $V_{1-x}Mo_xB_y$ films with different Mo concentration and B/TM ratio. We discuss the relationship between chemical composition, structure formation and structure evolution during vacuum annealing up to 1300°C. We further investigate the influence on hardness, elastic modulus, and friction coefficient at elevated temperature in air. Our results are supported by density functional theory calculations.

[1] A. Erdemir et al., Wear 205 (1997) 236-239

[2] B. Alling et al., Scientific Reports 5 (2015) 9888

[3] W. Gulbiński et al., Wear 254 (2003) 129–135

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Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific D - Session H2-2-WeM

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II

Moderators: James Gibson, RWTH Aachen University, Germany, **Olivier Pierron**, Georgia Institute of Technology, USA

9:40am **H2-2-WeM-6 Abnormal Grain Growth in Ultrafine Grained Ni Under High-Cycle Loading**, ***Olivier Pierron (olivier.pierron@me.gatech.edu)***, Georgia Institute of Technology, USA

Abnormal grain growth can occur in polycrystalline materials with only a fraction of grains growing drastically to consume other grains. Here we report abnormal grain growth in ultrafine grained metal in a rarely explored high-cycle loading regime at ambient temperature. Abnormal grain growth is observed in electroplated Ni microbeams with average initial grain sizes less than 640 nm under a large number of loading cycles (up to 10^9) with low strain amplitudes (< 0.3%). Such abnormal grain growth occurs predominantly in the family of grains whose <100>orientation is along the tensile/compressive loading direction. Micromechanics analysis suggests that the elastic anisotropy of grains dictates the thermodynamic driving force of abnormal grain growth, such that the lowest strain energy density of the <100>oriented grain family dominates grain growth. These results are compared to other recent investigations of cyclic-induced grain growth in metals. In order to establish the general applicability of abnormal grain growth in metals controlled by the elastic anisotropy of single-crystal grains, a high-throughput technique to perform systematic characterization of cycle-induced grain growth in ultrafine grained metallic films with varying degrees of elastic anisotropy is presented.

11:00am **H2-2-WeM-10 Superlattice Effect on the Mechanical Properties of Transition Metal Diboride Coatings**, ***Rainer Hahn (rainer.hahn@tuwien.ac.at)**, A. Tymoszuk,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* 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*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

PVD deposited superlattice structures enable the simultaneous enhancement of hardness and fracture toughness of thin ceramic coatings – evading the strength-ductility trade-off dilemma [1]. While a deeper understanding of this effect has been gained for transition metal nitrides (TMN) [2], hardly any knowledge is yet available for diborides (TMB_2). Here we show that superlattices can—similarly to the nitrides—increase both mechanical properties of diboride coatings. For this purpose, we developed non-reactively sputtered TiB_2/WB_2 and TiB_2/ZrB_2 superlattice coatings, the former is characterized by a high difference in shear modulus (ΔG ~112 GPa), and the latter features a high lattice mismatch (Δa ~0.14 Å) of the participating layer materials.

Nanoindentation, as well as in-situ microcantilever bending tests, yield a distinct increase in hardness (up to 45.5 ± 1.3 GPa) for the TiB_2/WB_2 system but no increase in fracture toughness. Contrary, TiB_2/ZrB_2 shows no increase in H, while K_{IC} increases by ~ 20% up to 3.70 ± 0.26 MPa·$m^{1/2}$. Similar behavior is observed for cube-corner-based fracture toughness evaluation, however, under the influence of corresponding residual compressive stresses. X-ray diffraction studies show a preferred (001) orientation for most of our coatings, the only exception thereby are the TiB_2/WB_2 superlattices with a bilayer period Λ > 9 nm, where we observe increasing (101) orientation with an increasing bilayer period. Furthermore, the number of satellite peaks and their intensity hints towards sharp interfaces, later confirmed by our HR-TEM studies. These results are discussed and complemented by an extensive literature review.

Keywords: Hard Coatings, Diborides, Physical Vapor Deposition, Micromechanical Testing, Fracture Toughness

[1] R. Hahn, M. Bartosik, R. Soler, C. Kirchlechner, G. Dehm, P.H. Mayrhofer, Scr. Mater. 124 (2016) 67–70.

[2] R. Hahn, N. Koutná, T. Wójcik, A. Davydok, S. Kolozsvári, C. Krywka, D. Holec, M. Bartosik, P.H. Mayrhofer, Commun. Mater. 2020 11 1 (2020) 1–11.

11:20am **H2-2-WeM-11 Fatigue Behavior of Gold Thin Films at Elevated Temperature Studied by Bulge Testing**, ***Anna Krapf (anna.krapf@fau.de)***, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

Microcomponents, such as microchips, actuators and sensors, are often based on metallic thin films that must endure cyclic thermomechanical loading during their lifetime. The mechanical properties of these thin films are usually different from bulk materials and so are their thermomechanical fatigue mechanisms. For this reason, an advanced bulge setup was used to cyclically load gold thin films of 150 nm thickness at temperatures in the range 25 °C – 100 °C. The stress-controlled experiments highlight the significance of the interface character for the fatigue lifetime. The presentation will discuss the fatigue properties and damage mechanisms of gold thin films – freestanding and with brittle sublayer - as a function of the microstructure, temperature and stress amplitude.

11:40am **H2-2-WeM-12 Tensegrity Metamaterials - Towards Failure Resistant Engineering Systems**, ***Jens Bauer (jens.bauer@uci.edu)***, University of California, Irvine, USA **INVITED**

Failure of materials and structures, including ductile metals, brittle ceramics, discrete foams and space-trusses, is typically preceded by highly localized deformation. Formation of shear bands and crack surfaces, and buckling of walls and struts thereby cause a chain reaction of locally confined damage events, while large parts of the system do not experience critical loads. In lightweight structures, localized deformation causes catastrophic failure, limiting application to small strain regimes. To ensure robustness under real-world non-linear loading scenarios, over-designed linear-elastic constructions are adopted.

Breaking with this established paradigm, we present three-dimensional (3D) tensegrity metamaterials which delocalize deformation, demonstrating a pathway towards superior, failure resistant load bearing systems. In a tensegrity system, isolated rigid compressive bars stretch a continuous mesh of tethers forming a free-standing lightweight, truss structure. We demonstrate that the unique isolation of compressive members in tensegrity systems suppresses the propagation of instable deformation mechanisms. This facilitates a delocalized deformation pattern, which is free from localized under- or over-use. As a result, tensegrity metamaterials possess unprecedented failure resistance, with up to 25-fold enhancement in deformability and orders of magnitude increased energy absorption capability without failure over same-strength state-of-the-art lattice architectures. These findings provide important groundwork for design of superior engineering systems, from reusable impact protection systems to adaptive load-bearing structures.

Special Interest Talks
Room Town & Country A - Session SIT3-WeSIT

Special Interest Session III
Moderator: Samir Aouadi, University of North Texas, USA

1:00pm **SIT3-WeSIT-1 Tribological Coating Solutions and Lubrication Strategies for Gas Turbine Engines***, Pantcho Stoyanov (pantcho.stoyanov@concordia.ca),* Concordia University, Canada **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 bombardment 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 and lubrication strategies employed in several sections of gas turbine engines. After a general review of aircraft engine tribology, the talk will focus on tribological coatings and materials used to minimize fretting type of wear. 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 the future strategies of tribological coating solutions in gas turbine engines.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B5-2-WeA

Hard and Multifunctional Nanostructured Coatings II

Moderators: Rainer Hahn, TU Wien, Institute of Materials Science and Technology, Austria, **Tomas Kozak**, University of West Bohemia, Czechia

2:00pm **B5-2-WeA-1 Design of Coatings for Harsh Environments by Computation and Experiment (Virtual Presentation)**, ***Efstathios "Stathis" I. Meletis (meletis@uta.edu)***, University of Texas at Arlington, USA **INVITED**

One of the great challenges in engineering science is to protect a material at its surface from chemical reactions and mechanical degradation such as high temperature oxidation, impact and wear. Applying a hard coating, which bonds strongly to the surface of the material, prevents excessive abrasion and provides the needed shield towards mechanical impact. At high temperatures in an oxidative environment, however, many hard boride, carbide and nitride coatings quickly deteriorate due to thermal instability and chemical degradation. An overview is presented of our recent efforts under the materials genome initiative to develop a new class of protective ceramic coatings, coalescing computational investigation and experimental realization and characterization. The efforts focus on several transition metal quaternary (Zr,Hf,Si)BCN and ternary (Hf,Ta)SiN amorphous and nanocomposite coatings for severe environment applications. Compositional and structural atomistic simulations using density-functional theory and large-scale molecular dynamic calculations were conducted to explore thermal, oxidation and mechanical properties. A number of complementary experimental characterization techniques were used to study the thermal, mechanical and oxidation resistance of the coatings. Atomistic and local structure characterization and image simulations were conducted by using HRTEM to develop a comprehensive understanding of the synthesis-structure-property relationship in these high potential coating systems.

2:40pm **B5-2-WeA-3 Microstructure and Properties of PVD Synthesized Super-hard Ti-B-N Coatings**, ***Rebecca Janknecht (rebecca.janknecht@tuwien.ac.at)***, *R. Hahn, A. Kirnbauer,* TU Wien, Institute of Materials Science and Technology, Austria; *P. Polcik ,* Plansee Composite Materials GmbH, Germany; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Ternary transition-metal boron nitride Ti-B-N has emerged as an outstanding material system in the field of protective coatings due to its high hardness and temperature stability. In particular, its large number of equilibrium and metastable phases offers numerous possible compositions for investigating and understanding structural effects and their influence on mechanical properties.

With prior interest in chemical compositions close to the TiN-TiB line in the corresponding equilateral concentration triangle, Ti-B-N coatings were prepared using a Ti-TiN-TiB_2 target containing 10 at.% B.

Focusing on the investigation of single-phase structured super-hard (H≥40 GPa) Ti-B-N coatings, the influence of various deposition conditions on the structure and mechanical properties during non-reactive DC magnetron sputtering - compared to nanocrystalline Ti-B-N - comprises this study. The results show - consistent with previous ab initio calculations - that up to 10 at.% B can be incorporated into the face-centered cubic (fcc) TiN lattice.

3:00pm **B5-2-WeA-4 Enhanced Mechanical Performance of Nanostructured B-Dopednitride Coatings Deposited by HiPIMS With Positive Pulses**, *P. Diaz-Rodriguez, A. Mendez, J. Santiago,* ***Ivan Fernandez (ivan.fernandez@nano4energy.eu)***, *A. Wennberg, J. Endrino,* Nano4Energy, Spain; *E. Chacon, A. Guzman, M. Panizo,* Universidad Politecnica de Madrid, Spain; *M. Monclus, J. Molina,* IMDEA Materiales, Spain

In recent years, due to the advancement of high-speed machining(HSM), more demanding specifications on cutting tool coatings' hardness, chemical inertness materials, wear resistance,anti-abrasion, and also thermal and oxidation resistance are required. In order to overcome the detrimental effects associated with high temperatures during HSM on tool life and workpiece surface finishing, nanostructured coatings based on multilayers or nanocomposites have been proposed [1, 2]. In this work, we present nanostructured AlTiBN and AlCrBN coatings deposited by HiPIMS with positive pulses. The optimization of the coatings was carried out by tailoring metal ion fluxes and energies. More energetic process conditions have been provided by adjusting height and width of positive pulses. Coatings' microstructure has been studied and related to HiPIMS parameters. The formation of nanocrystalline grains embedded in an amorphous boron-rich phase provides enhanced toughness and wear resistance[3]. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained in nanoscratch testing. High temperature nanoindentation and micropillar splittingwere used to evaluate toughness and thermal resistance of the coatings. Finally, micromilling tests were carried out to assess the performance of these nanostructured coatings in micromachining of stainless steel and titanium alloys.

[1] J. Musil,Surface and Coatings Technology 125 (2000) 322–330

[2]P. Mayrhofer et al.,Progress in Materials Science 51 (2006) 1032–1114

[3] A.Mendez et al., Surface and Coatings Technology 422 (2021) 127513

3:20pm **B5-2-WeA-5 Development of TiB_2 Coatings in a New Generation Industrial Reactor Based on Hybrid DC-pulsed and HIPIMS Magnetron Sputtering on HSS Steels – Tribological Study at Room, Medium and High Temperature**, *E. Arias,* Asociación de la Industria Navarra, Spain; ***Gonzalo Garcia fuentes (gfuentes@ain.es)***, Asociación de la industria Navarra, Spain; *H. Gabriel,* PVT Plasma und Vakuum Technik GmbH, Germany; *I. Fernández,* N4E, Spain; *J. Fernández Palacio,* Asociación de la Industria Navarra, Spain

Titanium di-boride (TiB_2) coatings exhibit excellent combination of hardness and low adhesion to cutting metal alloys such as these based on Ti, Al or Ni, and it has been used since a decade on cutting tools in the aerospace sector. TiB_2 is well known to exhibit low moderate toughness, which limits it applicability under complex 3D shaped cutting tools, or tools subject to very high loads. Pulsed DC sputtering as well as other conventional vapor deposition techniques are being developed to this purpose. In our approach, a hybrid industrial scale system equipped with 4 magnetron sputtering sources and a 600/350 mm Height/Diameter effective volume is chosen to implement TiB2 coating formulations. The system is equipped with pulsed DC and HIPIMS V+ PSUs. The target configuration is chosen in the unbalance mode while the BIAS pulse is synchronized with the HIPIMS PSU so to enhance the Me+ ion bombardment ratio. The HIPIMS V+ parameterization will be focus to provide an enhanced coating-to-substrate adhesion strength, but also microstructural strength to the TiB_2 matrix. Optical emission probes will provide valuable information about the concentration ratio of Me/Ar ionized species for different pulsing/power deposition conditions. The characterization of the coatings is carried out using glow discharge emission spectroscopy, x-ray diffraction, scanning electron microscopy and nanoindentation. The friction and wear is characterized using different conditions of temperature, and load. In particular, the surface contact interaction with Ti-alloys and Al-alloys will be discussed in terms of the galling of the testing materials for different conditions.

3:40pm **B5-2-WeA-6 Study the Effect of Nozzle Geometry on Spray Coating by Aerosol Deposition Method**, ***Bahareh Farahani (bahareh.farahani@csulb.edu)***, California State University, Long Beach, USA; *M. Jadidi,* Ryerson University, Canada; *S. Moghtadernejad,* California State University, Long Beach, USA

The Aerosol Deposition (AD) method, also known as Vacuum Cold Spraying (VCS), is an emerging spray coating technology to fabricate a dense thick/thin ceramic or metal layer on a substrate through the kinetic impaction and cumulative deposition of ultrafine solid particles under near-vacuum conditions [1]. AD is a Room Temperature Impact Consolidation (RTIC) mechanism that causes negligible oxidation or degradation to the feedstock powders making it a desirable candidate for applying coatings on lower-melting and temperature-sensitive substrates such as glass, metal, and polymers. This high-velocity deposition technique is a promising coating process for industrial applications, such as solid oxide fuel cells, solid-state lithium batteries, bio-component coatings, and surface protection [1]. One of the challenges of this method is achieving successful deposition of the particles with high coating quality. It should be noted that coating quality can be significantly improved by optimizing the particle impact velocity. As such, the focus of this project is to study the effect of nozzle geometry and operating parameters such as range of pressure ratios and standoff distance on particle impact velocity using the method of Computational Fluid Dynamics (CFD).

In this work, a de Laval nozzle with two axisymmetric geometries of 1) sharp and 2) rounded edge will be modeled to generate a supersonic gas flow to accelerate particles toward a substrate using CFD. To simulate the gas flow behavior in the jet stream leaving the nozzle, a realizable k-epsilon turbulence model will be used. Results will be validated by comparing the locations of the Mach disks in highly under-expanded free-jet conditions with the experimental data of nozzles with the same geometries. In addition, a Eulerian-Lagrangian based discrete-phase model will be used to study the particle trajectory and velocity upon impact with the substrate. The effect of drag coefficient and thermophoretic force on in-flight particles behavior will be also evaluated to improve the particles deposition formation upon impact. The simulation results will lead to understanding the effects of nozzle geometry and operating parameters on the particle impact velocity and distribution. This ultimately provides the baseline to design and optimize an AD system with enhanced coating quality.

[1] D. Hanft, J. Exner, M. Schubert, T. Stöcker, P. Fuierer, and R. Moos, "An overview of the Aerosol Deposition method: Process fundamentals and new trends in materials applications," *J. Ceram. Sci. Technol.*, vol. 6, no. 3, pp. 147–181, 2015, doi: 10.4416/JCST2015-00018.

4:00pm **B5-2-WeA-7 Thick Ceramic Coatings Deposited by Supercritical Fluid Chemical Deposition (SFCD)**, ***Erwan Peigney (erwan.peigney@icmcb.cnrs.fr)***, *G. Aubert,* ICMCB-CNRS, France; *M. Cavarroc,* SAFRAN, France; *A. Poulon-Quintin, C. Aymonier,* ICMCB-CNRS, France

Requirements for the elaboration of ceramic coatings are constantly evolving, especially when it comes to depositing high thicknesses on complex shaped substrates. In this way, traditional deposition methods do not fully meet the new challenges, notably directional processes such as PVD. Liquid-phase processes suffer also many limitations, including contamination issues and poor mass transport. Likewise, non-directional gas-phase processes such as CVD encounters precursor volatility constraints, which lead to mass transport-limited conditions, poor step coverage and non-uniformity for submicrometer-patterned substrates.

To overcome all these difficulties, new processes have shown great interest in recent decades. Among this, Supercritical Fluid Chemical Deposition technology (SFCD) stands out thanks to its advantages. Indeed, supercritical fluids have hybrid thermophysical properties, intermediate between liquids and gases, which are continuously adjustable with small variations of pressure and temperature. For instance, they exhibit gas-like viscosities and diffusivities while having liquid-like densities allowing the dissolution of a wide range of metallic precursors with substantial concentrations. SFCD process proposes to deposit thick inorganic films with uniform coverage of complex shaped substrate, complete filling of narrow high aspect ratio features, reduction in process temperatures and this with a high growth rate deposition.

The present work concerns the development of thick ceramic coatings on complex shaped metallic substrates using a cold-wall reactor filled with different mixture of fluids at sub- and supercritical conditions. Depending on the precursor selected, the fluid composition and the deposition parameters, the coating properties are tuned in terms of adhesion to the substrate, hardness, roughness and corrosion resistance. The material microstructure and crystallinity are also impacted. They are characterized through GIXRD, TEM, XPS and Raman spectroscopy.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B6-2-WeA

Coating Design and Architectures II

Moderator: Paul Heinz Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria

2:00pm **B6-2-WeA-1 Industrial Antibacterial Decorative Coatings**, ***Ivan Kolev (ikolev@hauzer.nl)***, *P. Immich, A. Fuchs, H. Vercoulen, D. Doerwald,* IHI Hauzer Techno Coating B.V., Netherlands

Anywhere large numbers of people gather, touch-based contamination contributes to the spread of bacterial infections. Coatings with antibacterial effect could have an important public health benefit. This includes door handles, bathroom taps and other high-touch elements in public and private buildings. Already for decades these elements have commonly had a PVD decorative finish, which provides them with an attractive look and increased wear and corrosion resistance. The next generation decorative coating should also include antibacterial properties.

In this work, decorative antibacterial coatings on industrial scale are presented. The antimicrobial properties are realised by doping of the standard decorative coatings with Cu and Ag. To verify the efficacy, the coatings are tested for their kill rate against two of the most common bacteria *Escherichia coli* and *Staphylococcus aureus*. The testing shows excellent results – kill rate of up to 100% within one hour. The effect on the doping upon standard properties, such as colour, wear and corrosion resistance are also discussed

2:20pm **B6-2-WeA-2 Few Thoughts about Hard Coatings and Machining Industry**, ***Aharon Inspektor (ainspekt@andrew.cmu.edu)***, Carnegie Mellon University, USA

The development of cutting tools is a traditional proving ground for the design and testing of new materials, new coatings and new concepts in materials science. Recently we witnessed rapid development of innovative hard coatings with superior mechanical properties, thermal stability and chemical resistance. The new coatings are well suited for machining materials at significantly higher speeds and feed rates and play important role in machining industry. Nevertheless, "older" coatings such as TiN, TiCN and TiAlN are also still in use at many small and large machining centers. Why it is so? What is the reason for this wide range of hard coatings in the cutting tools industry? And how this affect development and introduction of novel coatings? In this paper we will discuss these questions, present selection criteria of hard coatings in the industry and examine how the Fourth Industrial Revolution will affect future hard coatings and machining landscape. We will start with "machining wear maps" that display the relationships between machining parameters and tool's wear: the starting point for tools' selection, and for the resultant wide range of hard coatings in the industry. Then we will examine how the Fourth Industrial Revolution, Industrial Internet of Things (IIOT) with multi-level connectivity of sensors, machines and systems, will likely changes this manufacturing landscape. We will conclude the talk by discussing the germane trends and ensuing future development of hard coatings for metal cutting industry.

2:40pm **B6-2-WeA-3 Effect of Coating Architecture on Stress Relief Mechanism of TiZrN Coatings on Si Substrate (Virtual Presentation)**, ***Jia-Hong Huang (jhhuang@ess.nthu.edu.tw)***, *M. Liu, Y. Chiu,* National Tsing Hua University, Taiwan **INVITED**

Hard coatings deposited by physical vapor deposition are usually subjected to high residual stress. To relieve the residual stress, it is commonly introducing a metal interlayer between coating and substrate or by further coating architecture design. However, the underlying stress relief mechanism of coatings with architecture has not been fully understood. The purpose of this study was to investigate the extent of stress relief achieved by employing different types of interlayers or coating architecture, and explain the stress relief mechanism in each coating architecture using a simple energy-balance model. Themodel was based on the concept that the relief of stored energies from both coating (ΔG_f) and Si substrate (ΔG_{Si}) was converted to the plastic work by the metal interlayer. TiZrN/TiN/Ti tri-layer coatings and TiZrN bi-layer coatings with Ti, TiZr and TiZr/Ti interlayers on Si substrate were chosen as the model systems, which were deposited using unbalanced magnetron sputtering. Laser curvature method and the average X-ray strain method combined with nanoindentation were used to measure the residual stress of the entire specimen and individual layers, respectively. For the TiZrN specimens with different interlayers, the results showed that increasing the metal interlayer thickness may not be an effective way on increasing stress relief efficiency in the coating. Since plastic deformation of the interlayer could only occur in part of the interlayer near the TiZrN/interlayer interface, increasing the interlayer thickness did not substantially increase the effective deformation thickness. Furthermore, plastic deformation became difficult for the metal interlayer with higher strength coefficient (k). Therefore, ΔG_f may decrease by using high-k interlayer with the same thickness. However, the high-k interlayer could act as a channel to transfer the stress to the Si substrate, if proper interlayer thickness was used. For the specimens with coating architecture, the results revealed that the extent of stress relief in TiZrN coating with TiN/Ti architected interlayer was larger than that with only a single Ti interlayer. The TiN transitional layer served as an energy channel that effectively transferred the stored energy in TiZrN to the Ti interlayer and alleviated the large stress difference at the original TiZrN/Ti interface, thereby increasing the plastic deformation capacity of the underlying interlayer; therefore, a larger fraction of residual stress in TiZrN was relieved.

Functional Thin Films and Surfaces
Room Town & Country D - Session C2-1-WeA

Thin Films for Electronic Devices I

Moderators: Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Jörg Patscheider**, Evatec AG, Switzerland

3:20pm **C2-1-WeA-5 Developing Electronic Materials With an Eye Towards Packaging**, ***Marcel A. Wall (marcel.a.wall@intel.com)***, Intel Corporation, USA **INVITED**

Heterogeneous integration of multiple types of Integrated circuit chips on a single package is an emerging area in advanced packaging that has made significant impact to High Performance Computing (HPC) devices. In this presentation, we will discuss the evolution of heterogeneous System in Package (SIP) packaging technologies. We will provide an overview of key drivers and metrics for enabling advanced die to die and on package interconnect technologies . We will cover the areas of innovation needed in materials, equipment, process and design in advancing the next generation of heterogeneous SIP packaging technologies. Finally, we will cover some of the unique requirements needed of basic thin film materials used in electronics, as it applies to packaging.

4:00pm **C2-1-WeA-7 Crystallographic Study of Non-polar $Al_{0.7}Sc_{0.3}N$(11-20) Grown on r-plane Al_2O_3 Using Magnetron Sputter Epitaxy**, ***Akash Nair (akash.nair@iaf.fraunhofer.de)***, *L. Kirste,* Fraunhofer Institute for Applied Solid State Physics IAF, Germany*; N. Manuel Feil,* University of Freiburg, Germany*; M. Prescher, A. Žukauskaitė,* Fraunhofer Institute for Applied Solid State Physics IAF, Germany

Aluminium scandium nitride (AlScN) has emerged as a promising material for fabrication of bulk acoustic wave (BAW) and surface acoustic wave (SAW) devices by virtue of its high piezoelectric properties and improved electromechanical coupling. Despite the high interest, AlScN remains relatively unexplored material in terms of the structural properties and device applications. We recently demonstrated that non-polar $Al_{0.77}Sc_{0.23}N$ offers a pathway for further improvement in electromechanical coupling for SAW resonators by aligning the acoustic wave along the c-axis direction with the largest piezoelectric response[1]. The metastable nature of $Al_{1-x}Sc_xN$ at higher scandium concentrations, that causes formation of abnormally oriented grains (AOG) protruding from surface of the films, has been a challenge for its adoption for SAW applications. We succeeded in achieving the growth of completely AOG-free non-polar in-plane oriented $Al_{1-x}Sc_xN$ films with even higher Sc content of x=0.3 by reactive magnetron sputter epitaxy. Various sputtering process conditions were investigated focusing on the $Al_{0.7}Sc_{0.3}N$(11-20)/Al_2O_3(1-102) film. Surface quality and films with RMS roughness less than 0.5 nm could be obtained. The atomic force microscopy (AFM) and x-ray diffraction (XRD) studies of films show a unique striated grain morphology along the c-axis of the film revealing in-plane anisotropy. While the XRD measurements confirm the in-plane orientation of $Al_{0.7}Sc_{0.3}N$(11-20), the φ scans also reveal a distorted wurzitic structure and structural anisotropy. The structural anisotropy is studied by combining transmission electron microscopy, high resolution XRD and AFM. Furthermore, the optimized $Al_{0.7}Sc_{0.3}N$(11-20) films were used to fabricate SAW resonator test structures. Different in-plane SAW propagation directions were used to map the angular distribution of effective electromechanical coupling as well as piezoelectric properties of non-polar AlScN thin films and correlated to the results of structural anisotropy study.

[1] A.Ding, et al., APL 116(10), 101903 (2020).

4:20pm **C2-1-WeA-8 Tuning Barrier Properties of Metal Nitride Thin Films for GaN Transistor Applications**, ***Clemens Nyffeler (clemens.nyffeler@evatecnet.com)***, *B. Attarimashalkoubeh, J. Patscheider, B. Heinz,* Evatec AG, Switzerland

Due to their thermal stability and barrier properties, conductive metal nitrides are often used in the fabrication of electronic devices, such as contact layers on the surface of a field-effect transistor's (FET) gate region. Specifically, in the case where a metal nitride layer is in direct contact with a semiconductor's surface, for example in heterojunction FETs made from III-V materials such as Gallium Nitride, the barrier function requirements are twofold. The material must prevent both, migration of metal species (diffusion barrier), and also electrical conduction into the semiconductor (Schottky barrier), thus preventing shorts between gate and channel and ensuring efficient device operation.

In this context, we investigate the mentioned barrier function, electrical conductivity, and other relevant properties of thin TiN_x and WN_x layers (t < 200nm) deposited by reactive magnetron sputtering. Sputter deposition was performed on an Evatec Clusterline® 200II industrial production system for automated processing of 200mm substrates at high throughput.

Our experiments show that good barrier properties in tungsten nitride are achieved for a sub-stoichiometric, nitrogen-deficient composition of WN_x with a nitrogen content of only 20at% showing a predominant phase of (111)-oriented W_2N. For TiN_x on the other hand, we see evidence for diffusion through the barrier layer in annealing experiments for sub-stoichiometric films only. Conversely, the barrier remains effective for films deposited in a nitrogen-rich ambient, with a N2:Ar gas-flow ratio of larger than 1:1, resulting in over-stoichiometric films.

The diffusion experiments are conducted on stacks of 25nm Ti / 100nm TiN_x / 75nm Al layers (top-to-bottom, on Si substrates). Four-point probe measurements before ex-situ annealing at temperatures up to 400°C and after annealing exhibit a significant change of the measured sheet resistance. These changes are correlated to failure of the Schottky barrier function.

4:40pm **C2-1-WeA-9 Advancements in Metallic Interconnects for the Semiconductor Industry**, ***Thomas Ponnuswamy (Thomas.Ponnuswamy@lamresearch.com)***, Lam Research Corp, USA **INVITED**

The semiconductor industry is advancing from a SoC (system on ship) approach towards developing various integration schemes involving SiP (system in package) to meet the future requirements of performance and cost. This is commonly referred to as heterogeneous integration and is being utilized for 2.5D/3D chip stacking, high density fanout and chiplets. All these approaches rely on the use of metallic interconnects including TSVs (through-silicon vias), micropillars, fine line RDL, and hybrid bonding.

In the case of 3D stacking with TSVs for memory, we see an increase in the number of stacking layers and reduction of critical dimensions to accommodate higher I/O counts. The interconnects in high density fanout comprise of fine line RDL and megapillars. To meet the performance requirements line dimensions are shrinking from 5x5µm to sub 2x2µm L/S, along with incorporation of a multilayer approach. Megapillars typically range from 100 to 200µm CD with varying aspect ratios depending on the integration scheme and performance needs. Copper pillars with sub-40µm pitch are referred to as micropillars which will eventually need to be replaced by hybrid bonding as the dimensions shrink below 10µm.

Scaling requirements for each of these interconnects pose challenges that need to be addressed by making process, materials, and integration changes. In the case of TSVs, higher aspect ratios necessitate the need for alternate metallization schemes. For micropillars, increase in bump density results in challenges to assembly yield and reliability, while for fine line RDLs stress induced damage and topography control needs to be solved. Finally, in the case of hybrid bonding the key requirement of lower thermal budget for yield improvement needs to be addressed for die-to-wafer and wafer-to-wafer stacking.

This presentation will cover how select deposition processes and material changes provide solutions to the scaling challenges posed by interconnects utilized in various heterogenous integration schemes.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E1-3-WeA

Friction, Wear, Lubrication Effects, and Modeling III

Moderators: Noora Manninen, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, **Andreas Rosenkranz**, Andreas Rosenkranz, Universidad de Chile

2:00pm **E1-3-WeA-1 Critical Materials-Free Cermet Coatings by Thermal Spraying: Sliding and Abrasive Wear Behaviour (Virtual Presentation)**, ***Giovanni Bolelli (giovanni.bolelli@unimore.it)***, Unimore, Italy **INVITED**

Cermet coatings provide resistance against sliding and abrasive wear in e.g. petrochemical valves, papermaking rolls and blades, pump parts, rotary joints and sliding elements of high-speed automatic machinery, etc.

The better-known compositions are based on WC and/or Cr_3C_2. WC-Co-based compositions possess excellent wear resistance at room and moderate temperatures; however, they present two types of criticalities. W and Co are regarded as critical raw materials by many industrialized countries, due to the risk for supply shortages (primary production being concentrated in few manufacturing countries) together with their strategic relevance. On the other hand, Co is now labelled as probable human carcinogen (cat. 1B). This increases the workplace safety requirements. There might also be risks for end-users if fine particulate debris is released. Synergistic effects between Co and WC increase further the inhalation health risk.

Cr_3C_2-NiCr, employed for high-temperature applications and/or corrosion resistance, could alleviate the issues with W and Co, despite the hazardousness of Ni itself, and the potential release of volatile Cr compounds during spraying. However, its low-temperature wear resistance is no match for WC-based materials.

This contribution summarises the authors' recent research on potential alternatives, following two distinct approaches:

-Coatings from commercially available or experimental powder formulations based on WC with Co-free (or nearly Co-free) matrices based on Ni (e.g. WC-NiMoCrFeCo) and/or Fe (e.g. WC-FeNiCrMoCu, WC-FeCrAl).

-Coatings where both Co and WC are replaced. The work has mostly been focused on TiC-based compositions with matrices such as Ni-20Cr, Fe-Cr-Al, or Fe-Ni-Cr alloys.

Results obtained so far show that, in sliding wear applications and/or under corrosive conditions, WC-based hardmetals with Co-free matrices can be a viable replacement for WC-CoCr, matching or sometimes even surpassing its performance. The sliding wear resistance of TiC-based coatings is intermediate between WC-CoCr and Cr_3C_2-NiCr ones, and they are serviceable up to at least 400 °C. So, they could suit a range of low- to intermediate-temperature applications, when the extreme wear resistance of WC-based materials might not be needed. Drawbacks and limitations to be overcome include the tendency of TiC-based formulations to oxidize during thermal spraying, which induces brittleness and impairs the resistance to coarse particles' abrasion.

2:40pm **E1-3-WeA-3 Tribological Behavior of Zirconium Coated Ti-6Al-4V by Pack Cementation***, Beyza Öztürk (beyza.oeztuerk@dechema.de), L. Mengis,* DECHEMA Research Institute, Germany*; D. Dickes, U. Glatzel,* University of Bayreuth, Germany*; M. Galetz,* DECHEMA Research Institute, Germany

The Ti-6Al-4V alloy is used in aerospace, automotive or biomaterial applications due to its excellent mechanical strength and corrosion resistance as well as biocompatibility. However, its poor tribological behavior limits its applications. In this study, zirconium coatings are produced on Ti-6Al-4V by pack cementation process at 700, 900 and 1050 °C for 5 h with the goal to form ZrO_2 on the surface. After that, coatings are examined by optical microscopy (OM), electron microprobe analysis (EPMA) and X-ray diffraction (XRD) techniques. The wear behavior of uncoated and zirconium coated Ti-6Al-4V against Si_3N_4 is studied under dry sliding conditions in the temperature range of RT-600 °C using a ball-on-disc tribometer. Finally, the wear mechanism of the tribopair is investigated by scanning electron microscopy with an energy dispersive X-ray analyzer (SEM/EDX) and profilometry.

3:00pm **E1-3-WeA-4 Study of Electrochemical and Tribological Properties of Electrophoretic Deposited Thin and Thick Graphene Coatings on Pure Titanium Substrate***, Madhusmita Mallick (madhusmita1509@gmail.com), A. N,* Indian Institute of Technology (IIT), Madras, India

Titanium and its alloys have been used widely in various sectors owing to their exceptional properties of light weight, high strength and biocompatibility. However, their poor abrasion and corrosion resistance behaviors are major cause of concern. To mitigate these problems, graphene protective coatings were applied. Therefore, this study focusses on improvement of both corrosion and wear resistance properties of commercially pure-Ti (grade 2) by electrophoretic deposited (EPD) graphene coatings. The effects of different coating thickness and morphology on the electrochemical and tribological performance were investigated. The test results revealed that the smooth and compact microstructure of thin graphene coating of thickness 2.16 µm exhibited superior corrosion resistance and lubricating properties (COF=~0.02) compared to thick graphene coating of thickness 11.8µm (COF=~0.17). However, thick graphene coating demonstrated higher durability of its lubricating behavior and good wear resistance property. Nevertheless, both graphene coatings showed significant improvement in both corrosion and wear resistance properties of bare Ti substrate for various industrial applications.

New Horizons in Coatings and Thin Films
Room Pacific D - Session F1-WeA

Nanomaterials and Nanofabrication

Moderators: Diederik Depla, Ghent University, Belgium, **Vladimir Popok**, Aalborg University, Denmark

2:00pm **F1-WeA-1 Polymer Films with Gas-Phase Aggregated Nanoparticles: Formation and Applications***, Vladimir Popok (vp@mp.aau.dk),* Aalborg University, Denmark **INVITED**

In the last couple of decades, nanoparticles (NPs) have been widely used in various research fields and industrial branches. Among many physical and chemical ways of nanoparticle synthesis, the gas-phase aggregation method, also known as cluster beam technique, [1, 2] provides a number of advantages allowing for a very good control of composition because ultra-pure targets are used and the particles are aggregated in vacuum. Formation of not only homo-atomic but alloy and compound NPs with tunable structure and shape (core@shell, Janus- and dumbbell-like, spherical or cubic etc.) is possible. Adjusting the aggregation parameters and adding mass-filtering systems brings a capability of size selection. One more advantage is easy tuning the surface coverage or filling factor of NPs on/in the films. Finally, yet importantly is a capability to form patterned nanostructured films or coatings with gradients of NP surface density.

Polymers are very attractive hosting or supporting media for NPs due to plasticity, flexibility, easy processing, low weight and also low cost. Use of polymers also allows to add required functionality [3, 4]. The talk will overview several most important directions, namely on: (i) tuning resistance of the composite films by controlling the coverage or filling factor of metal NPs and use such materials as elastomeric electrodes, strain gauges and gas sensors; (ii) utilizing localized surface plasmon resonance of NPs to design polymer-based metamaterials with controllable transmittance as well as matrices for enhanced sensing and detection; (iii) polymer coatings with ferromagnetic particles demonstrating excellent absorption of GHz waves as well as tunability of magnetic properties; (iv) utilization of polymer films with NPs as advanced membranes in filtering as well as bactericidal media in food packaging and in medicine.

11. V.N. Popok, E.E.B. Campbell, Rev. Adv. Mater. Sci. 11(1) (2006) 19-45.
12. V.N. Popok, O. Kylian, Appl. Nano 1 (2020) 25-58.
13. V.N. Popok, Cluster Beam Synthesis of Polymer Composites with Nanoparticles, in: Polymer-based Multifunctional Nanocomposites and Their Applications, Eds. K. Song, C. Liu and J.Z. Guo, Elsevier, 2019, 35-76.
14. O. Kylián, V.N. Popok, Frontiers of Nanoscience, 15 (2020) 119-162.

2:40pm **F1-WeA-3 Stress Evolution in Particle Strengthened Metal-Oxide Nanolaminates: Insights from in-Situ Synchrotron Diffraction Experiments***, Barbara Putz (barbara.putz@unileoben.ac.at),* Montanuniversität Leoben, Austria*; A. Sharma,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; K. Gradwohl,* Leibniz-Institut für Kristallzüchtung , Germany*; P. Gruber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM)-WBM, Germany*; D. Többens,* Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Germany*; X. Maeder, J. Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Understanding deformation mechanisms of metal-ceramic nanolaminate coatings (NLC) is crucial in order to exploit their promising mechanical, physical and chemical properties, useful for a wide range of thermal, mechanical and environmental conditions (1). We have fabricated unique, particle strengthened metal/oxide nanolaminates, combining three different deposition techniques: Atomic Layer (ALD), Physical Vapor (PVD) and Nanoparticle (NP) Deposition. Ultrathin oxide layers (<1nm, Al_2O_3) confine the grain growth of metallic PVD films (50nm, Au), for grain sizes distinctly lower than the total film thickness (150nm), improving strength and ductility, while incorporated NPs (W, diameter 4 nm) further enhances mechanical properties. The multilayer microstructures and NP concentrations were confirmed and characterized by cross-sectional transmission electron microscopy (TEM). Stress evolution in the nanocomposites was studied with X-ray diffraction and sin^2psi analysis during in-situ tensile experiments on flexible polymer substrates. Two different nanocomposite geometries (Au/Al_2O_3 and Au + W-NP/Al_2O_3, total thickness 150nm) as well as single Au films (50nm and 150nm) with and without NP reinforcement were investigated to study and isolate the influence of layer thickness and nanoparticle concentration. Results indicate a clear strengthening of 150 nm Au films through multi-layering (Au/Al_2O_3), which can be further increased through the addition of NPs (Au+W-NP/Al_2O_3). Post mortem scanning electron imaging (SEM) of the deformation pattern as well as electrical resistance measurements recorded in-situ during straining indicate that no significant embrittlement was introduced by neither ALD nor NP addition. In summary, the novel manufacturing approach and resulting nanocomposites are promising candidates for multifunctional components in next-generation nano-devices.

(1) A. Misra, J.P. Hirth, R.G. Hoagland, Length-scale-dependent deformation mechanisms in incoherent metallic multilayered composites, Acta Mater. 53 (2005) 4817–4824. https://doi.org/10.1016/j.actamat.2005.06.025.

3:00pm **F1-WeA-4 Structure-Processing Relationships of Chiral Organic-Inorganic Thin Films for Circularly Polarized Light Detection***, Katherine Burzynski (katherine.burzynski.ctr@afrl.af.mil),* AFRL / Azimuth Corp., USA*; E. Muller,* AFRL / UES, USA*; A. Trout,* The Ohio State University, USA*; W. Kennedy,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA

Photonic quantum information systems (pQIS), optical imaging systems, and analytical spectroscopy tools all benefit from sensitivity to the polarization state of light. Particularly of interest is the detection and discrimination of circularly polarized light (CPL). Currently, the main method to detect CPL requires complex optical systems that cannot easily be incorporated into on-chip circuitry. Direct detection of CPL has been demonstrated by chiral organic semiconductors and metamaterials but suffer from low quantum efficiencies. Chiral organic-inorganic materials are promising for CPL detection due to their ease of fabrication and chiral optoelectronic properties. To date, a limited number of chiral organic metal halide systems possessing intrinsic optoelectronic response to CPL are reported in literature, leaving many chiral systems unexplored. The chiral organic cations, R-(+)- and S-(−)-1-(1-naphtyl)ethylamine (R- and S-NEA+) were incorporated into the lead iodide system. A variety of growth techniques, including spin-coating, confined crystallization, and hydrothermal crystallization, as well as annealing conditions were investigated in an effort to reliably produce functional thin films for CPL photodetection. The fabrication techniques that promote the chiral organic metal halide crystallization and reduce the amount of lead iodide crystallites result in strong chiral optical responses, and ultimately, efficient CPL detection via polarization sensitive photocurrent in thin film devices.

3:20pm **F1-WeA-5 Bio-Inspired Antibacterial Metasurfaces Fabricated by Glancing Angle Deposition***, Chuang Qu (chuang.qu@louisville.edu), J. Rozsa, H. Jung, M. Running, S. McNamara, K. Walsh,* University of Louisville, USA

The goal of this research is to propose an easy and cost-effective fabrication approach of Glancing Angle Deposition (GLAD) for creating antibacterial surfaces, which are inspired by cicada wings. Antibacterial surfaces are known to be applied in a variety of specific interfaces, such as medical implants and food packaging. As Ivanova et al pointed out, bio-inspired surface structuring for antibacterial requires 'further comprehensive and systematic studies'.

This research begins with the examination of the wings of Neotibicen canicularis (an annual cicada in North America, also known as the dog-day cicada, see Fig 1a). Using a scanning electron microscope (SEM), one can observe that the cicada wing is covered nanopillar cone nanostructures, with the tips of the cones sub-100 nm in diameter, and the height of the cones approximately 200 nm (see Fig 1b). The nanopillar cones are semi-hexagonally distributed on the cicada wings with ~170 nm between the neighboring pillars. These antibacterial surfaces compose of appropriately spaced nanopillars cone features, which puncture into bio cells falling on top and keep the surface bacteria-free. Given the nano-level three-dimensional features on the surface of cicada wings, it is extremely difficult to replicate these naturally occurred nanostructures using conventional top-down nanofabrication processes, especially cost-effectively and in large areas. For this reason, we propose to use GLAD combining self-assembly of nanospheres to solve the fabrication problem. GLAD is a versatile bottom-up process that uses physical vapor deposition while maneuvering with incident angle and rotation of the substrate. Although the GLAD approach has been proposed over decades, there is still a lot to discover about this technique, such as the effective seeding rules. This paper will introduce the new seeding rule and scheme for GLAD to replicate the nanopillar cone structures, along with the whole fabrication process using GLAD. Figure 2 presents our initial effort to replicate the cicada wing nanopillar cone structures using GLAD. Finally, gram-negative bacteria (E Coli) are applied on top of the surface for antibacterial testing. Our preliminary results show the effectiveness of the antibacterial property of our synthetic nanostructured film. The proposed GLAD process with the new seeding scheme provides the flexibility in design and optimization of three-dimensional nanofeatures with periodic/random distributions, which allows the further exploring of functional bio-inspired nanostructures.

3:40pm **F1-WeA-6 Polymer Templates-Assisted Design of ZnO Films via Swelling-Assisted Sequential Infiltration Synthesis (SIS) and Swelling Based Infiltration (SBI): Properties, Adsorption Characteristics, and Performance***, Khalil Omotosho (khalildolapoomotosho@my.unt.edu),* University of North Texas, USA

In this paper, we report the properties and adsorption characteristics of ZnO coatings designed with polymer templates-assisted infiltration approaches and their reactions with the environment. For this, we investigated the infiltration of polymer of amphiphilic block copolymer (BCP) templates with ZnO by comparison of 2 infiltration approaches, the swelling-assisted sequential infiltration synthesis (SIS) and the swelling-based infiltration (SBI), followed by polymer templates removal by oxidative thermal annealing for the design of porous ZnO films. Using the quartz crystal microbalance (QCM), we compared the infiltration efficiency of both methods. The XRD and XPS data revealed that the SBI-based porous ZnO films have a more disordered structure with a high surface concentration of OH groups, leading to a more hydrophilic film. We monitored the chemical interactions of the polymer templates before and after infiltration using the FTIR. Our results indicate that the performance of the ZnO coatings is highly dependent on the infiltration approach adopted, the templates, and their interactions with organic molecules. These results suggest new ways to efficiently design highly porous metal oxide coatings that can be adapted for various applications.

4:00pm **F1-WeA-7 Pulsed Aerosol Assisted Plasma Deposition: Process and Film Composition Characterization Using Nanoparticles Optical Properties***, Adèle Girardeau (adele.girardeau@laplace.univ-tlse.fr),* LAPLACE, LCC, Safran Tech, France*; G. Carnide,* LAPLACE, LCC, IMRCP, France*; A. Mingotaud,* IMRCP, France*; M. Cavarroc,* Safran Tech, France*; M. Kahn,* LCC, France*; R. Clergereaux,* LAPLACE, France

Aerosol-assisted processes enable to deposit thin films, homogeneous[1,2] or nanocomposite[3–6]. For example, the nebulization of colloidal solutions, i.e. liquid solutions containing nanoparticles, in plasma processes have been widely used for nanocomposite thin film deposition. In this work, an alternative method, called direct liquid reactor-injector (DLRI) of nanoparticles, is applied. It allows to synthesize nanoparticles prior to their injection in the plasma in a pulsed injection regime[7].

In a low-pressure RF plasma coupled with DLRI of ZnO nanoparticles, it enables to form nanocomposite thin films with really small (<10 nm in diameter) and highly dispersed nanoparticles embedded in a matrix[7] that exhibits the classical optical properties of ZnO (absorbance at their band-gap - 3.37 eV and fluorescence when illuminated by ultraviolet light - 320-360 nm[8–10]). However, the volume fraction of nanoparticles embedded in the matrix is 5 times lower than expected. Indeed, in-situ optical emission spectroscopy (OES) of the plasma presents the characteristic luminescence of ZnO nanoparticles suggesting that nanoparticles are efficiently confined in the plasma volume during the process and does not participate to the nanocomposite formation.

To estimate the number of nanoparticles confined in the plasma volume and the global process balance of matter, one must establish the relation between the absorption / fluorescence and the number of nanoparticles. Here, we report an abacus obtained with ZnO nanoparticles synthesized by an organometallic approach: it shows that the optical characteristics of the ZnO nanoparticles follow the classical Beer-Lambert and luminescence laws, a useful tool for in-situ analyses. It also enables to determine the absorptivity and the quantum yield of the ZnO nanoparticles produced.

New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-2-WeA

New Horizons in Boron-Containing Coatings II

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

2:00pm **F4-2-WeA-1 Understanding and Optimizing the Properties of Superhard Metal Borides**, ***Sarah Tolbert (tolbert@chem.ucla.edu)***, University of California, Los Angeles, USA **INVITED**

In this talk, we will examine a family of super-hard materials based on late transition metal borides.These materials are exciting because, unlike diamond, they can be synthesized at atmospheric pressure.The materials were initially constructed using three very simple design rules:1) use late transition metals to create high electron density so that the materials are incompressible; 2) add boron to build strong covalent bond to prevent slip and generate hard materials; 3) use solid-solution effects to further tune materials properties.While these ideas is incredibly simple, they have also proven to be very effective.In this talk, we will thus use a combination of materials synthesis, indentation measurements, and high-pressure diffraction to gain an understanding of how the hardness in this family of materials can be tuned based on chemical composition and bonding motifs.We will specifically take advantage of non-hydrostatic high pressure X-ray diffraction methods to directly probe both elastic lattice deformations and the onset of plastic deformation in a wide range of materials in a lattice specific manner.To gain a global understanding of the family of materials we will move from metal (M) rich MB phases, to more conventional MB_2 and MB_4 type materials, and finally to very high boron content MB_{12} type materials.In all cases, the goal will be to correlate structure and bonding with hardness.Finally, we will end with some new studies on nanoscale versions of these materials, where nanoscale architecture is combined with bonding constraints to further improve hardness.

2:40pm **F4-2-WeA-3 Si alloyed Transition Metal Diborides - A Novel Class of Oxidation Resistant Coating Materials**, *T. Glechner, L. Zauner, R. Hahn, A. Bahr, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; **Helmut Riedl (helmut.riedl@tuwien.ac.at)**,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Surface protection of highly stressed components used in aviation or energy production is of great interest, especially to extend the operation ranges in oxidative high-temperature environments. Here, transition metal (TM) ceramics are a suitable class to resist such conditions. However, studies on a drastic improvement of the oxidation resistance of TM-diborides based coatings are relatively rare, as up to now many studies focus on the synthesis and mechanical properties of such films.

Therefore, within this study we suggest the combination of TM-boride based coating materials – as a high temperature stable ceramic – with the excellent oxide former Si, resulting in coatings with outstanding oxidation resistance, tested up to 1500 °C. Various TM-Si-$B_{2\pm z}$ (TM=Ti, Cr, Hf, Ta, W) films have been sputter deposited and subsequently oxidized in a DTA/TG setup to study their oxidation kinetics. Above certain Si contents, Ti-Si-$B_{2\pm z}$, Cr-Si-$B_{2\pm z}$, and Hf-Si-$B_{2\pm z}$ coatings exhibit strongly retarded oxidation kinetics obtaining k_p values below 10^{-11} $kg^2m^{-4}s^{-1}$ at 1100 °C. Long term oxidation tests at 1200 °C (up to 60 h in ambient air on hard substrates) confirmed the superior protective capability of these coatings, with i.e. $Hf_{0.20}Si_{0.23}B_{0.57}$ possessing an oxide scale thickness of only 1.5 µm after 60 h. Along with a broad set of high-resolution characterization techniques (i.e. HR-TEM, APT) the study introduces this new class of hard coatings for oxidation protection at ultra-high temperatures.

Keywords: Oxidation Resistance; Transition Metal Ceramics; Thin Films; Borides; UHTC;

3:00pm **F4-2-WeA-4 High-Power Impulse Magnetron Sputter Deposition of TiB_x Thin Films: Effect of Pulse Length and Peak Current**, ***Niklas Hellgren (nhellgren@messiah.edu)***, Messiah University, USA*; I. Zhirkov,* Linköping University, IFM, Thin Film Physics Division, Sweden*; M. Sortica,* Uppsala University, Sweden*; A. Petruhins, G. Greczynski,* Linköping University, IFM, Thin Film Physics Division, Sweden*; I. Petrov,* University of Illinois at Urbana-Champaign, USA*; L. Hultman, J. Rosen,* Linköping University, IFM, Thin Film Physics Division, Sweden

We report on titanium boride, TiB_x, thin films grown by high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target. Commonly HiPIMS studies are conducted in constant power mode, so when the pulse length in changed, so is the peak current and/or frequency. Here we independently vary pulse length (t_{on} = 50 – 200 µs) and peak current density (J_{peak} = 0.5 – 2 A/cm^2), while keeping the pulse frequency constant at f = 100 Hz. Thus, the total power vary depending on deposition condition. All other parameters were kept constant; substrate-target distance d = 6.5 cm, Ar pressure p_{Ar} = 10 mTorr, substrate temperature T_s = 500 °C, and substrate bias V_s = - 60 V.

The resulting films are all under-stoichiometric with B/Ti ranging from 1.3 to 1.9, as determined by ToF-ERDA and RBS. For any given t_{on}, the B/Ti ratio increases monotonically as J_{peak} increase from 0.5 to 2 A/cm^2. The trend is more complex as a function of t_{on}; in most cases, the highest B/Ti is observed for t_{on} = 100 µs, and decreases for both higher and lower t_{on}. The exception is for J_{peak} = 2 A/cm^2, where B/Ti increased slightly when increasing t_{on}.

The trends are discussed in terms of variations in both the total atom deposition flux, as determined from ERDA and RBS, and B^+, Ti^+ and Ar^+ ion flux measured by time- and energy-integrated mass spectrometry. Especially the Ti and Ti^+ fluxes saturate for the highest values of t_{on} and J_{peak}, which explains the highest film B/Ti ratios. This is also accompanied by a transition from strongly 001-textured films to predominantly 101-texture.

3:20pm **F4-2-WeA-5 Effect of Ar Particles on the Growth and Mechanical Properties of ZrB_{2+x} Films**, ***Tomas Fiantok (tomas.fiantok@fmph.uniba.sk)***, *T. Roch,* Comenius University, Bratislava, Slovakia*; P. Svec,* Academy of Science, Bratislava, Slovakia*; M. Truchly, V. Sroba, M. Mikula,* Comenius University, Bratislava, Slovakia

Highly demanding aerospace applications create an opportunity to exploit the promising potential of transition metal diboride based thin films (TMB_2, where TM = Ti, Zr, Nb, Ta, Mo, W) due to their high hardness and wear resistance. But their real use is still limited by brittle character and low oxidation resistance at elevated temperatures. TMB_2 films are most often prepared by physical vapor deposition (PVD) methods such as magnetron sputtering from stoichiometric compound targets in an inert argon atmosphere. The deposition processes are accompanied by (i) different angular distribution of sputtered boron, and metals, respectively, leading to the growth of overstoichiometric TMB_{2+x} films; (ii) the energy of reflected Ar neutrals causing resputtering and lead to grow a substoichiometric vacancy-containing TMB_{2-x} films. Here, we would like to demonstrate the effect of Ar particles on the structure, mechanical properties, and oxidation resistance of ZrB_{2+x} films. The films were deposited by high target utilization sputtering (HiTUS) technology where it is possible to independently change the kinetic energy of the argon ions accelerated toward the target (steering of target voltage) while maintaining the same amount (constant target current). Therefore, we have grown nanocrystalline ZrB_{2+x} films over a wide concentration range (x ~ 0.02 ÷ 2.1) with hardness values in range of 45.5GPa ± 1.2 GPa ÷ 8.3 GPa ± 0.3GPa. The films have a brittle character, expressed by Young's moduli, with the highest value of 480.9 GPa ± 8.8 GPa for $ZrB_{2.11}$. X-ray diffraction analysis confirmed the presence of hexagonal ZrB_2 phase with different preferred orientations depending on stoichiometry of the films. The highest oxidation resistance exhibited $ZrB_{2.27}$ films with onset temperature of ~ 750°C. Due to better understanding of the obtained results a deeper insight into nanostructure via transmission electron microscopy was performed. Mechanical behavior of ZrB_{2+x} was explained by density functional theory calculations.

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3:40pm **F4-2-WeA-6 Accurate Composition Depth Profiling of Light Elements in Thin Films Using Ion Beams - What Can Be Achieved?**, ***Daniel Primetzhofer (daniel.primetzhofer@physics.uu.se)***, Uppsala University, Sweden **INVITED**

For compound materials, subtle differences in stoichiometry often significantly alter the material properties of interest. This fact becomes particular important for compound systems for which a wide range of different compositions is accessible during synthesis as exemplified by transition metal carbides and borides. However, while accurate data on the composition on such compound samples containing light chemical species is thus of critical relevance, only very few methods can accurately provide the information requested. Ion beam-based analysis offers a unique toolbox to access the sample chemistry of such systems by a number of different non-destructive composition depth profiling techniques.

In this contribution we will illustrate the potential of ion beam analytical techniques in the characterization of light species ranging from hydrogen to oxygen while simultaneously providing reliable concentration depth profiles of the heavier constituents. Particular emphasis will be given to boron containing systems of different nature, i.e. thin films as well as multilayered or ion-implanted systems. At first, the underlying principles of ion-beam based analysis will be reviewed, illustrating the general characteristics and advantages of the methodology. These include amongst others minimum sample-preparation, non-destructive analysis, as well as typically fast measurements and analysis.

Subsequently, we will present a number of different ion-beam based methods by showcasing how they can answer specific scientific questions ranging from lattice location of hydrogen interstitials in energy storage materials to accurate measurements of the stoichiometry of borides as used for hard coatings. The methods presented will include tools capable of high-resolution depth profiling of specific isotopes as in nuclear resonance analysis or elastic backscattering spectrometry as well as methods providing composition depth profiles of the whole sample inventory on nanometer depth scales as enabled by Time-of-Flight Elastic Recoil Detection Analysis. We will discuss the achievable accuracy as well as limitations of the techniques also in comparison to other analytical approaches. Finally, we will also discuss, how a combination of methods can be employed to further increase the accuracy of analysis.

Topical Symposia
Room Town & Country B - Session TS3-WeA
Electrochemical Cells – Hydrogen and Batteries

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Klaus Böbel**, Bosch GmbH, Germany

3:20pm **TS3-WeA-5 Current and Future Trends in Materials for Advanced Lithium Batteries***, O. Kahvecioglu, **Carrie Siu (b294370@anl.gov)**,* Argonne National Laboratory, USA **INVITED**

The story behind lithium-ion batteries is nothing less than a quest for a new better performing materials and more reliable, safer devices. As far back as the late 1970s, a team of pioneering scientists began research on an invention that is known today as the lithium-ion battery or LIB. This rechargeable electrical energy storage device powers everything from hand-held electronics to power tools to electric vehicles and, in the near future, possibly even large vehicles and aircrafts. In 2019, the three brilliant minds behind LIB development, John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino were recognized for their discovery with the award of the Nobel Prize in Chemistry. Like any other great discovery, early LIBs were not perfect. The first experiments that used electrodes made from titanium disulfide and lithium metal were less than successful. After these early batteries short-circuited and caught fire, it was decided to halt the experiments. Not for long. John B. Goodenough came up with another idea. In the early 1980s he substituted lithium cobalt oxide (LCO) for the cathode instead of titanium disulfide. This new material was so successful that modern-day cell phone batteries still use it.

To satisfy market demands, the quest for new materials rages on. Although Li-ion batteries are proven and reliable technologies, they are not perfect, and suffer from performance degradation over time, limited shelf life and most importantly, some hazards associated with their use. Scientists and engineers are constantly making improvements to mitigate these issues, however performance decay and thermal runaways have not entirely been solved. Most of today's research effort is focused on cathode active materials. Coating and doping are the most frequently used techniques to improve material performance. Atomic layer deposition (ALD), for example, is by far most the popular technique for depositing nano-scale conformal layers on powder surfaces.

Current and future battery materials development for electric vehicles (EVs) must address the range limits (longer), cycle performance (stable), energy density (higher) and safety (flammability). Achieving all of these parameters at the desired level with a single material is challenging. Li-ion battery fires seen all over the world drive battery researchers to discover safer materials. One promising technology is the all solid state battery (ASSB), which can potentially address all these issues. Massive efforts seek to address the interfacial problems between the cathode and electrolyte.

The presentation will discuss current trends in battery materials.

4:00pm **TS3-WeA-7 Application of Bipolar Hipims to Enhance the Durability Performance of Carbon Coatings in Metallic Bipolar Plates***, J. Santiago , I. Fernandez, **Pablo Diaz-Rodriguez (pablo.diazr@nano4energy.eu)**,* Nano4Energy, Spain*; M. Panizo, M. Morales-Furio, C. Molpeceres,* Technical University Madrid, Spain*; J. Sanchez-Lopez,* CSIC-University Sevilla, Spain*; L. Mendizabal,* Tekniker, Spain*; G. Sevilla, M. Sanchez, N. Rojas,* Spanish Hydrogen National Center, Spain

Metallic bipolar plates (BPPs) are a promising candidate to replace conventional graphite BPPs due to higher power density and lower costs in proton exchange membrane fuel cells (PEMFCs). However, great challenges still exist for the application of metallic BPPs since they are working in acidic, humid, warm and polarized environment that reduce the lifetime of BPPs. The application of coatings is essential to enhance interfacial conductivity and corrosion resistance.

In this study, four different metal-doped amorphous carbon coatings (a-C:Cr, a-C:W, a-C:Nb and a-C:Ti) have been deposited by bipolar HiPIMS on stainless steel. The influence of HiPIMS parameters on coating-substrate interface, as well as the coating properties have been evaluated. SEM and TEM microscopy have been used to evaluate the coating interface. Raman analysis has been carried out to analyze the influence of metal content on carbon structure. The sp3-sp2 ratio has also been assessed with EELS spectroscopy. XPS analysis was used to evaluate the formation of metal carbides. Potentiodynamic and potentiostatic tests have been conducted to evaluate the corrosion resistance of the coated samples. Interfacial contact resistance (ICR) has been measured before and after corrosion tests.

Coatings deposited by bipolar HiPIMS improve coating-substrate contact interface and allow optimizing sp3-sp2 carbon structure, reducing ICR and enhancing corrosion resistance, as compared with carbon coatings deposited by conventional sputtering techniques. The results show that coatings follow the requirements established by DoE and are of great potential for application in PEMFC.

4:20pm **TS3-WeA-8 Coatings for Fuel Cells and Electrolyzers: From Materials to Processes, Challenges and Opportunities***, **Etienne Bouyer (etienne.bouyer@cea.fr)**,* Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), Grenoble, France **INVITED**

Hydrogen technologies are booming according to the benefit such technologies can bring for decarbonisation of as an example energy intensive industry and mobility sectors.

One has to distinguish between hydrogen conversion to produce electricity and hydrogen production in itself for further valorization of this carbon free fuel. The first topic concerns fuel cells for electricity generation from hydrogen and oxygen whereas the second topic is related to electrolyzers that allow to produce clean hydrogen through water splitting. Both electrochemical devices are based on a multilayer system.

The first illustration relates to fuel cell that convert the chemical energy contained in a fuel into electrical energy. As all electrochemical devices, a fuel cell is composed by two electrodes (anode and cathode) separated by an electrolyte. Between the two electrodes, ions pass through the electrolyte (ionic conductor and electronic insulator). Fuel cell is an open electrochemical generator (unlike batteries that are closed systems). Proton Exchange Membrane Fuel Cell (PEMFC) is a fuel cell operating at around 60 to 80°C and, to maintain a reasonable kinetic noble-metals catalyst are needed.

The second illustration focuses on high temperature electrolyzers that are made of multilayer ceramic materials. It has the same structure (anode/electrolyte/cathode) than a PEMFC. The hydrogen production reaction is not spontaneous, therefore electrical energy must be supplied to the system to produce hydrogen in an electrolyzer. Such system operate at high temperature (600-800°C): increasing the temperature decreases electricity demand thanks to thermodynamics and improves electrochemical kinetics.But limitations due to materials are occurring.

An overview of materials as well as associated processes to shape such components as layers or coatings will be presented and discussed. A special emphasis will be put on the remaining challenges (which slow down development of such technologies) and on the potential solutions. This contribution will also pay attention on the use of the so-called critical raw materials, on the way to minimize their content or -even better- to substitute them by more abundant materials and to save material through an optimization of the shape forming processes.

5:00pm **TS3-WeA-10 Electrochemically Stable PVD Coatings With Low Interfacial Contact Resistance for Proton Exchange Membrane Electrolyzer Bipolar Plates***, **Nathan Kruppe (kruppnth@schaeffler.com)**, E. Schulz, M. Öte, N. Bagcivan, J. Hackner, S. Rüth,* Schaeffler Technologies GmbH & Co. KG, Germany

In the scope of worldwide energy transition, the industrial availability of alternative energy sources is increasingly becoming the focus of attention - not least due to urgent legislative requirements. In the proton exchange membrane water electrolysis (PEMWE) water is electrochemically decomposed by an applied current. In this way, hydrogen is produced. PEMWE is characterized by its high-power density, the lack of hazardous chemicals and - a major advantage for the production of green hydrogen in particular - its ability to follow load changes almost instantaneously.

The core of the electrolyzer is the stack, in which numerous cells are stacked and interconnected via bipolar plates. The load collective acting on these bipolar plates is particularly harsh. Under warm and humid conditions, high electrochemical potentials, simultaneously low pH values, i.e. acidic environment as well as oxygen formation on the anode side and hydrogen formation on the cathode side, the materials are exposed to corrosive attacks on the one hand and hydrogen embrittlement on the other. The use of expensive solid materials such as titanium is not sufficiently suitable for the large series production of scalable, efficient, durable and robust PEMWE electrolyzers. Especially on the anode side, corrosive loading on stainless steel leads to reduced performance of the entire stack.

Surface technology offers a solution when stainless steel, which is significantly less expensive than titanium, is protected from corrosive attacks and hydrogen embrittlement by thin high-performance coatings. At the same time, a low contact resistance can be achieved in the long term. Within the scope of this contribution, it will be shown which requirements are placed on coating systems for PEMWE bipolar plates in order to realize electrochemical stability on the one hand and a sufficiently low interfacial resistance on the other hand. Results will be presented which prove the high potential of Schaeffler Technologies coating solutions for this application.

Awards Convocation and Honorary Lecture
Room Town & Country A - Session HL-WeHL

Bunshah Award Honorary Lecture

Moderator: Ivan G. Petrov, University of Illinois at Urbana-Champaign, USA

5:45pm **HL-WeHL-1 R.F. Bunshah Award and ICMCTF Lecture Invited Talk: Functional Coating and Surface Engineering for Real Life**, ***Jolanta-Ewa Klemberg-Sapieha (jsapieha@polymtl.ca)*** [1], Polytechnique Montréal, Canada **INVITED**

Over the past several decades, we have witnessed significant advances in numerous scientific and technological sectors thanks to the development of new thin-film and coating systems and surface engineering approaches, frequently based on the use of plasma processes. In many cases, the ever-increasing requirements involve an "ideal" combination of the mechanical, tribological, corrosion, thermal, and other characteristics, as well as high durability that can only be satisfied by using specifically tailored film architectures including nanocomposite, nanolaminate, multilayer, and graded layer systems. Such progress has been possible based on an in-depth understanding of the evolution of the microstructure during the film growth, of the intimate relationship between the microstructure on the atomistic and nanometer scales and the macroscopic properties, and the physical and chemical effects involved in plasma-surface interactions.

This presentation will highlight a journey of the development of plasma processes and functional and multifunctional coatings in our laboratory, involving numerous students and collaborators, that has been motivated by curiosity, by real-life/practical applications, coating systems performance and durability, and the prospects for sustainable future. In particular, I will illustrate my contributions to the field of surface engineering by taking examples from four main periods of activity, namely (i) high-frequency plasma for surface activation and plasma polymerization, (ii) functional coatings on plastics with a tailored optical, barrier, and anti-scratch characteristics and resistance to the outer space environment, (iii) hard and elastic, wear-resistant nanocomposite protective coatings for manufacturing applications, and (iv) protective coatings for harsh environments providing high resistance to solid particle erosion, ice accumulation and high-temperature oxidation suitable for aerospace applications.

[1] **R.F. Bunshah Awardee**

Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B1-1-ThM

PVD Coatings and Technologies I

Moderator: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), Germany

8:20am **B1-1-ThM-2 Optimization of RF Magnetron Sputter Deposition of Ultrathick Boron Carbide Coatings***, **Alison Engwall (engwall1@llnl.gov)**,* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; L. Bayu Aji, S. Shin, P. Mirkarimi, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Boron carbide is a material of interest as an ablative layer for inertial confinement fusion (ICF) applications due to its robust physical properties and uniform amorphous structure. However, growing boron carbide films to thicknesses of >50 µm, as needed for ICF, presents many challenges. Our approach to the optimization of two main process parameters (the target-to-substrate distance and Ar gas pressure) for the deposition of boron carbide coatings by RF magnetron sputtering is based on a combination of film characterization, plasma diagnostics, and modeling. Monte Carlo simulations of ballistic sputtering and gas-phase atomic transport are benchmarked by selected measurements of the deposition rate, residual film stress, and plasma parameters monitored with an electrostatic probe. We describe results of this study of parameter space and ultimately demonstrate the deposition of >50 µm-thick boron carbide coatings with close-to-zero residual stress.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

8:40am **B1-1-ThM-3 Hybrid Technologies for Wear Protective Coatings With Adaptive Behavior***, **Andrey Voevodin (andrey.voevodin@unt.edu)**,* University of North Texas, USA **INVITED**

Physical Vapor Deposition (PVD) technologies offer a suite of methods for surface engineering, where the broad range controls of the deposited flux chemical composition, density, ionization state and energy allow for the growth of wear reducing materials with complex compositions and structures tailored for an adaptive behavior in variable environments and temperatures.For example, the hybridization of magnetron sputtering and pulsed laser deposition had led possibility to embed transition metal dichalcogenides into hard ceramic matrices which had open a range of adaptive coating capable to operate over the broad range of environment humidity and temperature by self-changing the contact surface chemistry and structure in response to the environment change. The hybrid processes for the formation of adaptive wear protective coatings were further expanded to include combinations of PVD methods with other methods, e.g. laser texturing and electro-spark deposition, had led to additional avenues for realization of robust wear protective coatings with adaptive behavior to operate under high contact loads and speeds.The presentation reviews developments of adaptive wear protective coatings produced with hybrid PVD methods and places perspectives for future opportunities.

9:20am **B1-1-ThM-5 Cylindrical Magnetron Deposition of TiAlN Coatings with HiPIMS***, **Veronika Simova (veronika.simova@polymtl.ca)**, O. Zabeida, L. Varela Jimenez, J. Qian, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Rotating cylindrical magnetrons have several important benefits in comparison with widely used planar magnetrons, making them interesting for large-scale industrial applications. Due to their rotation, target erosion is uniform that results in a much higher target utilization (70% or more) and a high stability during reactive sputtering processes. Moreover, better cooling efficiency allows one to use higher power densities and, consequently, higher deposition rates can be achieved. This makes cylindrical magnetron sputtering (CMS) well adapted for HiPIMS.

In the present work, we investigated the use of CMS for the fabrication of $Ti_{0.5}Al_{0.5}N$ as a model hard coating extensively used for the protection against harsh environments such as those seen in aerospace and manufacturing. We studied the effect of pulsed-DC and HiPIMS deposition conditions (frequency of 0.91 kHz, duty cycle of 91% and 9.1%, respectively) on the microstructure, mechanical properties, residual stress and stress depth profiles. In addition, *in situ* real-time plasma monitoring by optical emission spectroscopy (OES) was applied for the study of the process and of the film growth conditions.

By applying the substrate bias, the coating hardness increased from 20 GPa (no bias) up to 30 GPa for a bias of -60 V without any additional heating. This increase in hardness is in good correlation with the increase in compressive stress from -0.9 GPa to -5.5 GPa and corresponding decrease in the grain size (from 16 nm to 9 nm). The stress depth profiles clearly show a steep gradient in compressive stress increasing from the substrate interface towards to the coating surface.

Substrate heating results in further enhancement of the mechanical properties, accompanied by a considerably lower compressive stress and its gradient. Consequently, when combining substrate heating with substrate biasing, hard TiAlN coatings with even lower compressive stress can be produced (-2.3 GPa).

The results clearly show that the substrate bias and heating can effectively be used to tune the mechanical properties and residual stress and stress depth profiles of TiAlN coatings.

9:40am **B1-1-ThM-6 Development of VC-based Early Transition Metal Carbide Superlattices via Compound Target Magnetron Sputtering***, **Barbara Schmid (barbara.schmid@tuwien.ac.at)**, N. Koutná, R. Hahn, J. Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; S. Kolozsvari,* Plansee Composite Materials, Germany*; E. Pitthan Filho, D. Primetzhofer,* Uppsala University, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Transition metal carbides are known to feature high thermal and mechanic stability as well as high melting points, sometimes above 3500 K, and can be regarded as ultra-high temperature ceramics (UHTC). The huge downsides to those materials is the high inherent brittleness.

Superlattice architecture describes the alternation of coherently grown nanolayers of two or more materials. By creating such superlattices, optical, magnetic, electronic, tribological, or mechanical properties can be influenced. The hardness but also the toughness of superlattice materials can be significantly higher than their monolithically grown components.

Therefore, we developed superlattice structures of selected transition metal carbides combined with VC as well as performed bilayer period variations between 2 and 50 nm.

The selected carbide combinations are based on density functional theory simulations, which revealed VC containing films as most promising candidates to have an improved toughness behavior due to the superlattice structure.

All coatings are developed via DC magnetron sputtering using the respective ceramic targets. Their characterization includes X-ray diffraction, scanning and transmission electron microscopy, energy dispersive X-ray spectroscopy, elastic recoil detection analysis, nanoindentation and in-situ micromechanical investigations.

10:00am **B1-1-ThM-7 New Approach to Ceria-Based Electrolyte Deposition by Reactive Magnetron Sputtering***, **Kamel Ouari (kamel.ouari@utt.fr)**, E. Zgheib, S. Achache,* LASMIS, University of Technology of Troyes, France*; M. Arab Pour Yazdi, A. Billard, P. Briois,* FEMTO-ST, University of Technology of Belfort-Montbéliard, France*; F. Sanchette,* LASMIS, University of Technology of Troyes, France

Low-Temperature Solid Oxide Fuel Cells (LT-SOFC) represent a future technology for clean and efficient power generation from renewable sources. Low-temperature operation can make SOFC technology technically useful, i.e. less manufacturing cost and with more stable long-term performance. However, it also brings significant challenges in cell fabrication, especially in producing thin and dense electrolyte films with good mechanical and electrical properties. Magnetron sputtering is one of the advanced techniques used to develop micrometer coatings. Although it is a scalable industrial process, it also has drawbacks, such as low oxide deposition rates. Ceria-based electrolytes, Ce(Gd, Sm)O2, are one of the most promising alternatives to the conventional SOFC electrolyte, Yttria-Stabilised Zirconia (YSZ), due to their high ionic conductivity at low temperatures (< 600°C). Thus, in this work, optimized electrolytes for LT-SOFCs are deposited by reactive pulsed DC magnetron sputtering. The objective is to obtain dense coatings of a few micrometres with high deposition rates. Coatings were deposited using an DEPH 4 system (DEPHIS, Etupes, France) to prove their feasibility on a large scale. We report two new methods for depositing high-quality electrolyte layers by reactive magnetron sputtering, one involving sub-stoichiometric coating and the other stoichiometric without using any control systems (e.g. optical emission spectroscopy, target voltage, mass spectrometry, or other). The sub-stoichiometric films require ex-situ annealing to fully oxidize them. The deposition rates are in the order of that of the metal mode of the reactive deposition method. Moreover, the discharge voltage and overall pressure stabilize after a few minutes. Investigations are focused on growth, physico-electrochemical characterizations of Gd- and Sm-doped ceria as a function of deposition parameters (bias, O2 flow rate, etc.), and performance tests of LT-SOFCs with 2, 5 and 10 µm thick sputtered electrolytes.

10:20am **B1-1-ThM-8 Sputter-Deposited Zr-Cu Thin Film Metallic Glasses: Microstructure and Properties Control of as-Deposited Films and Impact of Ultra-Short Pulsed Laser Irradiation Treatments on the Film's Structure***, **Alejandro Borroto (alejandro.borroto@univ-lorraine.fr)**,* Institut Jean Lamour - Université de Lorraine, France*; M. Prudent,* Laboratoire Hubert Curien - Université de Lyon, France*; S. Bruyère,* Institut Jean Lamour - Université de Lorraine, France*; F. Bourquard,* Laboratoire Hubert Curien - Université de Lyon, France*; D. Pilloud, D. Horwat,* Institut Jean Lamour - Université de Lorraine, France*; M. Leroy,* IREIS, Groupe HEF, France*; P. Steyer,* MATEIS, INSA Lyon, Université de Lyon, France*; J. Colombier, F. Garrelie,* Laboratoire Hubert Curien - Université de Lyon, France*; J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

Owing to their amorphous structure, metallic glasses (MGs) have emerged as a new class of materials with remarkable properties compared with their crystalline counterpart. Using physical vapor deposition methods such as sputtering, MGs can be prepared in the form of thin film metallic glasses (TFMGs). Thus, the microstructural control inherent to the sputtering process can be exploited to tailor the properties of TFMGs. Meanwhile, laser irradiation is a well-established technique for surface functionalization, allowing the generation of ripples known as laser-induced periodic surface structures (LIPSS).However, a lack exists on the laser-induced surface functionalization of MGs, most of the studies are focused on the laser irradiation-crystalline material interaction.

Here, sputter-deposited Zr-Cu thin films, largely known for their good glass forming ability, are used as a model system and studied over a wide range of compositions. Our results are divided into two parts. First, we report on the influence that the energy of the sputtered atoms arriving at the substrate (controlled here through the deposition pressure) has on the structure, microstructure, and properties of the deposited films. We demonstrate that by increasing the deposition pressure, a composition-dependent transition from a denser to a columnar microstructure occurs. This microstructural transition directly affects the residual stress state as well as the electrical and optical properties of the deposited TFMGs. In particular, we show that there is a threshold in the deposition pressure below which the resistivity of the films remains constant. Second, we report on the laser-induced structural changes occurring at the surface and near-surface in Zr-Cu thin film metallic glasses. Hence, we study the influence that the alloy composition has on the crystallization process induced by laser irradiation. Transmission electron microscopy is used to study the evolution of the film's structure, microstructure, and composition after laser irradiation. In particular, we demonstrated the feasibility of laser treatment to obtain periodic surface structures of different geometries in TFMGs. Our results shed new light on the laser-amorphous material interaction process, opening a new avenue for future applications.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B8-1-ThM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

Moderators: Tiberiu Minea, Université Paris-Saclay, France, **Martin Rudolph**, Leibniz Inst. of Surface Eng. (IOM), Germany

8:00am **B8-1-ThM-1 the Role of He (23S1) Metastable Atoms to Generate High Current Density in Pulsed Magnetron Discharge***, **Abderzak FARSY (abderzak.el-farsy@universite-paris-saclay.fr)**,* Laboratoire de Physique des Gaz et des Plasmas (LPGP), University Paris Saclay -CNRS, Orsay, France*; E. Morel,* SuperGrid Institute, France*; T. Minea,* Laboratoire de Physique des Gaz et des Plasmas (LPGP), University Paris Saclay -CNRS, Orsay, France

Magnetically enhanced plasmas are used in various applications of low-temperature plasmas including magnetron sputtering and Hall-effect thrusters. In magnetron discharge technologies for sputtering applications, the use of the magnetic field allows the electron confinement yielding for the increase of the plasma density by 1-2 orders of magnitude and the increase of the deposition rate. High power impulse magnetron sputtering (HIPIMS) is a recent ionized physical vapor deposition where a pulsed power supply delivers a huge peak power during a short pulse to achieve a very high ionization degree (>50%) of the metallic sputtered vapor.

In this contribution, we focused on the time-resolved characterization of gas temperature and the density of He (2^3S_1, 19.82 eV) metastable atoms in the ionization region of magnetron plasma operated with a graphite target (2 inch in diameter) and a high current density range (10-20 A/cm^2) within a pulse of 50 µs. Those characterizations are combined with the electrical ones of the cathode voltage and the discharge current. The temporal evolution of He metastable atoms velocity distribution functions (AVDFs) was measured using Time Resolved Tunable Diode Laser Absorption spectroscopy (TR-TDLAS), see figure 1 in supplemental document. A diode laser, accorded to provide 30 pm wavelength range without mode hop and centered at λ_0=1082.909 nm, was used to probe the He $2^3S_1 – 2^3P_0$.

In our conditions, the measured TR-TDLAS profile is affected only by the Doppler broadening; all other mechanisms are negligible. Thus, from the analysis of TR-AVDFs, the gas temperature and He metastable atoms density are calculated (figure 2b in supplemental document), we assumed that the He ground state and the He metastable have the same temperature. The main result obtained by those diagnostics is that the He metastable atoms density reaches the maximum by a time-shift with the current maximum. The He metastable atoms density reaches the maximum at 20 µs whereas the discharge current at 31 µs. In the presentation, this behavior will be used to discuss the role of the He metastable atoms to generate the high current density. Since the measurements were carried out in the ionization region, the He metastable atoms density is affected by electron density and temperature and also by the gas rarefaction effect. Therefore, the effect of cathode voltage, the gas pressure and the discharge current will be presented and discussed.

8:20am **B8-1-ThM-2 Transport of Ions and Neutrals in HiPIMS Studied by Particle-Based Simulations***, **Tomas Kozak (kozakt@ntis.zcu.cz)**,* University of West Bohemia, Czechia

High-power impulse magnetron sputtering (HiPIMS) technique is being increasingly used for deposition of films due to its ability to deliver more energy into the growing film via target material ions. The sputtered target material atoms are ionized in the high-density plasma above the target. Some of these ions return onto the target due to the structure of the plasma potential above the target. To understand the effect of the pulse shape and other discharge parameters on the ion return probability is very important for the optimization of the ionized fraction, the energy and the total flux of film-forming atoms on the substrate.

A 3D computer simulation employing the direct simulation Monte Carlo (DSMC) method was developed to bridge the gap between existing volume-averaged (less detailed) and particle-in-cell (very detailed) models. The presented simulation can directly calculate the return probability and the related ionized fraction of the target material species on the substrate for a given (time-dependent) spatial distribution of the plasma potential which is estimated based on recent experimental studies. Moreover, the simulation provides time- and space-resolved densities of atoms and ions in the discharge plasma and their fluxes to various surfaces (including energy distributions). The calculated densities are in a good agreement with density maps obtained by optical methods. The ionized fraction on the substrate is found to strongly depend on the plasma potential drop across the ionization region above the target while the ion return probability changes only weakly (around the value of 0.9). This highlights the importance of accurate determination of the ion return probability. By comparing the simulation results with experimental data (such as, ionized fraction, deposition rate), other unknown discharge parameters can be determined.

The simulation also provides quantitative evaluation of the gas rarefaction effect which is found to significantly reduce the process gas density between the target and the substrate (during and after the HiPIMS pulse). Additionally, the effects of various collisional processes in the plasma or the effect of varying plasma potential (*e.g.*, due to spokes) can be studied by the simulations.

8:40am **B8-1-ThM-3 Kinetic Investigation of Electron Heating in HiPIMS Discharges***, **Bocong Zheng (bcong.zheng@gmail.com)**,* Fraunhofer USA*; Y. Fu,* Tsinghua University, China*; K. Wang, T. Schuelke,* Fraunhofer USA*; Q. Fan,* Michigan State University, USA **INVITED**

We provide a self-consistent and complete description of discharge characteristics of high power impulse magnetron sputtering (HiPIMS) through fully kinetic 1d3v particle-in-cell/Monte Carlo collision (PIC/MCC) simulations. As HiPIMS employs much higher transient power than conventional DC magnetron sputtering (DCMS), more physical processes need to be considered in its simulations, such as Coulomb collisions between charged species, sputtering winds, i.e. gas rarefaction due to momentum exchange between the sputtering species and the background gas, ionization of metal ions from the sputtering species, and secondary electron emission induced by these multi-charged metal ions. This study considers all of the above processes and on this basis provides a detailed description of the HiPIMS discharge characteristics, including discharge runaway, electron dynamics, and sputtering winds. Some important conclusions previously obtained from the global model are confirmed by this *ab initio* kinetic simulation. During the discharge runaway process, i.e., the transition from the low-current DCMS regime to the high-current HiPIMS regime, metal ions gradually replace gas ions as the dominant ones, and the electron energization transitions from sheath energization to Ohmic heating of the ionization region. These results are beneficial for the design and optimization of HiPIMS discharges in practical applications.

9:20am **B8-1-ThM-5 The Influence of the Magnetic Field on the Discharge Parameters of a High Power Impulse Magnetron Sputtering Discharge***,* ***Martin Rudolph (martin.rudolph@iom-leipzig.de)****,* Leibniz Institute of Surface Engineering (IOM), Germany*; N. Brenning,* KTH Royal Intstitute of Technology, Sweden*; H. Hajihoseini,* University of Iceland*; . Raadu,* KTH Royal Institute of Technology, Sweden*; T. Minea,* Université Paris– Saclay, France*; A. Anders,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Gudmundsson,* University of Iceland*; D. Lundin,* Linköping University, IFM, Sweden

The magnetic field of a magnetron is crucial for the working principle of magnetron sputtering. This becomes apparent in particular for high power impulse magnetron sputtering (HiPIMS), where changes in the magnetic field are known to strongly affect the discharge current and voltage waveforms. For examples, for discharges with the peak discharge current kept constant, the discharge voltage decreases with stronger magnetic fields. Simulating these discharges using the Ionization Region Model provides insights into the discharge physics. We reveal that the decreasing discharge voltage has the effect that a higher fraction of the input power is used for electron heating rather than for accelerating ions. This is because stronger magnetic field increases the fraction of the discharge voltage that drops over the ionization region which enhances Ohmic heating. As a result, the discharge voltage can be lower to reach the same peak discharge current. For discharges operated with the discharge voltage kept constant, the peak discharge current increases for stronger magnetic fields. The reason is again that a higher fraction of the input power is directed to the electrons, the discharge becomes more energy efficient. This increases the electron density which lowers the discharge impedance and enables the discharge to run at a higher discharge current. Indeed, we find a close link between the evolution of the electron density and that of the discharge current during the pulse. This suggests that the discharge current can be used as a handle to adjust the electron density of a HiPIMS discharge and by that, to adjust the probability that a sputtered atom is ionized in the ionization region.

9:40am **B8-1-ThM-6 Digitalisation Strategies for a Digital Twin of the Synthesis of Functional Materials by High Power Impulse Magnetron Sputtering and Other Plasma PVD Processes***,* ***Arutiun Ehiasarian (a.ehiasarian@shu.ac.uk)****, A. Arunachalam Sugumaran, P. Hovsepian,* Sheffield Hallam University, UK*; C. Davies, P. Hatto,* Ionbond UK

Optical emission spectroscopy (OES) was combined with process parameters to monitor all stages of both High Power Impulse Magnetron Sputtering (HIPIMS) and conventional magnetron sputtering processes to provide a robust method of determining process repeatability and a reliable means of process control for quality assurance purposes. Strategies for the in-situ real-time monitoring of coating thickness, composition, crystallographic and morphological development for a CrAlYN/CrN nanoscale multilayer film were developed.Equivalents to the ion-to-neutral ratio and metal-to-nitrogen ratios at the substrates were derived from readily available parameters including the optical emission intensities of Cr I, N_2 (C-B) and Ar I lines in combination with the plasma diffusivity estimated from the ratio of substrate and cathode current densities.The optically-derived equivalent parameters identified the deposition flux conditions which trigger the switch of dominant crystallographic texture from (111) to (220) observed in XRD pole figures and the development of coating morphology from faceted to dense for a range of magnetron magnetic field configurations.

The work paves the way to implementation of machine learning protocols for monitoring and control of these and other processing activities, including coatings development and the use of alternative deposition techniques.The work provides essential elements for the creation of a digital twin of the PVD process to both monitor and predict process outcomes such as film thickness, texture and morphology in real time.

10:00am **B8-1-ThM-7 Decrease of the Interfacial Adhesion to Polymers and Pharmaceuticals Through Modification of Steel Surfaces by PVD and CVD Techniques***,* *M. Lima,* University of Minho, Portugal*; R. Silva,* University of Aveiro, Portugal*; F. Ferreira,* University of Coimbra, Portugal*; F. Oliveira, R. Silva,* University of Aveiro, Portugal*; A. Cavaleiro,* ***Sandra Carvalho (sandra.carvalho@dem.uc.pt)****,* University of Coimbra, Portugal

The adhesion is a thermodynamic parameter that quantifies the interatomic and intermolecular interaction between two surfaces and involves chemical, physical, and rheological phenomena [1]. Many industrial processes are affected by adhesion phenomena occurring during the contact of two surfaces with different properties.

An example is the demolding stage of the injection molding process because small fractions of the polymers frequently remain adhered to the mold surface, producing defective polymeric parts (~2 % of the injected parts are rejected) and reducing the mold lifetime [2].

On the other hand, the production of pills and tablets in the pharmaceutical industry is limited by the interaction between the punch and the powder. Different factors such as chemical composition, excipients, particle sizes, melting and compression points of the pharmaceuticals, and the surface properties of the punch determine the success of the drug compaction. The compaction and surface finishing of the pills will directly influence the disintegration and drug dissolution leading to diverse and undesired drug absorption kinetics [3].

Solving adhesion problems in these specific industries will reduce the generation of waste and increase productivity.

There are different ways to optimize the demolding process, such as temperature and humidity optimization, applied demolding and molding forces, or modification of the steel surface using physical vapor deposition (PVD), plasma treatments, and chemical vapor deposition (CVD) methods.

This work will report the development of coatings deposited by atomic layer deposition as well as magnetron sputtering onto steel surfaces to reduce the adherence of both polymeric and pharmaceutical materials. Coatings with different chemical and physical properties presented different surface energy values and this parameter was related to the adhesion of the polymers or the pharmaceuticals to the surfaces. Additionally, the steel coated surfaces were characterized by different techniques (SEM, XRD, FTIR, XPS, nanoindentation, OCA) to disclose the adhesion mechanisms. The coated surfaces with the lowest surface energy showed in a simulated injection process (polymers) and a powder compression machine (pharmaceuticals), the most promising results.

References

[1] R. Matjie et al., Fuel, 181 (2016) 573-578.

[2] M.J. Lima et al., ACS Appl. Nano Mater., 4 (2021) 10018-10028.

[3] V. Mazel et al., Int. J. Pharm., 442 (2013) 42-48.

10:20am **B8-1-ThM-8 Target Erosion Effects During Hipims Deposition of Ultrathick Au-Ta Alloy Films***,* *J. Bae,* General Atomics, USA*; A. Engwall, L. Bayu Aji, S. Shin, A. Baker, J. Moody,* ***S. O. Kucheyev (kucheyev@llnl.gov)****,* Lawrence Livermore National Laboratory, USA

Gold-tantalum alloy films are of interest for biomedical and magnetically-assisted inertial confinement fusion (ICF) applications. Here, we systematically study properties of Au-Ta alloy films deposited by high-power impulse magnetron sputtering (HiPIMS) from alloyed targets. By varying substrate tilt, bias, and HiPIMS pulsing parameters, properties of Au-Ta films can be controlled in a very wide range, including residual stress from -2 to +0.5 GPa, density from 12 to 17 g/cm^3, and electrical resistivity from 50 to 4500 micro-Ohm cm. Emphasis of this presentation will be on understanding and controlling effects of target wear/erosion, which strongly influences film properties during the long runs required for depositing >10-micron-thick coatings for ICF hohlraums. This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

Functional Thin Films and Surfaces
Room Pacific D - Session C2-2-ThM

Thin Films for Electronic Devices II

Moderators: Julien Keraudy, Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein, **Jörg Patscheider**, Evatec AG, Switzerland

9:00am **C2-2-ThM-4 Thermal, Plasma-enhanced and Spatial Atomic Layer Deposition as an Enabling Nanotechnology for Electronic Devices*, Erwin Kessels (w.m.m.kessels@tue.nl),*** Eindhoven University of Technology, Netherlands **INVITED**

Atomic layer deposition (ALD) is a true enabling nanotechnology that allows for the preparation of high-quality thin films on challenging surface topologies with excellent step coverage and precisely controlled nanometer dimensions. The semiconductor industry has been the main driving force behind the industrial implementation of ALD in high-volume manufacturing in the last 2 decades as it has been key for the materials- and 3D-enabled scaling to continue Moore's law in computing and data storage. Yet currently processing at the nanoscale has also become critical for other electronic devices including power electronics, microsystems and photonics.

In this presentation, the method of ALD will be introduced including a description of its underlying mechanisms, key features and hallmarks. Subsequently major developments in the field of ALD for electronic devices will be discussed covering thermal, plasma-enhanced and spatial ALD. Aspects that will be addressed include: the use of (spatial) ALD in advanced patterning, area-selective deposition using inhibitor molecules in advanced ALD-cycles, conformal deposition and gap-filling in high-aspect ratio structures including the role of surface recombination of radicals for plasma ALD, the role of ions and their energy (with respect to damage and microstructure control) in plasma ALD, etc. Examples will be given for a variety of materials systems and device applications.

9:40am **C2-2-ThM-6 Effects of Annealing Conditions on Temperature Coefficient of Resistance of Pt/AlO_X Thermistors*, Atasi Dan (atasi.dan@nist.gov)***, *E. Antunes, C. Yung, N. Tomlin, M. Stephens, J. Lehman,* Applied Physics Division, National Institute of Standards and Technology (NIST), Boulder, USA

The emergence of microfabricated, uncooled microbolometer arrays incorporating vertically-aligned carbon nanotube (VACNT) absorbers is opening opportunities for monitoring the Earth's radiative energy budget using electrical substitution techniques. In microbolometers, a thermistor having high sensitivity to temperature changes is an important component. In the present work, Pt/AlO_x thermistors are fabricated on $SiN_x/SiO_2/Si$ substrates using magnetron sputtering. In order to achieve enhanced adhesion of Pt film (175 nm), an AlO_x layer with a thickness of 10 nm is deposited as an interlayer on the substrate via reactive high-power impulse magnetron sputtering (HiPIMS), while the Pt layer was deposited by direct current (DC) sputtering process. To maximize the negative temperature coefficient of resistance (TCR), Pt/AlO_x is subjected to different annealing conditions by varying annealing temperature, time, and environment. With an increase in the annealing temperature and duration, Pt/AlO_x exhibits a significant improvement in TCR. The microstructural and morphological investigations suggest that the improvement in TCR is related to the recrystallization process of Pt and the increase in grain size. The fabricated Pt/AlO_x thermistor with a high negative TCR and provides a great potential for its use in microbolometer applications as well as ensures its capability while performing any post-processing step at high temperature.

10:00am **C2-2-ThM-7 Ultrathin Transition Metal Silicides Investigated In Situ Using Ion Scattering*, Philipp M. Wolf (philipp.wolf@physics.uu.se)***, *H. Bruce, W. Hallén, E. Pitthan, Z. Zhang,* Uppsala University, Sweden*; C. Lavoie,* IBM T. J. Watson Research Center, USA*; T. Tran, D. Primetzhofer,* Uppsala University, Sweden

Transition metal silicides are an essential building block of MOSFETs, where their low resistivity makes them the preferred choice for contact metallization.[1] As the silicide layer thickness continues to decrease with the reduction in the size of MOSFETs, methods with a high sensitivity to the outermost atomic layers are needed to investigate potential differences in phase transitions of ultrathin films as compared to thicker films. Here, we utilize a time-of-flight low-energy ion scattering (ToF-LEIS) approach capable of resolving structure and composition of ultrathin films with a sub nm resolution[2] to study phase transitions of ultrathin silicides. Our ToF-LEIS setup is connected to a preparation chamber equipped with an e^--beam evaporator for thin film deposition, a heating filament, an ion sputter gun, an Auger electron spectrometer and a low-energy electron diffraction setup, enabling us to perform in situ characterization. Additional ex situ measurements, including time of flight medium-energy ion scattering, Rutherford backscattering spectrometry and transmission electron microscopy are performed to provide additional information on total areal densities, crystallographic structures and phases present in the films.

We present detailed studies of two relevant silicide systems, ultrathin Ni and Ti silicide films, grown on Si(100). For Ni silicide films with an initial Ni thickness of 3.6 nm, using the above-described approach, we found an unprecedented direct transition from orthorhombic δ-Ni_2Si, displaying long-range order covering the whole film thickness, to epitaxial $NiSi_{2-x}$ at 290°C skipping the intermediate NiSi phase observed for thicker films.[3] Considering previous studies we suggest that the ordered δ-Ni_2Si phase occurs regardless of the initial Ni film thickness but is limited in thickness by competing orientations of the δ-Ni_2Si crystal. Whether or not the NiSi phase is found absent, depends on whether the formed δ-Ni_2Si can consume all deposited Ni or not. For Ti silicide, formed from a Ti thickness of 6 nm annealed in steps up to 680°C, we do not observe an epitaxial phase but instead agglomeration of the silicide film. Further, an even thinner Ti silicide film, with an initial Ti thickness of 3 nm, is annealed in situ and characterized. Together these results show the analytical power of the presented approach and the increasing need for methods with a sub nm resolution in the field of thin film electronics.

[1]S.-L. Zhang and Z. Zhang, Met. Films for Electron., Opt. and Magn. Appl., Elsevier, 244–301, 2014
[2]M. Draxler et al., Phys. Rev. A, 68, 022901, 2003
[3]P. M. Wolf et al., Small, 2106093, 2022

10:20am **C2-2-ThM-8 Synthesis of a New Ternary Nitride Semiconductor - Zn_2VN_3: A Combinatorial Exploration of the Zn-V-N Phase Space***, S. Zhuk,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Kistanov,* University of Oulu, Finland*; S. Boehme,* ETH Zürich, Switzerland*; N. Ott, M. Stiefel,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M. Kovalenko,* ETH Zürich, Switzerland; ***Sebastian Siol (sebastian.siol@empa.ch),*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nitrides are promising functional materials for a variety of applications. Despite their technological importance, many promising theoretically predicted metal nitrides are yet to be discovered. This is partly rooted in their challenging synthesis as compared to oxides. Non-equilibrium PVD in UHV conditions, such as reactive RF-magnetron sputtering, provides ideal prerequisites for the formation of novel metastable nitride thin films.

In this work, a computationally guided combinatorial PVD screening of the entire Zn-V-N phase space is performed, resulting in the synthesis of the previously unreported ternary nitride Zn_2VN_3.[1] Reactive RF co-sputtering of Zn and V targets is performed in Ar/N_2 atmosphere with N_2 is supplied directly to the sputter plasma to increase the N_2 dissociation rate and consequently increase the N chemical potential. The combinatorial libraries are grown with composition and deposition temperature gradients to quickly cover large areas of the synthesis phase space. A comprehensive automated mapping characterization of the sample is performed to investigate the structure, composition, chemical-state as well as optoelectronic properties. XRD mapping analysis reveals the presence of a wurtzite $Zn_{1-x}V_xN$ phase over a large compositional range from Zn_2VN_3 to $ZnVN_2$, with a narrow process window for single-phase Zn_2VN_3.

Following the combinatorial screening we isolate the phase and synthesize single-phase polycrystalline Zn_2VN_3 thin films with wurtzite structure on conventional borosilicate glass substrates. In addition, we demonstrate that cation-disordered, but phase-pure (002)-textured wurtzite Zn_2VN_3 thin films can be grown using epitaxial stabilization on α-Al_2O_3 (0001) substrates at remarkably low growth temperatures well below 200 °C as evidenced by (S)TEM analysis. The composition as well as chemical state of the constituent elements are studied using RBS/ERDA as well as XPS/HAXPES methods. These analyses reveal a stoichiometric material with no oxygen contamination, besides a thin surface oxide.

We find that Zn_2VN_3 is a weakly-doped p-type semiconductor demonstrating broadband room-temperature PL spanning the range between 2 eV and 3 eV, consistent with the bandgap of similar magnitude predicted by density functional theory-based calculations. In addition, the electronic properties can be tuned over a wide range via isostructural alloying on the cation site, making this a promising material for optoelectronic applications.

[1] S. Zhuk *et al.* 2021 arXiv:2109.00365

10:40am **C2-2-ThM-9 Theoretical and Experimental Approaches for the Determination of Functional Properties of a New Semiconductor: $MgSsnN_2$**, ***Agathe Virfeu (agathe.virfeu@univ-lorraine.fr)***, *F. Alnjiman, S. Diliberto, J. Ghanbaja,* Institut Jean Lamour - Université de Lorraine, France*; E. Haye,* University of Namur, Belgium*; S. Migot, J. Pierson,* Institut Jean Lamour - Université de Lorraine, France

III-N materials are commonly used as active layers in LEDs, transistors, solar cells and mechanical devices. The main spinneret is based on the use of InGaN alloys. However, such layers contain indium and gallium. Significant volatility in their price and supply over the last years has led to considerable concern given their critical roles and their use in a wide range of large-scale electronic devices. It is important to study and develop new earth abundant materials with optimized properties for the realization of innovative optoelectronic devices that could be competitive cost for mass production. Over the past 10 years, the study of Zn based II-IV-N_2 family has shown that they are interesting semiconductors due to the tunability of their properties. However, oxygen contamination and high vapor pressure of zinc make it difficult to control the stoichiometry and the structure order. In this work, we aim at developing a new kind of inexpensive, indium/gallium-free, nitride material that could be the basis of new way for optoelectronic applications. The studies are focusing on $MgSnN_2$ thin films (bandgap energy ≈ 2 eV) that is a good candidate for green emitters in LEDs and an absorber material in tandem photovoltaics.

$MgSnN_2$ thin films have been deposited by magnetron co-sputtering at different substrate temperatures (up to 500 °C).The Mg/Sn atomic ratio has been controlled by the current applied to the Mg and Sn targets. The structure of the films has been studied by X-ray diffraction. Whatever the deposition temperature, the films crystallize in a wurtzite-like structure with a strong preferred orientation in the [002] direction. The columnar microstructure of $MgSnN_2$ thin films have been studied by transmission electron microscopy and the chemical environment of the Sn and Mg atoms has been investigated using Mössbauer spectrometry and X-ray photoemission spectroscopy.The optical band gap deduced from UV-visible spectroscopy is ranging in the 2.1 – 2.4 eV range. These experimental optical properties of $MgSnN_2$ films were compared to those obtained by *ab initio* calculations. Finally, the electrical resistivity, carrier concentration, type and carrier mobilityhave been measured by Hall effect.

11:00am **C2-2-ThM-10 Relative Effects of Pulsed Laser Deposition Parameters on the Stoichiometry of Multiferroic Thin Films**, ***W. C. McGinnis (wayne.mcginnis@spawar.navy.mil)***, *A. Hening, T. Emery-Adleman,* Naval Information Warfare Center Pacific, USA

Pulsed laser deposition has a reputation for maintaining the stoichiometry of the ablation target in the deposited film. Exceptions to this "rule" occur, however, for materials such as multiferroic $Bi_xDy_{(1-x)}FeO_3$ (BDFO), which contain elements with large differences in volatility, such as Bi and Fe. The relative effects of various pulsed laser deposition parameters on the resulting stoichiometry of BDFO films as a function of time (or number of laser pulses) has been examined using an interactive spreadsheet, as well as experimentally. The adjustable parameters include target composition, elemental ablation yield from the target, plume spreading effects, sputtering of the growing film by ablated atoms, and thermal evaporation of deposited atoms from the heated substrate. Examples of how the calculated film composition might evolve will be presented (as seen in the supplementary figure), along with experimental results showing how these deposition parameters individually affect BDFO film stoichiometry.

11:20am **C2-2-ThM-11 Effects of Carbon Addition on $Ge_2Sb_2Te_5$ Film Structure and Properties**, ***David Adams (dpadams@sandia.gov)***, *E. Lang, T. Clark, C. Sobczak, E. Scott, J. Custer,* Sandia National Laboratories, USA*; T. Beechem,* Purdue University, USA*; K. Hattar, M. Rodriguez,* Sandia National Laboratories, USA

Phase change thin film materials continue to attract interest for applications such as non-volatile electronic memory, sensors, and optical data storage, because the material can be rapidly switched between contrasted amorphous and crystalline states. In particular, the germanium antimony tellurium (GST) system remains a benchmark for many current studies wherein $Ge_2Sb_2Te_5$ has received much attention. Recent research has demonstrated how quaternary additions (C, N, Se, O) improve thermal stability. The addition of a few mol.% C, for example, increases crystallization temperature which positively impacts data retention. In this presentation, we examine additional consequences of carbon addition. We describe sputter-deposited $Ge_2Sb_2Te_5$ thin films fabricated with different amounts of carbon up to 12 mol.% and assess how this fourth species affects film phase, order, microstructure and key properties. Similar phase evolution is observed upon heating (amorphous –> face-centered cubic -> trigonal), and phase transformation temperatures are elevated when adding carbon. Grain size is also refined with increased carbon addition within the compositional range studied. The effects of carbon on thin film thermal properties are revealed by frequency domain thermoreflectance wherein a decreased thermal conductivity is observed even when adding small amounts (2 mol. % carbon). Finally, we investigate the response of C-doped GST films to heavy ion irradiation. Films have been irradiated to different doses with 2.8 MeV Au ions in order to explore the potential for ion-induced phase changes and modification of electrical resistivity and thermal conductivity.The response of films having different amounts of carbon (up to 6 mol.%) will be described wherein phase modifications are reported.

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Functional Thin Films and Surfaces
Room Pacific D - Session C3-1-ThM

Thin Films for Energy Storage and Conversion I

Moderators: Clio Azina, RWTH Aachen University, Germany, **Tushar Shimpi**, Colorado State University, USA

8:00am **C3-1-ThM-1 Designing Optimal Environments for Surface Catalytic Reactions in Perovskite Oxide Electrodes**, *L. Martin,* ***Abel Fernandez (abel_fernandez@berkeley.edu)***, University of California, Berkeley, USA **INVITED**

Solid-gas interactions at electrode surfaces determine the efficiency of solid-oxide fuel cells and electrolyzers. Of particular relevance are the local chemistry and electronic structure at the exposed electrode surface. Using epitaxial thin films as model systems, we studied the evolution of surface chemistry and electronic structure in perovskite electrodes with different surface orientations and epitaxial strain states. First, synthesizing $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ films on $SrTiO_3$ (001)-, (110)-, and (111)-oriented substrates wherein the surface orientation of the film is set by the substrates. Electrochemical impedance spectroscopy and electrical conductivity relaxation measurements reveal a strong surface-orientation dependency of the gas-exchange kinetics, wherein (111)-oriented surfaces exhibit an activity >3-times higher as compared to (001)-oriented surfaces. First-principles calculations suggest that the formation energy of vacancies and adsorption at the various surfaces is different and influenced by the surface polarity. Finally, synchrotron-based, ambient-pressure X-ray spectroscopies reveal distinct electronic changes and surface chemistry among the different surface orientations. Taken together, thin-film epitaxy provides an efficient approach to control and understand the electrode reactivity ultimately demonstrating that the (111)-surface exhibits a high density of active surface sites which leads to higher activity.[1] Outside of surface chemistry, manipulation of the surface electronic structure via epitaxial strain presents another route toward enhancing surface reaction rates. Combining high-temperature electrical-conductivity-relaxation studies and synchrotron-based X-ray absorption spectroscopy studies of $La_{0.5}Sr_{0.5}CoO_3$ and $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{-3}$ thin films under varying degrees of epitaxial strain reveals a strong correlation between orbital structure and catalysis rates. In both systems, films under biaxial tensile strain exhibit the fastest reaction kinetics, in agreement with previous reports. Films under tensile biaxial strain also possess the lowest electron occupation in the d_{z^2}orbitals, suggesting the orbital occupation plays an important role in determining the electrocatalytic properties of perovskite cathodes.[2]

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2. A. Fernandez *et al. Adv. Energy Mater.* 2102175 (2021).

8:40am **C3-1-ThM-3 Halide Perovskites: Advanced Photovoltiac Materials Empowered by a Unique Bonding Mechanism***, **Matthias Wuttig (wuttig@physik.rwth-aachen.de)**,* Sommerfeldstrasse, Germany*; C. Schön, M. Schumacher,* RWTH Aachen University, Germany*; J. Robertson,* University of Cambridge , UK*; P. Golub,* Heyrovsky Institute of Physical Chemistry, Czechia*; E. Bousquet,* Liege University, Belgium*; C. Gatti,* CNR-SCITEC, Italy*; J. Raty,* University Liege, Belgium

Outstanding photovoltaic (PV) materials combine a set of advantageous properties including large optical absorption and high charge carrier mobility, facilitated by small effective masses. Halide perovskites (ABX_3, where X = I, Br or Cl) are among the most promising PV materials. Their opto-electronic properties are governed by the B-X bond, which is responsible for the pronounced optical absorption and the small effective masses of the charge carriers. These properties are frequently attributed to the ns^2 configuration of the B atom, i.e. Pb $6s^2$ or Sn $5s^2$ ('lone-pair') states. Our analysis of the PV properties in conjunction with a quantum-chemical bond analysis reveals a different scenario. The B-X bond differs significantly from ionic, metallic or conventional 2c-2e covalent bonds. Instead it is better regarded as metavalent, since it shares about one p-electron between adjacent atoms. The resulting s–bond, formally a 2c-1e bond, is half-filled, causing pronounced optical absorption. Electron transfer between B and X atoms as well as lattice distortions open a moderate band gap resulting in charge carriers with small effective masses. Hence metavalent bonding explains favorable PV properties of halide perovskites, as summarized in a map for different bond types, which provides a blueprint to design PV materials.

M. Wuttig [https://arxiv.org/search/?searchtype=author&query=Wuttig%2C+M], C.-F. Schön [https://arxiv.org/search/?searchtype=author&query=Schoen%2C+C], M. Schumacher [https://arxiv.org/search/?searchtype=author&query=Schumacher%2C+M], J. Robertson [https://arxiv.org/search/?searchtype=author&query=Robertson%2C+J], P. Golub [https://arxiv.org/search/?searchtype=author&query=Golub%2C+P], E. Bousquet [https://arxiv.org/search/?searchtype=author&query=Bousquet%2C+E], C. Gatti, J.-Y. Raty [https://arxiv.org/search/?searchtype=author&query=Raty%2C+J]

Halide perovskites: third generation photovoltaic materials empowered by an unconventional bonding mechanism

Advanced Functional Materials, 202110166 (2021)

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E2-1-ThM

Mechanical Properties and Adhesion I

Moderators: Carsten Gachot, Vienna University of Technology, Austria, **Bo-Shiuan Li**, Oxford University, UK

10:40am **E2-1-ThM-9 Effect of Thin Film Properties on Delamination Behavior and Interface Adhesion***, **Alice Lassnig (alice.lassnig@oeaw.ac.at)**, S. Zak, R. Pippan,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; C. Mitterer,* Montanuniversität Leoben, Austria*; M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Understanding the factors affecting thin film delamination and quantifying thin film adhesion to their substrates is important to ensure reliable multi-material components which are widely encountered in several technological applications.
Of special interest are brittle-ductile interfaces separating thin ductile films from rigid substrates since they are particularly weak. Standard routes to quantify such interfaces are 4 Point Bending tests or - if applicable- buckle-driven delamination by means of the stressed overlayer technique [1]. Improving the interface stability for nanosized thin films on brittle substrates is therefore crucial to ensure reliable bi- and multi-material devices.

In a recent study [2] we could demonstrate that intrinsic film properties such as grain size can significantly influence interface adhesion. Nanoindentation results allowed to estimate the film yield stress of the films when bonded to the substrate. The mixed-mode adhesion energy for each film ranged from 2.35 J/m² for the films with larger

grains to 4.90 J/m² for their small-grained counterparts while all the films showed similar residual stresses and same film thicknesses. A newly developed focused ion beam (FIB) cutting technique allowed to decouple and quantify the amount of elastic and plastic deformation stored in the buckled thin film. This surprising result could be understood by introducing a new finite element modelling technique to further help understand plasticity contribution as a toughening mechanism during thin film delamination [3] and to further adapt established models, which currently only account for purely elastic film delamination.

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11:00am **E2-1-ThM-10 Buckling-Induced Delamination: Connection between Mode–Mixity and Dundurs´ Parameters***, **Stanislav Zak (stanislav.zak@oeaw.ac.at)**, M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Modern electronics and micromechanical devices consist of various combinations of layered materials and/or coatings with different material properties. In recent years, differences in the elastic moduli and Poisson's ratios are becoming more pronounced (e.g. when bendable electronic components are designed). Therefore, a strong push to investigate interface stability with a more in–depth view on the elastic material properties mismatch influence is needed. Measurements of the adhesion energy of the thin film on the different substrate materials can be made using the spontaneous (compressive stress induced) buckling method described by Hutchinson and Suo. This method induces lateral deformation of the thin film with respect to the substrate (to form delaminated buckles), which causes a significant shear loading contribution to the delamination crack front and therefore, the inevitable mode II appearance. Additionally, the shear loading can be highly influenced by the differences in deformations of the film and substrate due to their elastic mismatch which can be high for modern material combinations, such as those found in flexible devices. Therefore, the original approach to elastic mismatch by Hutchinson and Suo is revised and extended in this work. Since the elastic mismatch on the interface between two different materials can be described by the Dundurs' parameters, a wide range of parameters are used to evaluate the mode-mixity at the delamination crack front. Finite element (FE) modelling is combined with analytical solutions to evaluate parameters describing the mode–mixity of the delaminated buckles as a function of elastic mismatch (both according to Hutchinson and Suo and also with the use of more real-like models). The FE approach enables relatively simple and quick evaluation of stress intensity factors for arbitrary models via domain integration method. Therefore, several FE model configurations can be analysed together with numerically obtained stress/strain fields in the buckled samples. The resulting map of the mode-mixity as a function of Dundurs' parameters will lead to more precise experimental measurements of the mode I and mode II adhesion energy components for modern material combinations.

11:20am **E2-1-ThM-11 Colored Picosecond Acoustics Versus Scotch Tape Adhesion Test: Confrontation on a Series of Similar Samples With a Variable Adhesion***, A. Vital-Juarez,* IEMN UMR CNRS 8520, France*; J. Desmarres,* CNES, France*; **Arnaud DEVOS (arnaud.devos@iemn.fr)**,* IEMN UMR CNRS 8520, France

The study of the bonding at interfaces between thin layers is of great importance in optical and electronic applications as well as in the field of space exploration. A large number of methods have been developed to characterize the adhesion of a thin film to a substrate. Among them, Scotch Tape test is still one of the most popular methods.

Acoustic waves and especially ultra-high frequency acoustic waves are also sensitive to adhesion defects as they affect the way acoustic waves are reflected at the concerned interface.

In this paper, we prepare a dedicated series of identical thin-film samples with a variable adhesion at the interface between the film and its substrate. For that several avenues have been explored: introduction of a weak layer between the film and the substrate; reinforcement of the weak layer adhesion using ion beam implantation. The samples are then characterized using two much different techniques: colored picosecond acoustics for measuring thickness and acoustic reflection coefficient at the interface and scotch tape test to have an independent evaluation of the adhesion. An excellent correlation is found between techniques regarding adhesion that confirms the capability of APiC to perform adhesion test in a totally non destuctive manner and furthermore locally.

11:40am **E2-1-ThM-12 High-Throughput Screening of Adhesion and Friction of Solid Interfaces***, Maria Clelia Righi (clelia.righi@unibo.it),* University of Bologna, Italy **INVITED**
clelia.righi@unibo.it

High-throughput studies have become a valuable tool for material advancement, which is of tremendous importance for industry and closely tied to various societal challenges like clean energy production. We designed and implemented an advanced workflow, based on the FireWorks platform, to perform first principles calculations using the VASP package. Starting from two elemental solids, the workflow can generate the surfaces of interest and match them to form an interface. The interfacial adhesion, load-displacement curves, shear strength and charge displacements are automatically calculated and the results are stored in a public database [1].

In a first application of the high-throughput approach tohomogeneous interfaces we generated a database of the shear and cleavage strengths for over hundred interfaces formed by matching two equivalent surfaces of different elemental crystals [2]. We discovered the existence of a power-law between the adhesion and the shear strength for these interfaces. Moreover, the ratio of the strengths can provide an estimate of the material failure mode[3]. The analysis also showed that the mechanical properties of elemental crystals are closely related to their electronic structure [4].

In a more recent advancement, we created a database for heterogeneous interfaces focusing in particular to metal-on-metal surfaces relevant for technological applications and 2D layers adsorbed on solid substrates. The analysis of the overall trends and the comparisonof the data obtained for heterogeneous interfaces with the homogeneous counterparts improved the scientific and mechanistic understanding of interface mechanics and tribology [5].

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New Horizons in Coatings and Thin Films
Room Pacific E - Session F4-3-ThM

New Horizons in Boron-Containing Coatings III

Moderators: Marcus Hans, RWTH Aachen University, Germany, **Helmut Riedl**, TU Wien, Austria, **Johanna Rosén**, Linköping University, Sweden

8:40am **F4-3-ThM-3 Synthesis of MoAlB Thin Films ContainingMoB MBene Regions***, R. Sahu,* Max-Planck-Institut für Eisenforschung GmbH, RWTH Aachen University, Germany*; D. Bogdanovski, S. Evertz, P. Pöllmann, D. Holzapfel, E. Mayer, J. Achenbach,* RWTH Aachen University, Germany*; S. Zhang,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; C. Scheu,* Max-Planck-Institut für Eisenforschung GmbH, RWTH Aachen University, Germany*; **Jochen M. Schneider (schneider@mch.rwth-aachen.de)**,* Materials Chemistry, RWTH Aachen University, Germany

Two-dimensional (2D) inorganic transition metal boride nanosheets are emerging as promising post-graphene materials in energy research due to their unique properties. State-of-the-art processing strategies are based on chemical etching of bulk material synthesized *via* solid-state reaction at temperatures above 1000 °C. Here, we report the direct formation of MoB MBene domains in an MoAlB thin film by Al deintercalation from MoAlB in the vicinity of AlO_x regions. Hence, based on these results a straightforward processing pathway for the direct formation of MoB MBene-AlO_x-heterostructures without employing chemical etching is proposed here.

Furthermore, the nanolaminated ternary boride MoAlB exhibits a promising high-temperature oxidation resistance due to the formation of a dense alumina scale. While bulk synthesis of MoAlB requires temperatures larger than 1000 °C with up to 40% of excess Al in the feedstock, here we report the temperature range for the formation of single phase, orthorhombic MoAlB synthesized by magnetron sputtering from a stoichiometric target is 450 – 650 °C. Lower synthesis temperatures yield the formation of amorphous films, while at 700 °C, impurity phases form in addition to orthorhombic MoAlB. Amorphous MoAlB films were observed by in-situ X-ray diffraction to crystallize between 545 and 575 °C. Hence, we infer that the formation of orthorhombic MoAlB thin films issurface diffusion mediated below 545 °C. As bulk diffusion is activated between 545 and 575 °C the synthesis of fully dense MoAlB films with a maximum hardness of 15 ± 2 GPa and a Young’s modulus of 379 ± 30 GPa at 600 °C is surface and bulk diffusion mediated.

9:00am **F4-3-ThM-4 On the Surpassing Fracture Toughness of $TiB_2\pm_Z$ Thin Films***, **Christoph Fuger (christoph.fuger@tuwien.ac.at)**, A. Hirle, R. Hahn, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG , Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Their unique material characteristics make transition metal diboride-based thin films to perfect candidates for replacing state of the art protective and functional coatings. Not only machining tools but also high-precision components (e.g. turbine blades) within aircrafts and turbines used for energy production demand for surface improving materials. Mechanical properties like hardness, Young’s modulus and fracture toughness of the thin films are essential to protect the components from impacting mechanical stresses, especially against sudden impacts at high stress levels. Well-known for their superior hardness, various TMB_2 exhibit enhanced resistance against fracture exceeding K_{IC} values of well-established nitride-based coating materials (e.g. TiN or $Ti_{1-x}Al_xN$) and are therefore perfect aspirants for various industrial applications.

Here, we focus on magnetron sputtered non-stoichiometric $TiB_{2\pm z}$ exhibiting outstanding mechanical properties. Beside super hardness of 45.90 ± 1.20 GPa and Young’s modulus of 524.27 ± 14.10 GPa the coatings exhibit a fracture toughness of K_{IC} = 4.79 ± 0.57 MPa√m – tested via different micro-mechanical testing procedures. Detailed TEM and TEM-EELS investigations elucidate, that the distinct excess of boron predominates the constitution of the precipitating tissue phases around the columnar growth morphology. Due to covalently bonded boron-boron bonds the cohesive grain boundary strength is enhanced, impeding severe intercolumnar crack growth. The study highlights the great potential of $TiB_{2\pm z}$ for new applications in the field of high-performance components and reveal the importance of a detailed understanding of the grain boundary strength for fracture tough thin films.

Keywords: Fracture Toughness; Transition Metal Diborides; TiB_2; Tissue Phase; Micro-mechanical Testing;

9:20am **F4-3-ThM-5 Revealing the Beauty of Imperfection in Novel Diboride Coatings by Transmission Electron Microscopy*, Justinas Palisaitis (justinas.palisaitis@liu.se),*** Linköping Univ., IFM, Thin Film Physics Div., Sweden **INVITED**

Transition metal diborides (TMB_2) are considered as an extremely hard ceramics owning to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes TMB_2 coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1,2].Currently, magnetron sputtering is the primary technique for obtaining TMB_2 coatings. Typically obtained TMB_2 coatings are overstoichiometric in boron (B/TM>2) [3]. Recent addition of novel understoichometic variants of TMB_2 coatings (B/TM<2) have greatly widened their compositional range [3-8]. As the field of non-stoichiometric TMB_2 coatings is starting to open, this work offers the first systematic investigation into the different types of extended planar defects presented in the TMB_2 coatings throughout the wide compositional and elemental range. Atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects. Distinct types of planar defects residing on the {1-100} planes have been identified that are accompanied with or without local compositional changes. The characteristic atomic structures and factors leading to the formation of these planar defects in TMB_2 coatings will be presented.

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10:00am **F4-3-ThM-7 Thermally Induced Structure Evolution and Improved Oxidation Behavior of Ternary $Ta_{1-x}Al_xB_{2+\Delta}$ Hard Thin Films*, Viktor Šroba (viktor.sroba@fmph.uniba.sk),*** Comenius University, Bratislava, Slovakia*; T. Fiantok,* Comenius University in Bratislava, Slovakia*; M. Truchlý, T. Roch, B. Grančič,* Comenius University, Bratislava, Slovakia*; P. Švec,Jr.,* Institute of Physics, Slovak Academy of Sciences, Slovakia*; Š. Nagy,* Institute of Materials and Machine Mechanics SAS, Slovakia*; V. Izai,* Comenius University, Bratislava, Slovakia*; T. Glechner,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, Austria*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria*; P. Kúš, M. Mikula,* Comenius University, Bratislava, Slovakia

Diborides of transition metals (TMB_2) from IIIB to VIB group are due to their excellent mechanical properties and thermal stability promising materials for hard thin films used in extreme environments. Notable example being overstoichiometric $TiB_{2+\Delta}$ with value of hardness up to 60 GPa. However, formation of volatile boric acid (H_3BO_3) at elevated temperatures in air (450 °C for $TiB_{2+\Delta}$) and low fracture toughness expressed by high values of elastic modulus (500-600 GPa for $TiB_{2+\Delta}$) significantly reduce application potential of binary diboride coatings [1]. Alloying with aluminum to form ternary systems is well-proven method leading to improved oxidation resistance and higher hardness due to age hardening as a result of spinodal decomposition. This effect was theoretically predicted in $TiAlB_2$ by Alling et al. [2] and experimentally confirmed by Mockute et al. [3] in which decomposition of $TiAlB_{2+\Delta}$ films during annealing at 1000 °C led to increase in hardness from 32 to 37 GPa.

Here, we present structural evolution and oxidation behavior of ternary $Ta_{1-x}Al_xB_{2\pm\Delta}$ films. Experimental results obtained on magnetron co-sputtered $Ta_{1-x}Al_xB_{2\pm\Delta}$- films were supported by density functional theory (DFT) calculations on $TaAlB_2$ system. Addition of aluminum resulted in decrease of hardness from ~34 GPa for amorphous $TaB_{1.21}$ films to ~29 GPa for $Ta_{0.75}Al_{0.25}B_{2.14}$ films with typical 0001 texture of hexagonal α-AlB_2 type structure. Positive effect of aluminum alloying in improvement of oxidation behavior was observed during thermogravimetric analysis (TGA) with onset oxidation temperature of approx. 700 °C for $Ta_{0.75}Al_{0.25}B_{2.14}$ films compared to 600 °C for $TaB_{1.21}$ films.

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10:20am **F4-3-ThM-8 Mapping the X-B-C Systems: Search for the Elusive X_2BC Phase*, Pavel Soucek (soucek@physics.muni.cz),*** *S. Debnarova, M. Alishahi, S. Mirzaei, M. Kroker, L. Zabransky, V. Bursikova,* Masaryk University, Czechia*; Z. Czigany, K. Balazsi,* Centre for Energy Research, Hungary*; M. Hans, D. Holzapfel, S. Mraz, J. Schneider,* RWTH Aachen, Germany*; P. Vasina,* Masaryk University, Czechia **INVITED**

Binary borides and binary carbides have been known for many decades. Their outstanding mechanical, electrical and thermal properties made them indispensable in the industry, either in bulk or as thin films. The idea of combining these systems into a ternary X-B-C system naturally evolved. Such systems in the form of bulk have been investigated since the 1950s. The X has been from all of the s, p d and f blocks of the periodic table of the elements. Different structures were found. The orthorhombic Mo_2BC phase, being the first with the X_2BC stoichiometry, was described by Jeitschko in 1963 [1]. This structure attracted interest for its superconducting properties. Sixty years later, this is still the only synthesised X_2BC phase.

An interest in the X-B-C thin films can be traced to the mid-1980s, with experimental work accelerating in the 1990s. The focus was on the Ti-B-C system in the form of multilayers or in the form of a crystalline-crystalline nanocomposite. Superior mechanical properties of this system were described. A renaissance of the X_2BC phases, this time in the form of the thin films, has begun in 2009 when the Mo_2BC phase was prepared by direct current magnetron sputtering [2]. This phase was no longer studied for its superconducting properties, in which other materials superseded it, but for its highly unusual combination of high hardness and moderate ductility. Theoretical studies describing other crystalline ternary X_2BC phases predicting the thermodynamic possibility of their preparation together with even better mechanical properties followed [3]. Since then, several different systems from these predictions have been studied, including W-B-C, Nb-B-C and Ta-B-C. No definitive proof of the existence of any X_2BC phase apart from the original Mo_2BC phase was found. This contribution will cruise through the ups and downs of this research in the last decade. It will be shown that thin films from these systems can have interesting mechanical and thermal properties even without the formation of the desired and elusive X_2BC phase. It will be discussed why these phases won't form even under energetically very harsh conditions such as HiPIMS. We will also sketch the possibilities for the future directions of the studies of the X_2BCs.

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11:00am **F4-3-ThM-10 Industrial Deposition of W-B-C Coatings: Properties and Process Modelling*, Michael Kroker (kroker@physics.muni.cz),*** *P. Souček, L. Zábranský, V. Buršíková,* Masaryk University, Czechia*; V. Sochora, M. Jílek,* SHM s.r.o., Czechia*; P. Vašina,* Masaryk University, Czechia

W-B-C coatings have the potential to replace current state-of-the-art hard protective coatings in the industry owing to their unprecedented combination of high hardness and increased fracture resistance, as the brittle fracture is the most limiting shortcoming of the traditional hard protective coatings based on ceramics such as TiN, CrN, AlN, and their combinations. So far, only a few studies have dealt with industrial deposition of the W-B-C coatings.

This study shows the properties of W-B-C coatings industrially deposited by non-reactive magnetron sputtering using a system provided by SHM, Czech Republic. The system utilizes a single cylindrical sputter source fitted with a segmented target composed of tungsten, boron carbide, and graphite segments. The segmented target provides for the adaptation of the coatings' chemical composition by rearranging the position of individual segments. As an industrial standard, the planetary table capable of multi-axis rotation of substrates was used to simulate batch coating of the tools. The depositions were carried out in both stationary and single-axis rotation regimes to understand the differences between laboratory-like and industrial preparation of the coatings.

W-B-C coatings were studied over a broad range of chemical compositions. Although the coatings were mostly amorphous, they still exhibited high hardness (up to 29 GPa) and elastic modulus (up to 440 GPa). Detailed analyses of their mechanical properties proved their superior fracture resistance compared to current ceramic-based protective coatings. The comparison of the fracture resistance was possible using the instrumental indentation technique and indentation tip with a very small curvature radius (cube-corner diamond tip) and very thick coatings. This method induced cracking in the coating without the significant influence of the substrate.

To further ease the industrial utilization of these coatings, a simple yet powerful model was developed to predict the influence of the target setup and the influence of movement and placement of the substrates in the chamber. The modelling procedure was based on freeware SDTrimSP for the sputtering processes and SiMTra for the particle transport. The results showed very good agreement in terms of chemical composition as well as the relative thickness of the coatings. They were able to identify the crucial difference between the laboratory-like and industrial preparation of the W-B-C coatings.

11:20am **F4-3-ThM-11 Magnetron Sputter Deposition of Boron Carbide Films on Tilted Substrates***, Swanee Shin (shin5@llnl.gov), L. Bayu Aji,* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; A. Engwall, M. Nielsen, J. Hammons,* Lawrence Livermore National Laboratory, USA*; X. Zuo, B. Lee,* Argonne National Laboratory, USA*; X. Lepro Chavez, P. Mirkarimi, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Many applications of boron carbide films call for deposition onto non-planar substrates in the regime when the substrate normal is tilted away from the main deposition flux direction. Properties of boron carbide films deposited on such tilted substrates have not been previously studied, and the underlying physics of boron carbide film growth in the oblique angle deposition regime remains poorly understood. Here, we present results of our systematic study of the effect of substrate tilt on properties of boron carbide films deposited by direct current magnetron sputtering. The influence of the working gas (Ar vs Ne) on the deposition rate and film properties will also be discussed.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country B - Session G2-ThM
Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications

Moderators: Satish Dixit, Plasma Technology Inc., USA, **Heidrun Klostermann**, Fraunhofer FEP, Germany

8:00am **G2-ThM-1 Surface Engineering Opportunities: Harsh Environments Meeting New Strategies for Microstructural Designs (Virtual Presentation)***, Chris Berndt (cberndt@swin.edu.au),* Australian Research Council, Industrial Transformation Training Centre, Australia **INVITED**

Harsh and extreme environments arise when the operating regime is at high temperature under corrosive conditions. Examples of such environments are numerous as industries seek greater plant efficiencies and transportation platforms strive to operate under increasingly arduous conditions. That is, engineers desire greater productivity and length of operation before refurbishment: both commercial ambitions that rest on the component lifetime.

With the above pragmatic backdrop in mind, this presentation considers adding value and performance to traditional materials by surface engineering. Examples will be drawn from the biomaterial, mining and hypersonic vehicle sectors where Surface Engineering has provided solutions that address a variety of harsh and extreme environments.

The key issue in all cases, and which connects apparently disparate applications, is 'the microstructure'. Thus, the aim of this talk is to outline the highly defective nature of the coatings that enhance the performance of components. Although the focus will be on thermal spray technology, the theme of leveraging defects for their performance attributes crosses many areas of materials science and engineering. The defective nature is controlled by the processing variables of the surfacing method. Hence, process feedback loops are necessary so that the composite-like microstructural design can be controlled.

Acknowledgement: This work has been supported by the Australian Research Council (ARC). The Centre for Surface Engineering for Advanced Materials is funded under the Industrial Transformation Training Centre (ITTC) scheme via Award IC180100005. Many Colleagues have contributed to this effort.

8:40am **G2-ThM-3 Plasma Nitriding of Forming Tools for the Automotive Industry - Challenges and Opportunities***, Manuel Mee (manuel.mee@oerlikon.com),* Oerlikon Balzers Coating Germany GmbH, Germany **INVITED**

To increase the service life of forming tools, coatings by physical vapor deposition (PVD) or chemical vapor deposition (CVD) have been used for decades. However, upscaling to ensure robust processes for large tools is difficult. In this regard, hard chrome electrodeposition has proven to be a common practice. One disadvantage in particular is the limited durability, which in the context of service life, using the example of a car body side tool, is manifested in multiple decoating and recoating involving the use of environmentally critical chemicals. In contrast, plasma nitriding is a thermochemical diffusion process for surface hardening in which the surface layer of a workpiece or component is enriched with nitrogen at low to moderate temperatures. The technology used by Oerlikon allows a loading of up to 40 tons on an area of 3x10m. Thus, an environmentally friendly surface treatment is available even for massive tools, which, compared to hard chrome, requires only a single treatment.

Nevertheless, it should be noted and taken into account that in principle a start-up of these tools have already been done beforehand and therefore process-side interactions with impurities, passivation as well as any pre- and post-treatments are possible. This applies in particular to areas hardened and welded in advance, as well as to subsequent modifications where the already nitrided surface has to be welded. Possible consequences are material-specific and manifest themselves in tempering effects, outgassing and degradation phenomena.

The main topic of the presentation will be the requirements of users and manufacturers of forming tools and the resulting challenges. In addition to various applications and the respective restrictions with large forming tools whose mass can be far more than 10 tons, the measures derived from this to ensure process stability and quality will be discussed.

9:20am **G2-ThM-5 Enhanced Wear and Corrosion Properties of Stainless Steel by Electron Induced Plasma Nitriding***, Petros Abraha (petros@meijo-u.ac.jp),* Meijo University, Japan

In this study, we focus on recent advances in plasma source technology for materials processing applications. The plasma source used in conventional plasma nitriding treatment apply direct current, radio frequency, and microwave power between electrodes, and the potential difference accelerates electrons and ions in an electric field to generate plasma. In such a plasma source, normally, a high voltage of several kV is applied, and the generated plasma ions have high kinetic energy and large flux that bombard the surface of the sample.

Although high surface hardness can be obtained by conventional plasma nitriding treatment for austenitic stainless steel, the formation of chromium nitride reduces the chromium concentration of the base material and impairs corrosion resistance. In addition, sputtering due to ion collision also occurs, which significantly deteriorates the surface roughness. Therefore, there is a need for a nitriding method that improves the mechanical properties and corrosion resistance of austenitic stainless steel while maintaining the surface finish of the nitrided samples.

In this study, a low power plasma nitriding device with a relatively uniform plasma was used to nitride austenitic stainless steel. The results of our experiments show that the surface hardness of the nitrided samples were more than double the untreated sample while maintaining the roughness (RMS 10nm) of the mirror finished surface.

9:40am **G2-ThM-6 Tribological and Machining Performance of TiSiN(Ag) Coatings Deposited by HiPIMS***, **Diogo Cavaleiro (diogoacavaleiro@gmail.com)**, S. Carvalho, F. Fernandes,* University of Coimbra, Portugal

Titanium alloys are one of the most common materials used in the aerospace industry. The need to machine parts in this industry poses as one of the main problems, since these alloys are well-known to be difficult to machine materials, mainly due to their low Young's modulus and poor heat conductivity. The consequent restriction in the use of high cutting speeds limits the productivity which lead to the development of self-lubricant coatings as a promising way to improve the lifetime and performance of machining tools. The main focus of this work was to investigate the effect of Ag alloying on the high temperature tribological behaviour and machining performance of TiSiN coatings. The coatings exhibit relatively high hardness (32 to 15 GPa). Tribological behaviour was assessed in pin-on-disc tests at room temperature and at 900ºC, sliding against TiAl6V4 balls. Ag addition show a general decrease in the COF values across all the test temperatures. Increasing the Ag content and the temperature seems to show a beneficial effect in reducing the wear and the amount of adhered ball material. This is a promising result to reduce the built-up edge effect on the machining tests. The machining behaviour during turning of the TiAl6V4 alloy, showed that Ag additions had a beneficial effect on the machining performance of the films, especially for the higher cutting speeds. As observed for tribology, a clear reduce in the BUE was also found in machining when Ag was added to the coatings.

10:00am **G2-ThM-7 Crystal Structure, Localized Surface Plasmon Resonance and Sensing Properties of Infrared Transparent Conductive Thin Films***, **Liangge Xu (xuliangge@aliyun.com)**,* Harbin Institute of Technology, China

Tin oxide (SnO_2) has been widely explored for various applications due to its excellent n-type semiconductor properties, low resistance, and high optical transparency in the visible range. However, few studies on the preparation of SnO_2 films using high power pulsed magnetron sputtering have been reported. Oxygen content is a critical parameter in the practice of SnO_2 thin films by high-power pulsed magnetron sputtering. the average free range of Sn atoms is usually much smaller than O atoms. SnO_2 films deposited in a pure Ar atmosphere are likely to be oxygen-deficient and form O vacancies. and such oxygen vacancies will cause lattice distortion, which will affect the mobility of charge carriers in the SnO_2 film. Therefore, oxygen is the main factor affecting the electrical conductivity of SnO_2 films.

In this paper, the crystal structure and infrared transparent conductive properties of SnO_2 films prepared at 600°C were investigated at different oxygen partial pressures. Then, it is described that integrating SnO2 transparent conductive film into a multi-resonant surface enhanced infrared absorption (SEIRA) platform can overcome the shortcomings of poor selectivity and opacity of multi-gas sensing, and can simultaneously sense ultra-low concentrations of greenhouse gases on-chip. And realize the application in the transparent window scene. This strategy takes advantage of the near-field intensity enhancement (over 1500 times) of the multi-resonance SEIRA technology and the infrared light reflectivity that can be modulated by the SnO2 infrared transparent conductive film. Experiments have proved that the MOF-SEIRA platform realizes synchronous on-chip sensing of VOCs, with fast response time, high accuracy, high visible light transparency, and excellent linearity in a wide concentration range. In addition, the excellent scalability to detect more gases was explored. This work opens up exciting possibilities for the realization of integrated, real-time and on-chip multi-gas detection.

10:20am **G2-ThM-8 Research on the Anti-Reflection Performance of Tetrahedral Amorphous Carbon Coatings by Ga Doping***, **HoeKun Kim (ndkim2@naver.com)**, K. Lee, S. Lee,* Korea Aerospace University, Korea (Republic of)

The improvement of radiation resistance in the space solar cells(SC) is still of great importance. The main reason for space SC efficiency degradation under the action of solar wind is a reduction in carrier concentration of the base region, so that the space SC must be protected by coverglass with good protective and optical properties. However, it is very important to reduce SC weight, especially for interplanetary application. To achieve this aim relatively thin protective coating should be applied. For the decade, it has been shown that diamond-like carbon (DLC) coatings are very promising anti-reflection (AR) and protective coatings for solar cell. The advantages of DLC include high chemical stability, radiation stability and high hardness with the possibility of changing their optical properties by varying the deposition conditions. Especially, tetrahedral amorphous carbon (ta-C) coatings with extremely high hardness, smooth surface, excellent wear resistance, and better thermal stability than DLC have been paid much attention to an alternative protective coating materials. Additionally, optical properties of the ta-C coating could be improved by various metals doping. In this study, various contents of Ga were doped in the ta-C coating to improve the mechanical and optical properties of the ta-C coatings. Filtered cathodic vacuum arc (FCVA) and sputter hybrid system was co-deposited to synthesize the metal doped ta-C coating. Microstructure of the Ga doped ta-C coatings showed a columnar "moth-eye" structure that is especially useful for reducing reflections and increasing transmission between materials by the roll of light absorption. Raman spectroscopy analysis showed that all the coatings had high sp3/sp2 fraction over 56%, and the hardness showed high values of 48 GPa. The ta-C coating with high Si content showed improved transmittance than other carbon based coatings, and these results indicate that the metal doped ta-C top-coating could be applied for protective & AR coating of satellite solar cell.

Acknowledgement

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Thursday Lunch, May 26, 2022

Focused Topic Session
Room Town & Country C - Session FTS1-ThL

Focused Topic Session I

12:20pm **FTS1-ThL-1 The Art of Publishing***, Jörg Patscheider (joerg.patscheider@evatecnet.com),* Evatec AG, Switzerland

Good research deserves to be published, to be widely read, and to be recognized by your fellow researchers and community. The current research (and funding) climate makes it even absolutely necessary that you are successful in being able to be published: "Publish or Perish". This then raises the question: How can you achieve that goal?

"Success" essentially depends on three components: 1) the ability to determine the best possible publication strategy for your research findings, 2) the best possible way to write your article, and 3) the most effective interaction with editors. Key to success in this context is your ability to put yourself in the position of **readers**, **reviewers** and **editors**.

Key considerations in journal selection are a realistic assessment of the quality of the research and the audience you intend to reach. The art of manuscript writing is not just applying one "golden tip". It is essentially "telling your story" to your readers in an engaging way, and avoiding common mistakes and deficiencies including poor language. Avoidable mistakes can lead to unnecessary rejection of your manuscript. Finally, it is your open, non-defensive attitude towards the editors and the reviewer comments, that will not only increase the likelihood of getting your manuscript accepted for publication, it is also likely that your published paper has improved thanks to their comments.

By consistently applying these principles you are likely to become a more successful author.

Jörg Patscheider, Editor of the journal Surface and Coatings Technology, will give a presentation about "the Art of Publishing" from an editor's perspective. He will discuss the publication process, will outline the organization of a scientific journal, and will provide the important ingredients to get published.

Elsevier is the world's leading publisher of science and health information and publishes a number of journals that are highly relevant for ICMCTF attendees, such as "*Thin Solid Films*," "*Surface and Coatings Technology*," "Vacuum" and "*Applied Surface Science.*"

This FTS is aimed at new authors, but also at more experienced authors who want to hear how to bypass common publishing hurdles or have a discussion with the publisher and Editors who may be present during the session.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B1-2-ThA

PVD Coatings and Technologies II

Moderator: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), Germany

1:20pm **B1-2-ThA-1 Ultra-Precision Optical Surface Processing by Reactive Atmospheric Plasmas and Low Energy Ion Beams (Virtual Presentation)***,*
Thomas Arnold (thomas.arnold@iom-leipzig.de), Leibniz Institute of Surface Engineering (IOM), Germany*; J. Bauer,* Leibniz Institute of Surface Engineering (IOM), Germany , Germany*; G. Boehm, H. Müller,* Leibniz Institut of Surface Engineering (IOM), Germany **INVITED**

High-performance optical elements such as lenses and mirrors require high accuracy regarding figure error, waviness, and roughness. Furthermore, the complexity of surface shapes increases and an increasing demand for individually and complex shaped optical elements like non-standard aspheres, acylinders, or freeform elements is observed. In particular, the use of free-form elements in optical systems offers new functions in illumination and imaging applications and leads to fewer optical surfaces and thus more compact system designs. Recent advances in manufacturing technology are giving optical system designers more and more freedom. However, once the machinability of complex shaped surfaces is proven, tolerances become more stringent. Especially for scientific devices, e.g. space- and earth-based spectrometers or telescopes, or for laser beam shaping applications, high precision of free-form optical surfaces is required.

Depending on the material to be machined different non-conventional processing methods have been developed that are based either on atmospheric pressure reactive plasma jet etching or ion beam etching to deterministically remove material from the surface or for finishing.

Fluorine plasma jet-based methods are usually applied on materials like optical glasses, silicon, SiC or ULE. Here the specific chemical interactions between reactive radicals formed in the plasma and the surface constituents must be taken into account to achieve predictable results with respect to form accuracy, roughness, and laser damage threshold. The presentation gives an overview over different plasma jet based processing chains for precise freeform optical lens generation and finishing.

Ion beam etching technology has been recently shown to be applicable to aluminium surfaces. Increasing demands on applications of high-performance mirror devices for visible and ultraviolet spectral range call for new processing schemes. Reactively driven ion beam machining using oxygen and nitrogen gases allows direct figure error correction up to 1 µm machining depth while preserving the initial roughness. Machining marks originating from preliminary surface shaping by single-point diamond turning often limit the applicability of mirror surfaces in the short-periodic spectral range. Ion beam planarization with the aid of a polymeric sacrificial layer is shown as a promising process route for surface smoothing, resulting in successfully reduction of the turning mark structures. A combination with ion beam direct surface smoothing to perform a subsequent improvement of the microroughness is presented.

2:00pm **B1-2-ThA-3 A Combinatorial Approach to Developing Sputter-Deposited Heavy-Metal Alloy Films for Inertial Confinement Fusion Applications***,*
Leonardus Bimo Bayu Aji (bayuaji1@llnl.gov)*, A. Engwall,* Lawrence Livermore National Laboratory, USA*; J. Bae,* General Atomics, USA*; A. Baker, S. Shin, S. McCall, J. Moody, S. Kucheyev,* Lawrence Livermore National Laboratory, USA

Magnetically-assisted inertial confinement fusion (ICF) could push current National Ignition Facility (NIF) implosions closer to ignition. The application of a pulsed magnetic field to an ICF target requires the development ofnew hohlraums, which are sphero-cylindrical canswith wall thicknesses of over about 10 µm made from heavymetals. Magnetized ICF targets require heavy metal hohlraums with an electrical resistivity of over 100 µΩ cm at cryogenic temperatures of about 20 K. Such requirements cannot be met by the Au and depleted U hohlraums traditionally used for ICF. Here, we present results of our systematic study by combinatorial direct-current magnetron co-sputtering, aimed at developing a family of binary Au-Ta and Au-Bi films with the microstructure, stress, mechanical properties, and electronic transport favorable for ICF applications.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

2:20pm **B1-2-ThA-4 Machine Learning Based Model for Plasma Prediction in HPPMS Processes***,*
K. Bobzin, C. Kalscheuer, M. Carlet, ***Julia Janowitz (Janowitz@iot.rwth-aachen.de),*** Surface Engineering Institute - RWTH Aachen University, Germany

The coating development using Physical Vapor Deposition (PVD) is time intensive and expensive. The coating processes are usually developed and improved based on the operator's experience. In order to improve the understanding of the processes during coating deposition, methods of plasma diagnostics can be used in the coating process. However, this is also time intensive and requires the installation of special diagnostics. The aim of the current study is to build a model of PVD processes for prediction of the intensity of the plasma species during the coating process. Through this, a contribution to data based coating development can be achieved. Machine learning methods are used to build a model of the PVD process to predict the intensity distribution of the species in the plasma during coating deposition. Based on measured data of different coating processes, the models were trained and tested. Therefore, a broad database was established by measuring the ion intensities of the species in the plasma. The data was collected for chromium and aluminum based hard coatings using an industrial magnetron sputtering unit for coating deposition. The data was measured for hybrid processes of direct current (dcMS) and high power pulsed magnetron sputtering (HPPMS). Here, the gas flow of the reactive gases oxygen and nitrogen was varied. Ion intensities were measured using optical emission spectroscopy (OES) with six substrate side positioned collimators to measure the influence of all cathodes used. The data was measured time resolved during the coating process. The predictions of the intensities show similar trends for the measured intensities of the species within the coating chamber. The predicted intensity range is in good agreement with the measured data. The built models can be used for a more targeted process development. This can contribute to the application oriented adjustment of the coating processes and the coating properties. Within the scope of this study, it was possible to predict the intensities of the plasma species in the coating process for an industrial coating unit using hybrid processes dcMS/HPPMS.

2:40pm **B1-2-ThA-5 Oxidation Stability of Oxynitride CrAlON Hard Coatings***,*
K. Bobzin, C. Kalscheuer, Surface Engineering Institute - RWTH Aachen University, Germany*; G. Grundmeier, T. de los Arcos, S. Schwiderek,* Technical and Macromolecular Chemistry - University of Paderborn, Germany*;* ***Marco Carlet (carlet@iot.rwth-aachen.de),*** Surface Engineering Institute - RWTH Aachen University, Germany

Hard coatings like CrAlN deposited by physical vapor deposition are state of the art for wear and oxidation protection of cutting tools. High power pulsed magnetron sputtering (HPPMS) leads to a higher degree of ionization in plasma compared to direct current magnetron sputtering (dcMS). This enables the deposition of coatings with denser structures and smoother surfaces. Conducting a dcMS/HPPMS hybrid process combines the advantages of HPPMS with the high deposition rates of dcMS. Adding oxygen to CrAlN leads to the oxynitride coating system CrAlON. A reduced friction against steel was found for CrAlN coatings with an oxynitride CrAlON toplayer in previous studies. Since this decreases the thermal loadings on the coated cutting edge, it is beneficial during cutting. Nowadays, the interest of industry in oxynitride hard coatings is rising. However, the oxidation behavior of the quaternary oxynitride CrAlON has hardly been investigated yet. Therefore, the influence of the oxygen content in CrAlON hard coatings on the coating properties and on the oxidation stability was taken into account in the current study. The morphology of the coatings was investigated by scanning electron microscopy (SEM). The chemical composition of the bulk was measured by electron probe micro analysis and of the reaction layer by X-ray photoelectron spectroscopy. The phase composition of the coatings was investigated by X-ray diffraction (XRD) and the elastic-static properties by nanoindentation. Subsequently, the coated cemented carbide samples were heat treated at T = 900 °C and T = 1,000 °C for t = 0.5 h in ambient atmosphere. Finally, the heat treated samples were investigated by SEM and XRD again. A higher oxygen ratio of y = O/(N+O) of the coatings increased the indentation hardness and the resistance against plastic deformation. A moderate oxygen ratio of y = 13.2 % of the oxynitride coating increased the aluminum content of the reaction layer to x = Al/(Al+Cr) = 37.4 % compared to x = 27.3 % for the nitride coating and to x ≤ 30.2 % for the oxynitride coatings with higher oxygen contents of y ≥ 33.3 %. As shown by XRD, this enhanced the oxidation stability of the oxynitride coating with a moderate oxygen content of y = 13.2 % from T = 900 °C to T ≥ 1,000 °C.

Hard Coatings and Vapor Deposition Technologies
Room Pacific D - Session B3-ThA

Deposition Technologies and Applications for Carbon-based Coatings

Moderators: Konrad Fadenberger, Robert Bosch GmbH, Germany, **Frank Papa**, GP Plasma, USA

1:20pm **B3-ThA-1 Smooth and Wear-resistant Carbon Coatings Deposited by S3p™*, Julien Kéraudy (julien.keraudy@oerlikon.com),*** *K. Siegfried, D. Martin, S. Guimond,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Diamond-like carbon (DLC) coatings, namely hydrogenated amorphous carbon (a-C:H) coatings deposited by a PECVD process emerged years ago as the ideal solution for applications where component parts are under high loads or subject to extreme friction, wear and contact pressures with other parts. However, there are nowadays many tribological systems, in which the abrasion resistance of a-C:H coatings is at the limit or even insufficient. With its higher hardness, tetrahedral amorphous carbon (ta-C) would provide more abrasion resistance, a longer lifetime and enable a better performance for the related components. However, the state-of-the-art arc-deposited ta-C coatings (filtered or not) are simply too rough for many applications. Possible solutions to improve surface quality are post-finishing methods such as brushing or polishing, which however have a significant impact on the processing costs.

Recently, high power impulse magnetron sputtering (HiPIMS) was reported to be a suitable method to deposit dense hydrogen-free amorphous carbon (a-C) coatings. In this work, we report on the coating growth and properties of smooth and hard carbon coatings produced by the S3p™ (Scalable Pulsed Power Plasma) method in an industrial deposition plant. S3p™ technology enables scalability of the pulse power density and pulse length in a wide range and expands significantly the choice of the deposition parameters and process stability as compared to conventional HiPIMS technology. Smooth and hard hydrogen-free carbon layers were produced using graphite targets in Ar ambient. The thermal stability of the coatings in air and their tribological behavior in dry and lubricated environments were investigated and compared to the results of standard a-C:H and ta-C coatings. Furthermore, the influence of adding a C_2H_2 precursor in an Ar ambient atmosphere on the film properties and S3p™ reactive process was investigated.

Finally, selected applications where carbon coatings deposited by S3p™ outperformed common DLC coatings will be presented.

1:40pm **B3-ThA-2 New Developments on Hydrogen Free Carbon Coatings for Automotive, Industrial and Tool Applications*, Philipp Immich (pimmich@hauzer.nl),*** *L. Tegelaers, G. Negrea, R. Jacobs, G. Fransen,* IHI Hauzer Techno Coating B.V., Netherlands

Nanostructured and amorphous coatings play an important role in today's automotive, industrial and tool applications. There are huge areas for application for these kinds of coatings – first of all the automotive market, but also traditional applications like cutting or forming tools.

Today the focus is on the growing customer demand for coating properties like higher temperature stability and increased wear resistance in combination with low viscosity lubricants and fuels. In the last years therefore development work shifted to the group of hydrogen free DLC coatings like a-C and ta-C coatings.

To industrialize these coatings different developments routs were carried out in the last years, to ensure an economic and reliable way of deposition. The equipment design and even the selection of most suitable process technology are however also strongly determined by the productivity and the coating properties. In this regard we will demonstrate by using the different Hauzer high energetic pulsed technologies HIPIMS as well as new developed pulsed arc, that coatings can be more tuned and tailormade towards dedicated properties. We will also show that these technologies can be easy upscaled on different machine sizes and deliver here reliable industrial processes with a good ratio of coating cost per coated part and performance.

2:00pm **B3-ThA-3** ***Carbon-Based Coatings for Forming and Protection of Stainless Steel Sheets , Marcus Morstein (marcus.morstein@hightechzentrum.ch),*** Hightech Zentrum Aargau AG, Switzerland **INVITED**

Carbon-based coatings, because of their unique combination of low friction, low wear and chemical inertness, have a long-proven potential as coating materials. Both cutting and forming tools are coated with diamond-like carbon (DLC) coatings, as are components in the automotive sector, both for combustions engines and xEV components. Besides, its appealing dark black color renders DLC useful for decorative purposes.

For different applications different types of DLC coatings have been established, where hydrogen-stabilized DLC, despite its relatively low hardness, is the material of choice for components such as sliding or rolling bearings, or decorative coatings. On the high-performance end, tetrahedral amorphous carbon (*ta*-C) withstands tough conditions and provides superior hardness of up to about 60 GPa.

While the temperature- respectively, oxidation sensitivity limits the application range of carbon-based coatings, new applications keep being added and progress in deposition technology allows for (relatively) low-cost coating even of large-area parts with DLCs.

A recent example for the successful use of amorphous carbon as protective coating for stainless steel are metallic bipolar plates for proton-exchange membrane (PEM) fuel cells. These thin sheets of below 100 µm, often made from 316L (1.4404) steel, need to be protected from corrosion in order to achieve the desired stack lifetimes. For this purpose, chemically passive carbon-based coatings have been used with success.

Recently, precision forming processes have been developed for the economical mass production of these bipolar plates. In production-near tests, DLC coatings combined with an advanced surface treatment process for the steel tools have been shown to perform very well, compared to alternative PVD coatings

DLC coatings are also commonly applied as black color layer for e.g. household appliances. However, because of the imminent exposure to abrasive wear of those surfaces, the supporting properties of the otherwise soft stainless steel substrate need to be enhanced by mechanical of diffusion treatment.

Progress has been made in deposition technology, too. A novel hybrid deposition technique combining a microwave plasma with sputtering allows for the fabrication of high-hardness, non-hydrogenated diamond-like carbon coatings. The properties and morphology of the fabricated DLC films are comparedto those from pulsed-direct current magnetron sputtering (DCMS) or high-power impulse magnetron sputtering (HiPIMS), using techniques such as Raman spectroscopy, nanoindentation, X-ray reflectometry and scanning electron microscopy.

2:40pm **B3-ThA-5 DLC Coatings: Diamond Hardness & Graphite Lubrication Combined to Meet Industrial Application Requirements*, Hamid Bolvardi (h.bolvardi@platit.com),*** PLATIT AG, Switzerland*; J. Kluson, M. Jilek,* PLATIT a.s., Czechia*; R. Zemlicka, A. Lümkemann,* PLATIT AG, Switzerland

Dimond-like Carbon (DLC) coatings have unceasingly absorbed overwhelming interest from industry as well as academic research institutions within last years. High hardness and elastic modulus, chemical inertness, superior tribological properties and good corrosion resistance as well as high biocompatibility and resistance to bacterial colonization make DLC an engrossing coating system. Owed to the unique and broad range of properties, DLC coatings are constantly employed in new applications from cutting and forming tools to components; saw blades, end mills, micro-tools, punches, injection and extrusion molds and dies, automotive, decorative, medical applications are just some raised examples here. DLC coatings consist of a mixture of sp^3 (diamond) and sp^2 (graphite)bonds. The higher sp^3 bond fraction results in a higher density, hardness (at ambient and elevated temperature), thermal stability, oxidation resistance, higher residual stress and lower thermal conductivity. Hence, comprehending the correlation between DLC coating properties and industrial application requirements is a crucial prerequisite to a performance increase in industry. An attempt is made here to cover the range from DLC synthesis to its implementation in industrial applications and the obtained performance results thereof.

3:00pm **B3-ThA-6 Modeling of High Power Impulse Magnetron Sputtering Discharges With Graphite Target**, *H. Eliasson,* Linkoping University, Sweden*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; N. Brenning,* KTH Royal Institute of Technology, Sweden*; H. Hajihoseini,* University of Twente, Netherlands*; M. Zanaska,* Linkoping University, Sweden*; M. Adriaans,* Eindhoven University of Technology, Netherlands*; M. Raadu,* KTH Royal Institute of Technology, Sweden*; **Tiberiu Minea (tiberiu.minea@universite-paris-saclay.fr)**,* Universite Paris-Saclay, France*; J. Gudmundsson,* University of Iceland*; D. Lundin,* Linkoping University, Sweden

By using high power impulse magnetron sputtering (HiPIMS) to deposit tetrahedral amorphous carbon (ta-C) or diamond like carbon (DLC) thin films the aim is to increase the ionization fraction of the carbon atoms sputtered off the target, as it is known that energetic ion bombardment of the substrate is essential to deposit ta-C or DLC films with high sp^3 content. In fact the deposition of DLC films by HiPIMS has been explored extensively for deposition of DLC films. Here, the ionization region model (IRM) is applied to model a high power impulse magnetron sputtering (HiPIMS) discharge in argon with a graphite target. The model gives the temporal variation of the various species and the average electron energy, as well as internal discharge parameters such as the ionization probability, back-attraction probability, and the ionized flux fraction of the sputtered species. It is found that the discharge develops into working gas recycling and most of the discharge current at the cathode target surface is composed of Ar^+ ions, which constitute over 90 % of the discharge current, while the contribution of the C^+ ions is always small (<5 %), even for peak current densities close to 3 A/cm^2. For the target species, the time-averaged ionization probability $< \alpha_{t,pulse} >$ is low, or 13 - 27 %, the ion back-attraction probability during the pulse $\beta_{t,pulse}$ is high (> 92 %), and the ionized flux fraction is about 2 %. It is concluded that in the operation range studied here it is a challenge to ionize carbon atoms, that are sputtered off of a graphite target in a magnetron sputtering discharge, when depositing amorphous carbon films. It is concluded that it is a challenge to provide a high flux of ionized carbon from the HiPIMS process investigated here. This is due to a combination of a high ionization energy, a small ionization cross section and a low residence time of sputtered carbon in the ionization region. This requires fine-tuning of the process, for which the work suggests promising handles.

3:20pm **B3-ThA-7 Time Resolved Determination of Plasma Parameters, Ionization and Macroparticles in an Industrial Scale Ta-C Laser-Arc Coating System**, ***Mathis Klette (klette@physik.uni-kiel.de)**,* Kiel University, Germany*; M. Kopte, W. Fukarek,* VTD Vakuumtechnik Dresden GmbH, Germany*; H. Kersten,* Kiel University, Germany

The early 1990s marked the beginning of carbon laserarcs being used to deposit tetrahedral amorphous carbon (ta-C). Since then, many improvements to the process have been made [1,2]. Ta-C coatings provide the treated object with improved tribological and hardcoating properties, lowering friction and improving wear resistance. These properties make them ideal for automotive powertrain components, drill bits, cutting tools and other applications. While ta-C can be deposited using various techniques, the laserarc technology allows for a strong temporal and spatial control of the deposition process while providing high deposition rate and enabling up-scaling for industrial applications.

However, the up-scaling of deposition rate and process geometry has a profound impact on the physical process. In this contribution, we present measurements of a 100 µs pulsed 1-2 kA up-scaled carbon laserarc using various diagnostics to analyze this effect. A custom-tailored diagnostic setup enables Langmuir probe and Faraday cup measurements for electron and ion energy distribution functions, while spatially and time resolved optical emission spectroscopy yields ion species and densities. Of special interest is the characterization of C2+ ions which have been rarely observed so far.

The energy influx on the substrate is monitored by using calorimetric probes [3], while a force probe [4] and a high-speed camera analyze the neutral contributions and macro particles. This information can be used to estimate the individual contributions to the total energy influx and allows to optimize the particle filter.

Additionally, a second high-speed camera monitors the arc discharge at the cathode itself.

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3:40pm **B3-ThA-8 Fabrication of Hot Magnetron Carbon Targets for a High-Rate Films Deposition by Using Magnetron Sputtering Technique Under the Injection of Neon-Helium Gas Mixture**, ***Bartosz Wicher (Bartosz.Wicher.dokt@pw.edu.pl)**, R. Chodun,* Warsaw University of Technology, Poland*; Ł. Skowroński, M. Trzcinski,* Bydgoszcz University of Science and Technology, Poland*; K. Król,* Institute of Microelectronics and Optoelectronics, Warsaw University of Technology, Poland*; A. Lachowski,* Institute of High Pressure Physics, Polish Academy of Sciences, Poland*; K. Nowakowska-Langier,* National Centre for Nuclear Research (NCBJ), Poland*; K. Zdunek,* Warsaw University of Technology, Poland

A study of temperature of magnetron glassy carbon targets was performed for the case of gas injection magnetron sputtering (GIMS) of diamond–like carbon (DLC) and amorphous C–SiC films, by using unique geometry of the cathode source with increased temperature (HT – hot target). Cathode material was hollowed out for this purpose, from the bottom to the max. depth of 5 mm, which allowed to achieve target temperatures ranging from 790 to 1350 °C during the deposition of h-free carbon films. For the latter, four sockets were drilled in carbon target and then filled up with silicon carbide powder. In the second experiment, temporal evolution and spatial distribution of C–SiC cathode surface temperature were controlled by initiation of discrete pulse plasma discharges with power energies (Ei) changing from 122 to 403 J, which resulted in the temperature range from 730 to 1200 °C. The role of sputtering, sublimation and thermalized electrons in the increase of atoms removal from targets with limited heat conduction was clarified on the basis of an almost 4–fold increase in film deposition rate (up to 74 nm/min), compared to the completely cold process. For both variants of film deposition, GIMS were operated by generating as short as 400–ms and 250–ms plasma pulses at the frequencies of 1 and 2 Hz, respectively, thereby limiting the capability to cool targets operation over the neon–helium gas mixture. By contributing through the heat dissipation effect of HT, GIMS regime proved therefore to be an accurate in terms of increasing optical bandgap within DLC films, from 2.3 to 3.1 eV, which is derived from ordering of sp^2–graphene domains. The chemical and phase state of C–SiC films deposited from HT, revealed in turn, ~ 15 % of Si–C bonds, terminated in the 30 %–rich sp^3 carbon matrix, which puts its positive attribution to enhanced mechanical response, by means of 30.1 GPa hardness result.

Fig. 1. IR-thermogram of the studied targets' surface with its corresponding mean temperature; a, c) cold carbon and C–SiC targets, b, d) hot carbon and C–SiC targets, respectively.

Acknowledgment

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4:00pm **B3-ThA-9 Adjusting the Properties of ta-C by Doping with Metals and Non-metals**, ***Frank Kaulfuss (frank.kaulfuss@iws.fraunhofer.de)**, F. Hofmann, T. Kruelle, V. Weihnacht,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

Tetrahedral amorphous carbon coatings (ta-C) are characterized by their very high wear resistance and low friction under most conditions. However, the requirements in the various application areas differ significantly and there is a need for application-specific adaptations of the coatings in some cases.

Current investigations show that the Laser-Arc process can be used to produce doped carbon coatings via the evaporation of composite graphite cathodes. Cathodes with 5 at% dopant content were used for this purpose. Iron and molybdenum were investigated as metal dopants and boron and silicon as non-metal dopants. The processing conditions were kept identical for all doped cathodes, and an undoped ta-C reference was also prepared. It can be observed that the defect density of the resulting coatings are significantly lower than the reference, especially for boron and molybdenum doping. For example, a 5 µm thick boron-doped coating shows lower roughness than 1 µm ta-C. Significant differences are seen in the morphology of these coatings, with the defect density being significantly reduced. Excitation of boron in the plasma is similar to carbon, and amorphous coatings are formed with comparable hardness to the ta-C reference. In contrast, the very highly excited molybdenum reduces the hardness significantly. In the case of iron and molybdenum doping the coatings are then no longer completely amorphous, as crystalline clusters are formed. Under some lubricated tribological conditions, the ta-C:B and a-C:Mo show clear advantages over ta-C reference coatings with comparable hardnesses.

4:20pm **B3-ThA-10 Improved Tribological Properties of DLC Coatings by Pulsed Laser Hardening***, **Sylvain Le Coultre (sylvain.lecoultre@bfh.ch)**,* Berner Fachhochschule, Switzerland*; J. Matthey, C. Rieille,* HE-Arc, Switzerland*; B. Neuenschwander,* Berner Fachhochschule, Switzerland

For many applications in cutting tools or watchmaking industries, the need to develop new solutions in order to improve the lifetime and performances of the components requires new approaches and solutions. In a joint project between the (Berner Fachhochschule) BFH and the (Haute Ecole ARC) HE-ARC, promising results have been obtained with nanotextured graphite layers produced using a two step hybrid production technology. First, a graphite coating is deposited using magnetron sputtering technology. Second, the coating is treated at with high power pulsed laser at high repetition rate.

As pin-on-disc measurements show, laser nanotexturing not only lowers the friction coefficient of the graphite coating, but also eliminates the run-in phase and significantly reduces wear in dry conditions. In addition, the topography induced by the laser treatment generates an optical effect of iridescence which adds a decorative function.

These first result open possibilities to develop a new type of graphite coating modified by laser pulses for application on 2D or 3D products with sizes in the order of mm2 to a few cm2.

These are first results, further improvement are expected via appropriate texture patterns and doping of the carbon target. Under wet condition, microchannel with heights in the nanometer range between are expected to be beneficial for storing lubricant.

Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B8-2-ThA

HiPIMS, Pulsed Plasmas and Energetic Deposition II
Moderator: Martin Rudolph, Leibniz Inst. of Surface Eng. (IOM), Germany

1:20pm **B8-2-ThA-1 Diagnosing Bipolar HiPIMS Plasmas Using Laser Thomson Scattering (Virtual Presentation)***, **James Bradley (j.w.bradley@liv.ac.uk)**, M. Law,* University of Liverpool, UK **INVITED**

A laser Thomson scattering (LTS) experiment has been developed to measure the temporal and spatial evolution of the electron temperature T_e and density n_e in HiPIMS plasmas. The circular magnetron source furnished with a tungsten target has been operated in both unipolar and asymmetric bipolar pulsing modes. The LTS measurements made in the magnetic trap and on the centre-line are complemented by time-resolved Langmuir probe data as well as plasma optical emission measurements.

In conventional unipolar mode, during the HiPIMS pulse (on-time), the LTS measurements of n_e are seen to peak at 6.9×10^{19} m^{-3}, falling by two orders of magnitude some 300 µs into the afterglow. The value of T_e is seen to rise and fall during the negative pulse on-time as the discharge moves from one dominated by argon to metal vapour. Langmuir probe measurements are in good agreement with the LTS data.

When the source is operated in asymmetric bipolar pulsing mode, the pulse on-time results on the discharge centreline are similar to the unipolar case, however during the positive pulse periods we see significant electron heating in which T_e can rise to values comparable to the those measured in on-time. The on-set of the rises in T_e are significantly delayed relative to the start of the positive pulse, with the delay time decreasing with the magnitude of the positive voltage. The local electron density on the centreline n_e is seen to decay significantly more quickly in the afterglow than for the corresponding unipolar pulsing case. Optical emission intensities show the presence of W(I) lines well into the afterglow. The phenomenon of plasma electron heating in the positive pulse is believed to be due to the existence of a transient reverse discharge, in which the vessel walls become an effective cathode.

LTS measurements in the magnetic trap however, show no such anomalous electron heating in the positive pulse period. These observations are discussed in terms of electron cross-field transport from wall to different regions of the plasma.

2:00pm **B8-2-ThA-3 Time Resolved IEDF, EEDF and Q/M of a HiPIMS Discharge for Different Pulse Conditions, Pressures, and Probe Orientations***, Z. Jeckell,* University of Illinois at Urbana Champaign, USA*; D. Barlaz,* University of Illinois Urbana Champaign, USA*; W. Huber, T. Houlahan, I. Haehnlein,* Starfire Industries, USA*; **Brian Jurczyk (bjurczyk@starfireindustries.com)**,* Starfire Industries LLC, USA*; D. Ruzic,* University of Illinois Urbana Champaign, USA

Zachary Jeckell[1], David Barlaz[1], David Kapelyan[1], Wolfgang Huber[2], Thomas Houlahan[2] Ian Haehnlein[2], Brian Jurczyk[2], David N[1]. Ruzic[1]

[1] Department of Nuclear, Radiological, and Plasma Engineering, University of Illinois at Urbana-Champaign, Urbana, IL

[2] Starfire Industries, Champaign, IL 61820

This work investigates the temporal evolution of both the electron energies as well as the ion energies during a variety of high-power impulse magnetron sputtering conditions utilizing the positive voltage reversal, known as the Positive Kick, including pulse conditions and pressures ultimately to better understand the physics needed to tailor future depositions. This work was carried out using the HIDEN PSM probe which allows for time resolved ion energy and q/m measurements enabling differentiation between working gas ions and target ions, as well as identification of higher ionization states.Sputtered neutral distribution, low-energy sputtered ions, ionized process gases and accelerated ions from the near-magnetron magnetic trap influence the deposited film based off the modified Thornton-Anders diagram for HiPIMS plasmas. The differentiation between charged species showcases the time evolution of the $M_{magentictrap}^+/Ar_{magentictrap}^+$ and the $M_{bulkplasma}^+/Ar_{bulkplasma}^+$ ratios which are useful for optimizing pulse conditions to efficiently transport metal ions to the substrate and to aid in the selection of process recipes with suitable ratios. The IEDF measurements are paired with time resolved EEDF data acquired from a custom sampling circuit capable of discretizing increments of the duration of one HiPIMS pulse with the Positive Kick. Performed by sweeping voltages, an array for I-V-T are formed that allows for the EEDF to be calculated for all times t. Commentary on plasma potential evolution and expansion is given in relation to the measured IEDF at different on-axis and off-axis locations via linear motion feedthrough.

2:20pm **B8-2-ThA-4 Metal-Ion Synchronized Reactive HiPIMS of AlScN for Piezoelectric Applications***, **Jyotish Patidar (jyotish.patidar@empa.ch)**, K. Thorwarth, T. Amelal, S. Zhuk, S. Siol,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The growing demand for highly integrated piezoelectric micro-electro-mechanical systems motivates the development of novel piezoelectric thin films. AlN in wurtzite structure is a promising candidate for a number of piezoelectric applications due to its high temperature stability and linear frequency response. Isovalent alloying of AlN with Sc is a successful strategy to enhance its piezoelectric coefficient. The heterostructural nature of the alloy system, however leads to low miscibility and a high degree of structural frustration for high Sc concentrations. Consequently, to achieve highly textured AlScN films using conventional magnetron sputtering high deposition temperatures or epitaxial stabilization are needed.

In this work, we present the development of a metal-ion synchronized reactive high-power impulse magnetron sputtering (MIS-HiPIMS) approach for AlScN that could lead to advantages over the current state-of-the-art. HiPIMS is rarely employed for the synthesis of electro-ceramics or semiconductors, since the highly energetic synthesis environment often results in a large number of bulk defects. However, MIS-HiPIMS enables the control of the incident ions kinetic energy while simultaneously reducing the ion-implantation and consequently the bulk-defect concentration in the film. [1]

The MIS-HiPIMS approach presented here is based on reactive HiPIMS sputtering of Al combined with direct current (DC) sputtering of Sc in Ar/N atmosphere. The ion-energy-distribution at the substrate is recorded using a time and energy-sensitive quadrupole mass spectrometer. Subsequently, the negative substrate bias is synchronized on the Al-rich part of the pulse. The HiPIMS pulse pattern, as well as the timing of the synchronization is varied to tailor the microstructure and texture of the AlN thin films. In addition, the non-equilibrium solubility of Sc in AlN is investigated as a function of the incident ion kinetic energy. The materials are fully characterized with respect to their phase constitution, structure and composition using state-of-the-art techniques including high-resolution X-ray diffraction, Rutherford backscattering spectroscopy, elastic recoil detection analysis as well as hard X-ray photoelectron spectroscopy. For selected samples, the transverse piezoelectric coefficients $e_{31,f}$ are compared.

A successful demonstration of a MIS-HiPIMS process for highly textured AlScN could enable the deposition on temperature sensitive substrates, such as polymer foils, but also the functionalization of surfaces with high aspect ratios and would enable a variety of exciting new applications.

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2:40pm **B8-2-ThA-5 Selective Metal Ion Irradiation Using Bipolar HiPIMS: A New Route to Tailor Film Nanostructure and the Resulting Mechanical Properties***, **Ivan Fernandez (IVAN.FERNANDEZ@NANO4ENERGY.EU)**,* NANO4ENERGY SLNE, Spain

Metal ion irradiation combining HiPIMS discharges and pulsed bias synchronization has been demonstrated in the recent years to be a powerful method to achieve an accurate control on film nanostructure and phase control for the deposition of Transition Metal (TM) Nitrides [1]. It allows the deposition of films with optimum mechanical properties as well as reduced accumulated stress compared to the films deposited with gas-ion bombardment in Direct Current Magnetron Sputtering (DCMS). The selective attraction of metal ions at the substrate position optimizes the metal ion energy and momentum required during film growth.

In this presentation we extend this concept of selective metal ion irradiation by combining Bipolar HiPIMS with conventional DC magnetron sputtering operation and DC biasing. The concept of Bipolar HiPIMS was introduced some years ago by different groups and consist in applying a positive pulse with controlled pulse width and amplitude voltage after the conventional HiPIMS negative pulse [2]. This positive pulse allows the accurate acceleration of the positive metal ions towards the substrate, thus, promoting improved film properties such as reduced stress, higher film densification, improved mechanical properties - such as hardness or wear resistance- or better coverage of 3D complex parts. Moreover, it has been recently demonstrated that using bipolar HiPIMS with a substrate at ground potential (comparable to negative biased) results in a similar ion current profile as in conventional HiPIMS with a synchronized pulsed bias with the same delay and timing as the positive pulse [3].

This new coating process has been used for the deposition of hard, dense Transition Metal (TM) Nitrides commonly used in the metalworking industry. This manuscript studies the influence of Nb and Cr ion irradiation on the mechanical properties of TiAlN films, as they show a high large difference in mass. The description of the process as well as the resulting properties (microstructure, hardness, stress and texture) will be presented in this paper.

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3:00pm **B8-2-ThA-6 Ion Beam Sputter Deposition of Gallium Oxide Thin Films***, D. Kalanov, Y. Unutulmazsoy, **André Anders (andre.anders@iom-leipzig.de)**, C. Bundesmann,* Leibniz Institute of Surface Engineering (IOM), Germany

Ion beam sputter deposition (IBSD) is an energetic deposition technique, which provides unique opportunities to control the sputtering and growth processes and to study the correlations between them. The process provides intrinsic heating to the growing film by energetic particles, which can be used to tune various thin film properties, such as microstructure (incl. film density) and crystalline phase.

Gallium oxide is a material of high technological interest because of its unique properties, such as a wide bandgap and a high breakdown field strength. It enables the use of the material, for instance, in ultra-high-power electronics. To fully exploit the potential of gallium oxide thin films, high crystalline quality is needed. The IBSD is a process proven to be capable of growing films of such quality. In contrast to magnetron sputtering, IBSD does not have the unwanted highly energetic (several 100 eV) negative ion component, which causes defects.

The present report covers a systematic study of ion beam sputter deposition of gallium oxide thin films by investigating the fundamental correlations between (i) process parameters (sputtering geometry, ion species, ion energy, oxygen partial pressure), (ii) properties of secondary, sputtered and scattered particle species, and (iii) thin films.

The properties of secondary particles are studied by measuring energy distributions of ions, sputtered and scattered from the target. It is shown that changes in the sputtering geometry and energy of primary ions give control over the high-energy tail of the distribution. The composition of the film-forming flux is compared between processes with primary Ar^+ and O_2^+ beams, by varying the background oxygen pressure. Thin films are deposited for the same process configurations, and characterized regarding growth rate, density, roughness, crystallinity, and chemical composition. Presented systematic analysis may help to improve the process for depositing films of high crystalline quality at different substrate conditions (elevated temperatures, various substrate materials).

3:20pm **B8-2-ThA-7 The Promise of Data-Driven Methods for Diagnostics and Control of Plasma Interactions with Surfaces***, **Ali Mesbah (mesbah@berkeley.edu)**,* University of California Berkeley, USA **INVITED**

Data-driven methods can create unprecedented opportunities for real-time diagnostics and control of low-temperature plasmas (LTPs), which are increasingly used for treatment of heat and pressure sensitive (bio)materials in surface etching/functionalization, environmental, and biomedical applications. Some of the main challenges in modeling and control of LTP applications arise from their inherent complexity and variability. Firstly, the dynamics of LTPs are highly nonlinear and spatio-temporally distributed, which are hard to model due to their mechanistic complexity. Secondly, the LTP effects on complex surfaces are generally poorly understood. And thirdly, LTPs exhibit run-to-run variations and time-varying dynamics, whereby LTP treatments may be carried out under similar conditions, but yield different results. In this talk, we will demonstrate the usefulness of learning-based diagnostic and predictive control approaches for LTP treatment of complex surfaces. We will discuss how advanced machine learning and optimization methods can be leveraged to learn the complex plasma and surface dynamics in real-time, toward safe and high-performance LTP treatment of complex surfaces.

4:00pm **B8-2-ThA-9 Colored Random Noise of Cathodic Arcs: What Is It? Should We Care?***, **Andre Anders (andre.anders@iom-leipzig.de)**, K. Oh, D. Kalanov,* Leibniz Institute of Surface Engineering (IOM), Germany

Cathodic arcs are well established as the plasma source of a high-rate deposition technology, delivering hard and corrosion-resistant coatings, which are often based on nitrides but also on oxides, carbides, and multilayers and nanocomposites thereof.Through clever configurations of magnetic field, gas supply locations and choice of substrate location, the effects of arc plasma fluctuations or "noise" are mitigated and/or utilized. The physical origin of such noise lies in non-stationary cathode spot processes.Cathode spots, the small locations of current concentration and plasma generation, are known to be greatly affected by the chemical and microstructural properties of the cathode surface.Therefore, it should be expected that not all noise is equal but dependent on the cathode material and surface conditions.One can quantify the type of noise through their power spectral density and define a colored random noise (CRN) index, which lies between 1 (white noise) and 2 (brown noise), and it can even be greater than 2 when events are coupled due to strong feedbacks.In this contribution we summarize the findings, primarily based on FFT (fast Fourier transform) analysis of streak images of cathode spot plasma in vacuum, in argon, nitrogen, and oxygen.We show that the CRN index of cathode spots in vacuum is slightly larger than 2, indicating a general random walk behavior but with feedback, which is likely due to the influence of spot plasma on the ignition of the next spots.Argon as a process gas has no discernable influence on the CRN index, whereas nitrogen and especially oxygen reduce the index.This seems to be related to "easier" ignition of spots in the presence of a compound layer.A compound layer makes it easier for spots to ignite relatively far away from the original spot, but also to repeatedly ignite at about the same position.In the latter case, the spot may appear macroscopically stationary.The spot processes are orders of magnitude faster than the deposition duration and therefore, from a deposition point of view, the fluctuating plasma flow is generally considered with its “noise-averaged” properties.

Functional Thin Films and Surfaces
Room Town & Country C - Session C3-2-ThA

Thin Films for Energy Storage and Conversion II

Moderators: Clio Azina, RWTH Aachen University, Germany, **Tushar Shimpi**, Colorado State University, USA

3:00pm **C3-2-ThA-6 Atomic/Molecular Layer Deposition of Layer-Engineered Inorganic-Organic Thin Films for Emerging Energy Technologies***, **Maarit Karppinen (maarit.karppinen@aalto.fi),*** Aalto University, Finland **INVITED**

The ALD/MLD (atomic/molecular layer deposition) technique allows the combination of inorganic and organic layers into any arbitrary frequency pattern. We have exploited ALD/MLD for (i) textile-integrated thermoelectrics, (ii) photo-switchable high-coercivity magnets, (iii) artificial SEI layers for Li-ion batteries, and (iv) active components for Li-organic microbattery. For thermoelectrics, we pioneeredZnO:organic superlattice structures, in which monomolecular organic layers alternate with nm-scale thermoelectric ZnO layers, to drastically suppress the thermal conductivity without comprising the electrical conductivity; when deposited on textiles, these films coat the textile fibers conformally so that the entire textile becomes an active part of the thermoelectric device.[1,2]To realize flexible and photo-switchable magnets, we have combined nanoscale layers of the rarest trivalent iron oxide polymorph ε-Fe_2O_3 exhibiting giant coercive field values with azobenzene layers undergoing reversible trans-cis-trans isomerization reactions upon successive UV and visible light irradiations.[3,4] To mimic the composition of the naturally forming SEI layers in Li-ion batteries, we developed a three-precursor ALD/MLD process, Li-HMDS+ethylene glycol+CO_2, for the targeted lithium ethyl carbonate films.[5] Finally, for the Li-organic microbattery application, our new active-material arsenal comprises various intriguing intercalated-type layered Li-organic materialsthat experience minimal changes in crystal structure upon the electrochemical Li^+-ion intercalation.[6]

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3:40pm **C3-2-ThA-8 Transparent Niobium-Doped Titanium Dioxide Thin Films With High Seebeck Coefficient for Thermoelectric Applications***,* ***Joana Ribeiro (joanaribeiro93@hotmail.com)****, F. Correia, F. Rodrigues,* University of Minho, Portugal*; S. Reparaz, A. Goni,* Institut de Ciència de Materials de Barcelona-CSIC, Spain*; C. Tavares,* University of Minho, Portugal

The design of a transparent thermoelectric material is a promising technology for touch–screen displays and solar cell applications, rendering a more sustainable powering of the device. In order to enhance the thermoelectric performance, the material must have a high Seebeck coefficient, high electrical conductivity but low thermal conductivity [1]. Modifying the atomic structures of TiO_2 by deliberately introducing defects can enhance its properties to a great extent, while a cationic doping of TiO_2 has been documented to improve its electrical conductivity [2]. This work reports the production and characterization of optically transparent Nb-doped TiO_2 thin films with enhanced thermoelectric properties deposited on glass and Si by reactive d.c. magnetron sputtering in high vacuum. The purpose of these films is to harvest thermal energy from the environment and convert it to electrical energy. Several process parameters, such as reactive and working gas flow rate, deposition temperature, target current density and post-annealing conditions, directly affect the morphology and crystalline structure of the thin films. The optimization of these parameters results in thin films with thickness of 120-300 nm, maximum average optical transmittance in the visible range of 73 %, n-type electrical resistivity of 0.05 W·cm, thermal conductivity below 1.7 $W \cdot m^{-1} \cdot K^{-1}$ and a maximum absolute Seebeck coefficient of 223 $mV \cdot K^{-1}$. The resulting maximum thermoelectric power factor is 60 $mW \cdot K^{-2} \cdot m^{-1}$ and the maximum thermoelectric figure of merit is 0.014. Hence, modifying the optical, electric, thermal and thermoelectric properties of the thin films enables their suitability for applications as transparent electrodes in photovoltaic systems and touch displays, amongst other devices.

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4:00pm **C3-2-ThA-9 X-Ray Absorption Spectroscopy Study of Local Order in Transparent Thermoelectric Thin Films of Doped ZnO***, F. Correia, J. Ribeiro, F. Barbosa, M. Andritschky,* Centre of Physics of the Universities of Minho and Porto (CF-UM-UP), University of Minho, Portugal*; A. Kuzmin, I. Pudza,* Institute of Solid State Physics, University of Latvia*; A. Kalinko,* Deutsches Elektronen-Synchrotron − A Research Centre of the Helmholtz Association, Gibraltar*; E. Welter,* Deutsches Elektronen-Synchrotron − A Research Centre of the Helmholtz Association, Germany*; A. Mendes,* LEPABE, Faculty of Engineering of the University of Porto, Portugal*; A. LaGrow,* International Iberian Nanotechnology Laboratory (INL), Portugal*; O. Bondarchukat,* International Iberian Nanotechnology Laboratory (INL) , Portugal*; N. Sadrine, R. Correia, T. Monteiro,* i3N, Departamento de Física, Universidade de Aveiro, Portugal*;* ***Carlos J. Tavares (ctavares@fisica.uminho.pt)****,* Centre of Physics of the Universities of Minho and Porto (CF-UM-UP), University of Minho, Portugal

Ga, Bi- and Sb-doped ZnO thin films with thermoelectric properties were produced by magnetron sputtering. All undoped and doped films crystallise in a ZnO phase with the hexagonal wurtzite crystal structure. The local structure of the thin films was investigated by temperature-dependent X-ray absorption spectroscopy at the Zn, Ga, Sb K-edges, as well as at the Bi L_3-edge. The experiments were done in transmission and fluorescence modes at the P65 Applied XAFS beamline of the PETRA III storage ring. It was found that doping with Ga^{3+} and Bi^{3+} ions in the ZnO wurtzite structure produces a distinct effect on the thin film microstructure. The substitution of Zn^{2+} ions by smaller Ga^{3+} ions introduces a static disorder to the thin film structure, which is evidenced by an increase in the mean-square relative displacements (MSRD) σ^2(Zn-O) and σ^2 (Zn-Zn). At the same time, large Bi^{3+} ions do not substitute zinc ions, but are likely located in the disordered environment at the ZnO grain boundaries. This conclusion was directly supported by energy-dispersive X-ray spectroscopy combined with TEM and STEM observations as well as by resonant and non-resonant m-Raman experiments at room temperature, where the ZnO and ZnO:Bi spectra are similar, suggesting a lack of structural disorder in the wurtzite cell. Similar experiments were performed for ZnO:Sb_x (x=2-14 at%) thin films to determine the coordination environment of Sb impurities and their influence on the local structure and lattice dynamics of the ZnO matrix.XANES and EXAFS suggest that doping of ZnO by Sb impacts the crystallinity of the films leading to amorphization at high Sb concentrations. As a result, a significant increase of MSRD due to static disorder for higher Sb concentration has been found in the first and second coordination shells of zinc, when compared to crystalline w-ZnO.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E2-2-ThA
Mechanical Properties and Adhesion II

Moderators: Carsten Gachot, Vienna University of Technology, Austria, **Alice Lassnig**, Austrian Academy of Sciences, Austria

2:00pm **E2-2-ThA-3 Reliability Assessment of Thin Films and Multilayers in Electronic Packages (Virtual Presentation)**, ***Golta Khatibi (golta.khatibi@tuwien.ac.at)***, TU Wien, Austria **INVITED**

The rapid technological advancements and market demands in microelectronic sector requires highly accelerated and practice relevant reliability assessment methods. The devices are composed of a variety of dissimilar materials with different chemical, physical and mechanical properties and length scales. The structural integrity and reliability of the systems is related to the resistance of the constituent materials and their interfaces to alternating thermomechanical loads. Design and fabrication of functional and reliable electronics requires a knowledge of fatigue and delamination behavior of the structures and understanding of the related micro-mechanisms of damage. Recently isothermal accelerated mechanical fatigue testing has been proposed as an alternative to standard thermal cycling procedures for rapid evaluation of microelectronic devices. Dedicated dynamic testing set-ups are designed to simulate the dominating loading conditions in the devices while replacing the thermo-mechanically induced strains with equivalent mechanical strains. As a result, physically meaningful lifetime curves can be obtained and the vulnerable sites of the structures can be detected in a short time.

This talk includes a brief introduction on the application of the proposed method for evaluation of various type of multilayers followed by a case study on the effect processing parameters and environment on cyclic delamination behavior of thin films. The experiments were performed by using a dynamic four-point bending setup working in a broad frequency range, equipped with an environmental chamber. Static and dynamic tests were conducted on suitable sandwich type samples prepared from semiconductor tests structures consisting of Si/SiN/TiW/Cu/Polyimid films.Crack length as well as crack opening displacement was measured intermittently at different loading amplitudes. A fracture mechanics based method was applied to derive the relationship between the delamination growth rate (da/dN) and the cyclic energy release rate (ΔG). It was found that the cyclic interfacial delamination occurred at considerably lower values of energy release rate comparing to the critical adhesion energy of the same interface under quasi static loads. Furthermore, experimentally determined crack propagation rates were explained with a power law depending on the accumulated plastic strain per loading cycle by using FEM simulations.

2:40pm **E2-2-ThA-5 A Measurement Structure for *in-situ* Electrical Monitoring of Fatigue Delamination**, ***Sebastian Moser (sebastian.moser@k-ai.at)***, *D. Tscharnuter, M. Nelhiebel, M. Reisinger, J. Zechner,* KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Austria*; M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Semiconductor devices are comprised of multilayer material structures that undergo cyclic thermal loading with associated thermal stresses during service. A typical fatigue mode of such devices is delamination, which may result in impairment of the system's capability of passivating from environmental influences. At a certain stage, delamination might result in a loss of functionality in terms of mechanical, electrical, or thermal aspects sometimes leading to catastrophic failure of the device, for example, by means of bursting or local melting. It is apparent that in such a case, an accurate root cause analysis or localization of the failure is very challenging or even not possible. For this reason, the development of experimental methods capable of characterizing early-stage delamination is desired. This work introduces a specifically designed measurement structure that has been integrated into an actively heated microelectronic test chip and allows monitoring delamination *in situ* by means of electrical resistance measurements. The chip consists of a silicon substrate, a thin stack of functional layers, and a comparatively thick copper metallization (20 µm). Application of heat pulses causes significant thermo-mechanically induced strain in the copper due to its mismatch in coefficient of thermal expansion (CTE_{Cu} = 17 ppm/K) with respect to silicon (CTE_{Si} = 2.56 ppm/K). Under well-chosen experimental conditions, this drives cyclical delamination of the copper metallization from a functional barrier layer. The delamination monitoring structure presented is characterized by a layout with distinct geometric features that, when passed by the gradually advancing delamination crack front, result in characteristic responses in the electrically monitored signal. This allows a straightforward interpretation of the measurement data without having to rely on any separate calibration experiments. The functionality of the delamination monitoring structure has been proven, firstly, by a simple model that predicts the experimentally obtained curves very well and, secondly, by focused ion beam investigations at different delamination stages. A representative experimental study is presented quantifying the effect of different heating amplitudes, Δ*T*, and test environments, forming gas versus air, on the delamination rate.

3:00pm **E2-2-ThA-6 Modeling of Residual Stress Evolution in Thin Films: Effects of Growth Kinetics, Microstructural Evolution and Energetic Particle**, *E. Chason, T. Su, Z. Rao, S. Berman,* Brown University, USA*;* ***Diederik Depla (diederik.depla@ugent.be)***, Ghent University, Belgium

Residual stresses in thin films have significant effects on their performance and reliability.To control it, it is useful to understand how the stress is related to the processing conditions used for the film deposition.We describe an analytical model that we have developed that relates the stress to the physical processes occurring film deposition.The model explains the dependence on the growth conditions, microstructural evolution and energy of incoming particles.We have implemented this model in a least-squares fitting program to determine the kinetic parameters controlling stress.Modeling results are shown for numerous published results in the literature for different materials (Ag, Cu, Ni, Fe, Cr, Ti, Co, Mo) using evaporation and sputter deposition. The model is being developed into a web-based application that others can use to analyze their stress measurements and predict the stress under different processing conditions.

3:20pm **E2-2-ThA-7 Mechanical, Structural, Morphological and Biological Evaluation of Multilayer Coatings of HA-Ag/TiO2/TiN/Ti on Ti6Al4V Obtained by Magnetron Sputtering for Implant Application**, ***Julián Andrés Lenis Rodas (julian.lenis@udea.edu.co)***, *F. Bolívar Osorio, E. Contreras Romero,* University of Antioquia, Colombia*; A. Hurtado Macías,* CIMAV, Mexico*; P. Rico, J. Gómez Ribelles,* Valencia Polytechnic University, Spain*; M. Pacha Olivenza, M. Gonzales Martin ,* University of Extremadura, Spain

In the present study, multi-layer coatings of hydroxyapatite (HA) - Ag/TiO2-TiN/Ti were obtained on the Ti-6Al-4V alloy, by means of the magnetron sputtering technique. During its evaluation, the techniques of energy dispersive X-ray spectroscopy, X-ray diffraction (DRX), field emission scanning electron microscopy, transmission electron microscopy, micro scratch test, nano indentation, were used. The biological response was evaluated by means of I) cytotoxicity and adhesion of mouse mesenchymal stem cells, and II) adhesion and bacterial viability of Staphylococcus aureus strain. HA coatings with a Ca/P from 1.67 to 1.76 were obtained, whose structure was verified by means of DRX and Micro-Raman spectroscopy. Coatings evidenced a multi-layer architecture. A decrease in hardness and an increase in adhesion to the substrate of the coatings were obtained by incorporating the intermediate layers. The biological evaluation carried out indicated an antibacterial effect and potentially non-toxic character in the coatings.

Topical Symposia
Room Pacific E - Session TS4-ThA
Big Data, Machine Learning, Artificial Intelligence and High-Throughput Methods

Moderator: Igor Abrikosov, Linköping University, IFM, Sweden

1:20pm **TS4-ThA-1 New 3D and 2D Metal Borides from Materials Synthesis Guided by High-Throughput Simulations**, ***Johanna Rosen (johanna.rosen@liu.se)***, Linkoping University, Sweden **INVITED**

Exploratory theoretical predictions in uncharted structural and compositional space are integral to materials discoveries. A more recent addition to the family of laminated metal borides, so called MAB phases, is new types of chemically ordered quaternary borides, *i*-MAB ($M'_{4/3}M''_{2/3}AlB_2$) and *o*-MAB ($M'_4M''SiB_2$), in which the M-atoms are in-plane and out-of-plane chemically ordered, respectively. Both types of phases have been identified in high-throughput simulations followed by experimental synthesis, and they can be chemically exfoliated into 2D sheets, and selectively prepared in multilayer form, as delaminated single-layer sheets in colloidal suspension, or as additive-free filtered films. For example, Ti_4MoSiB_2 *o*-MAB can be used to derive 2D TiO_xCl_y of high yield.

$(Mo_{2/3}Y_{1/3})_2AlB_2$ and $(Mo_{2/3}Sc_{1/3})_2AlB_2$ *i*-MAB can be used for realization of so called boridene in the form of single-layer 2D sheets with ordered metal vacancies, $Mo_{4/3}B_{2-x}T_z$(T_z = -F, -O, -OH). The present talk will summarize the results to date of our predictive theoretical approach that have led to 2D materials synthesis from 3D quaternary metal borides, the mechanisms behind the realization of these 3D/2D materials, and evaluation of selected properties.

2:00pm **TS4-ThA-3 Machine Learned Moment Tensor Potentials for Hard Coatings***, **Ferenc Tasnádi (ferenc.tasnadi@liu.se)**, F. Bock, M. Odén, I. Abrikosov,* IFM Linköping University, Sweden

Refractory nitrides (TiN, Hf N , NbN etc.) nitride alloys ($Ti_{1-x}Al_xN$, etc.) or high-entropy alloys, such as TiZrHfTa are materials with high industrial relevance for hard coatings o f cutting tools [1] even for superconducting and plasmonic-based devices. M ajor objectives for their performance are the high-temperature the rmodynamic, dynamic and elastic properties. A recently developed combination of quantum mechanical calculations with machine-learning interatomic potentials (MLIP) [2], is utilized to calculate high temperature properties with high accuracy. On-the-fly training of moment tensor potentials allows us to perform the calculations with more than two orders less computational effort than using state-of-the-art ab initio molecular dynamics simulations. The calculated elastic constants are used to simulate surface acoustic waves and Brillouin light scattering (BLS) spectra. The results are compared with experiments. Furthermore, we investigate high-temperature bcc phase of titanium and predict very weak temperature dependence of its elastic moduli [3], called Elinvar effect, similar to the behavior observed for the so-called GUM metals . The effect in bcc-Ti is intrinsic and therefore unique.

[1] See, for example, F. Tasnádi et al., Phys. Rev. B 85, 144112 (2012); F. Tasnádi et al., Appl. Phys. Lett. 97, 231902 (2010); D. Holec et al. Phys. Rev. B 90, 184106 (2014); F. Tasnádi et al., Mater. Des. 114, 484 (2017); H. Huang et al., Adv. Mater. 5, 1701678 (2017). [2] I. S. Novikov et al., Mach. Learn.: Sci. Technol. 2 025002 (2021). [3] A. Shapeev et al., New. J. Phys. 22, 113005 (2020).

2:20pm **TS4-ThA-4 High-Throughput Rapid Experimental Alloy Development (HT-READ)***, **Kenneth Vecchio (kvecchio@eng.ucsd.edu)**,* UC San Diego, Dept. of NanoEngineering, USA **INVITED**

The development of high-throughput materials development strategies in the thin-film field have moved forward more quickly than bulk material high throughput strategies, primarily due to the need in bulk materials to account for microstructure effects on properties.In addition, the current bulk materials discovery cycle has several inefficiencies from initial computational predictions through fabrication and analyses. Much of the information and knowledge generated existed in isolated data silos making integrated approaches more challenging. This was the motivation for the 2011 Materials Genome Initiative, which sparked advances in many high-throughput computational techniques related to materials development. However, computational techniques ultimately rely on experimental validation.However, bulk materials are generally evaluated in a singular fashion, relying largely on human-driven compositional choices and analysis of the volumes of generated data, thus also slowing validation of computational models. Thus, increasing the rate of materials experimentation is fundamental to improving materials research, and requires parallelizing, automating, and miniaturizing key steps in experimental materials research, including computation, synthesis, processing, characterization, and data analysis.To overcome these limitations, we developed a High-Throughput Rapid Experimental Alloy Development (HT-READ) platform and methodology that comprises an integrated, closed-loop material screening process inspired by broad chemical assays and modern innovations in automation. Our method is a general framework unifying computational identification of ideal candidate materials, fabrication of sample libraries in a configuration amenable to multiple tests and processing routes, and analysis of the candidate materials in a high-throughput fashion. An artificial intelligence agent is used to find connections between compositions and material properties.New experimental data can be leveraged in subsequent iterations or new design objectives. The sample libraries are assigned unique identifiers and stored to make data and samples persistent, thus preventing institutional knowledge loss.This integrated approach paves the way for compositionally accurate and microstructurally informed bulk materials development in a highly-accelerated manner.

3:00pm **TS4-ThA-6 Finding Thermally Robust Superhard Materials with Machine Learning***, **Jakoah Brgoch (jbrgoch@Central.UH.EDU)**,* University of Houston, USA **INVITED**

Superhard materials with a Vickers hardness >40 GPa are essential in applications ranging from manufacturing to energy production. Finding new superhard materials has traditionally been guided by empirical design rules derived from classically known materials. However, the ability to quantitatively predict hardness remains a significant barrier in materials design. To address this challenge, we constructed an ensemble machine-learning model capable of directly predicting load-dependent hardness. The predictive power of our model was validated on eight unmeasured metal disilicides and a hold-out set of superhard materials. The trained model was then used to screen compounds in Pearson's Crystal Data (PCD) set and combined with our recently developed machine-learning phase diagram tool to suggest previously unreported superhard compounds. Finally, industrial materials often experience tremendous heat during application; thus, we are building a method for predicting hardness at elevated temperatures.

3:40pm **TS4-ThA-8 Rational Composition Optimization: Coupling Mixture Designs, Combinatorial Methods and Machine Learning***, **Elise GAREL (elise.garel@grenoble-inp.fr)**, H. VAN LANDEGHEM, J. PAROUTY, M. VERDIER, S. COINDEAU, R. MARTIN, F. ROBAUT, R. BOICHOT,* SIMAP, Grenoble-INP, CNRS, France

Multinary optimization has been at the heart of recent developments, either for High Entropy Alloy or for metallic glasses, amongst others. It represents a challenge that requires overcoming the usual method of "one sample at a time". Combinatorial approaches have been applied many times to N-element systems, and this study proposes to couple it to mixture design, in order to guarantee a uniform and systematic screening of the composition space, by elaborating and characterizing magnetron sputtered films with controlled gradients of composition.

This method was applied to the refractory high entropy alloy system Nb-Ti-Zr-Cr-Mo, on as-grown and annealed samples, as well as on a nitride pseudo-ternary, Ti-Al-Nb-N. The mechanical properties were measured by nanoindentation for both, while crystallinity was assessed using XRD — and EBSD in the case of the HEA. Conductivity measurements were performed on the nitride system. This high-throughput screening resulted in an experimental database covering the properties of 460 HEA compositions and 140 nitride compositions that was used to train Machine Learning models linking compositions, structures and properties.

In order to explore the possibilities offered by Machine Learning, several databases and different models were used. Raw experimental data and statistically processed database allowed delineating the performances of Machine Learning. Models with increasing complexity were tested: multilinear regression with interactions, Support Vector Machine, Random Forest and Neural Network, with previously adjust hyper-parameters. Random Forest and Neural Network show a very good accuracy, either on regression or on classification, for property prediction over the entire composition space. Multilinear regression, performing adequately as well, allows a rapid understanding of the weights of each component on the properties, as well as their interactions, which can be used to rationally examine the largely discussed hypothesis of the cocktail effect. For instance, the elastic modulus of as-grown RHEA system is well fitted by multilinear regression and coefficients show that it almost only results from a linear combination of the effect of pure elements. Hardness presents on the contrary much more complexity, with a high positive effect of binaries and principally a negative effect of ternaries and quaternaries, leading to higher values at the edges of the composition space than at its center.

Based on Machine Learning predictions, isovalue hulls and Pareto-optimal domains can be determined inside the composition space and used to identify the composition sets that show the best property compromises.

4:00pm **TS4-ThA-9 Transfer Learning of Thermodynamic and Elstic Properties of Hard-Coating Alloys**,
***Henrik Levämäki (henrik.levamaki@liu.se)**, F. Tasnadi, D. Sangiovanni,* Linköping University, IFM, Sweden*; L. Johnson,* Sandvik Coromant, Sweden*; R. Armiento, I. Abrikosov,* Linköping University, IFM, Sweden

Accelerated design of novel hard-coating materials requires state-of-the-art computational tools, which include data-driven techniques, building databases, and training machine learning (ML) models against the databases.

We present a development of a heavily automated high-throughput workflow to build a database of industrially relevant hard coating alloys, such as disordered binary and ternary nitrides [1]. We use Vienna Ab initio Simulation package (VASP) as the density functional theory calculator and the high-throughput toolkit (httk) to automate the calculation workflow. One of the key quantities in the computational study of hardness is the elastic tensor, and the challenge we face is that calculating the elastic tensor for disordered supercells is resource intensive, which makes building a large database of disordered hard-coating alloys slow. We therefore explore ways for ML techniques to support and complement our databases. We find that the crystal graph convolutional neural network (CGCNN) model [2] trained on ordered compounds from the Materials Project [3] has sufficient prediction accuracy for the disordered nitrides. This suggests that the existing public or commercial databases provide important data for predicting mechanical properties of qualitatively different types of material systems, which in our case are disordered hard-coating alloys that are not included in the original dataset.

[1] Can be found in arXiv under the title: "Predicting properties of hard-coating alloys using ab-initio and machine learning methods"

[2] Xie, Tian and Grossman, Jeffrey C., "Crystal Graph Convolutional Neural Networks for an Accurate and Interpretable Prediction of Material Properties", Physical Review Letters 120, 145301 (2018), doi: 10.1103/PhysRevLett.120.145301

[3] Jain, Anubhav and Ong, Shyue Ping and Hautier, Geoffroy and Chen, Wei and Richards, William Davidson and Dacek, Stephen and Cholia, Shreyas and Gunter, Dan and Skinner, David and Ceder, Gerbrand and Persson, Kristin A., "Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation", APL Materials 011002 (2013), doi: 10.1063/1.4812323

4:20pm **TS4-ThA-10 Data-Driven Search for Thermal Insulators Guided by Anharmonicity: From First Principles to Machine Learning**,
***Florian Knoop (florian.knoop@liu.se)**,* Linköping University, IFM, Sweden*; M. Langer,* Technical University of Berlin, Germany*; C. Carbogno,* NOMAD Laboratory at the Fritz Haber Institute of the Max Planck Society, Germany*; M. Rupp,* University of Konstanz, Germany*; M. Scheffler,* NOMAD Laboratory at the Fritz Haber Institute of the Max Planck Society, Germany

We present a systematic first-principles search for thermal insulators in materials space which covers hundreds of compounds, five lattice types and seven space groups, including simple rocksalt and zinc blende structures, up to complex perovskites. Using the high-throughput framework FHI-vibes [1] and a recently developed measure for the strength of anharmonicity [2], we identify 120 candidate materials with potential for low thermal conductivity at room temperature. We investigate the 60 most promising candidates with the ab initio Green Kubo method (aiGK) [3], enabling data-driven extraction of design principles for bulk materials with low thermal conductivity. The aiGK method provides an accurate framework to obtain thermal conductivities for materials, in particular strongly anharmonic ones such as thermal barrier coating ceramics like zirconia, since all anharmonic effects responsible for low thermal conductivity are included.We subsequently demonstrate how the first principles calculations can be complemented with the help of machine learning potentials to remove the computational bottleneck. For this task, we use message passing neural networks, a class of models that can accommodate implicit long-range interactions as well as directional information [4]. We present a systematic account of their performance for calculating the thermal conductivity of solid semiconductors and insulators and discuss implications for high-thoughput heat transport simulations and the discovery of novel thermal insulators.

[1] F. Knoop et al., J. Open Source Softw. 5, 2671 (2020)
[2] F. Knoop et al., Phys. Rev. Mater. 4, 083809 (2020)
[3] C. Carbogno, R. Ramprasad, and M. Scheffler, Phys. Rev. 118, 175901 (2017)
[4] K.T. Schütt et al., J. Chem. Phys. 148 241722 (2018)

4:40pm **TS4-ThA-11 2D Phase Mapping of Hf-Al-Si Refractory Complex Concentrated Alloy Produced using High-Throughput Magnetron Sputtering**,
***Sophia Cooper (sophiacooper@my.unt.edu)**, M. Dockins, M. Young, A. Voevodin,* University of North Texas, USA*; A. Ghoshal, V. Blair,* U.S. Army Futures Command, USA*; S. Aouadi,* University of North Texas, USA

Coatings for Use at High Temperatures
Room Golden State Ballroom - Session AP-ThP

Coatings for Use at High Temperatures (Symposium A) Poster Session

AP-ThP-2 Corrosion Induced Diffusion Pathways in Pvd $Al_{1-X}Cr_XN$ Coatings Investigated by Atom Probe Tomography*, Oliver Ernst Hudak (oliver.hudak@tuwien.ac.at),* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; V. Dalbauer,* Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; L. Shang, M. Arndt, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balzers, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany*; P. Felfer,* Department of Materials Science, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Corrosion processes are common phenomena in fields of engineering and there is nearly never an instance, where a material is totally inert to its environment. Therefore, corrosion and corrosion-resistance are essential variables that play a pivotal role in the development of protective coatings. Ingenuity of next generation PVD coatings has given rise to a wide range of material concepts set out to withstand all kinds of corrosive attacks (e.g. NaCl, HCl, SO_3 and O_2). While their performance is mostly assessed on descriptors such as mass change, impairment of mechanical properties, or variance in electrochemical surface potential, little work has been dedicated to understand corrosion driven diffusion pathways, specifically on an atomic scale.

Particularly the production of metallic-spits or "droplets" during PVD processes poses a significant drawback in light of the coating's corrosion resistive capabilities. In many regards, embedded macro particles, logged within the deposited coating matrix, serve a beneficial cause, when it comes to improved mechanical properties, such as hardness, fatigue resistance and fracture toughness. However, in light of corrosion behavior, macro-particles provide formations of voids and rugged grain boundaries that allow for fast-track diffusion of corrosive media to the substrate-coating interface.

This study showcases a systematic approach on highlighting preferred diffusion pathways of corrosive NaCl-rich media in PVD thin films. Intended as a model system, arc-evaporated- as well as sputtered AlCrN coatings were deposited on low alloy steel substrates and electrochemically investigated using a three-electrode set-up. With a Ag/AgCl reference electrode (RE), a Pt-counter electrode (CE) and the coated-steel sample as working electrode (WE), linear potentiodynamic polarization experiments were conducted in a 1M NaCl solution.

Next to SEM investigations, high resolution analytical techniques such as APT and TEM were consulted to help identify preferential diffusion paths, and highlight differences in the corrosion behavior of arced- and sputtered coatings.

Keywords: Corrosion Resistance; PVD coatings; Diffusion Pathways; Atom Probe Tomography

AP-ThP-8 Microstructure and Oxidation Behaviour of $MoSi_2$ Thin Films Grown by DCMS and HiPIMS*, Ahmed Bahr (ahmed.bahr@tuwien.ac.at),* *S. Richter, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Refractory transition-metal disilicides ($TMSi_2$) can be considered as promising candidates to be applied as protective coatings in high temperature applications as they have attractive combined properties such as high melting point, acceptable mechanical properties and especially high oxidation resistance in air.$MoSi_2$ exhibits an attractive mix of good mechanical properties and outstanding high temperature oxidation resistance due to the formation of a protective silicon-based oxide.

In our study, we employed direct current magnetron sputtering (DCMS) and High-power magnetron sputtering (HiPIMS) techniques to synthesize $MoSi_2$ thin films. We investigated the influence of the deposition parameters on the phase formation and the mechanical properties of the films. Moreover, the oxidation kinetics were analyzed at different temperature regimes up to 1500 °C. The coatings were characterized in terms of chemical composition, phase constitution, and mechanical properties using high-resolution characterization techniques.

Hard Coatings and Vapor Deposition Technologies
Room Golden State Ballroom - Session BP-ThP

Hard Coatings and Vapor Deposition Technologies (Symposium B) Poster Session

BP-ThP-1 Influence of Various Tool Steels and Cemented Carbide on Growth of PVD Hard Coatings*, K. Bobzin, C. Kalscheuer,* ***Marco Carlet (carlet@iot.rwth-aachen.de)****, D. Hoffmann,* RWTH Aachen University, Germany

In order to pursue lightweight construction, components are manufactured with high-strength materials. On the tool side, this leads to increased tool wear, e.g. on the punches of fine blanking tools. For this reason, high-strength and tough tool steels produced by powder metallurgy (PM) are increasingly used. Furthermore, PVD hard coatings are applied to increase tool life. In this study, the influence of the alloying elements as well as the manufacturing method of tool steels, whether powder or melt metallurgical (MM), is investigated on the coating growth and morphology. For this purpose, PVD hard coatings, particular the nanocomposite TiAlCrSiN, was deposited on various tool steels using an industrial coating unit. In the current study, PM and MM high speed steels (HSS) as well as MM cold work, hot work and plastic mold steel substrates were taken into account. In addition, cemented carbides were used as reference substrate material. Moreover, the influence of a TiAlN interlayer on the growth of the nanocomposite TiAlCrSiN toplayer is analyzed. The deposition of a CrAlN coating was investigated as reference to the nanocomposite. Confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) were used to analyze the coating topography. The coating morphology was examined by SEM and the crystal structure by X-ray diffraction (XRD). The indentation hardness and modulus were determined by nanoindentation. It can be seen that the coating growth of TiAlCrSiN is strongly dependent on the manufacturing process of the tool steel. On the PM HSS, the TiAlCrSiN coating exhibits a significantly rougher topography compared to all investigated melt metallurgical steel substrates and cemented carbide. Furthermore, it is evident in cross-sectional micrographs that the otherwise fine-crystalline, homogeneous morphology of the TiAlCrSiN coatings from the PM HSS substrate material exhibit cone-shaped grains. In addition to the nanocomposite TiAlCrSiN, the coating system CrAlN was deposited. Compared to the TiAlCrSiN nanocomposite, the CrAlN coating reveals no significant differences depending on the substrate materials. The findings can support the selection of suitable combinations of substrate materials and PVD hard coatings to improve tool life. In this work, it was shown that the coating growth of the PVD nanocomposite TiAlCrSiN is significantly dependent on the substrate material, in contrast to the ternary coating system CrAlN. Furthermore, the substrate influence of the coating growth cannot be suppressed by the prior application of an interlayer.

BP-ThP-2 Influence of Deposition Parameters on Chemistry, Structure and Mechanical Properties of Vanadium Carbide Thin Films*, Barbara Schmid (barbara.schmid@tuwien.ac.at),* *N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria*; E. Halwax,* TU Wien, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Cubic transition metal carbides generally exhibit high melting points as well as high hardness, which makes them especially interesting for the application as protective coatings. Vanadium carbide (VC) is not an exception to this trend with a melting point above 3000 K and up to 40 GPa in hardness.

However, the non-reactive synthesis of VC_x via DC magnetron sputtering is rare. The variation of deposition parameters such as working gas pressure (here, Ar), gas flow and sputtering power density applied to a stoichiometric VC compound target can result in drastically different thin film materials.

Varying these deposition parameters allowed to synthesise VC_x thin films with different chemistry, microstructure, as well as indentation hardness and modulus.

These material characteristics were investigated using electron probe microanalysis, X-ray diffraction, scanning and transmission electron microscopy, and nanoindentation. The obtained variation in lattice parameter and indentation modulus have been compared to density functional theory data for stoichiometric and non-stoichiometric VC_x. This allowed us to draw a clear picture of the deposition–structure–property relations for VC_x.

BP-ThP-3 Influence of High-Power Pulse Magnetron Sputtering Tantalum Nitride Film Characteristics and Protection Behavior*, **Yung-Chi Chang (vicky5062823@gmail.com)**, S. Hsu, C. Tu, D. Hong, F. Wu,* National United University, Taiwan

Nowadays quality requirements, such as higher hardness, wear resistance, sufficient toughness, adhesion strength and so ow, are focused for transition metal nitride, TMN, hard coating field. The selection of coating among various possible materials and related manufacturing processes is quite a challenge and requires careful consideration on the functions in the development systems. Among TMNs, with high hardness excellent tribological behavior, thermal and electrical performance, TaN. Has been chosen as a good protective layer for working components in versatile applications. In this study, and the enysfalline and metastable amorphous phase of tantalum nitride are fabricated using radio frequency, r.f., reactive magnetron sputtering technique. A multilayer film formed by alternating stacking of the above mentioned crystalline/amorphous layers is deposited through input power and gas inlet control. The adhesion of the tantalum nitride film is studied and compared with controlling parameters of interlayers with changes thickness, r.f. power, and high intensity power plasma. Compared with r.f., the single-layer film has a compact structure due to the higher energy of plasma power. The higher energy deposition, improves the crystallinity, and lead to a larger grain size. At the same time, the surface roughness of the film is reduced, and the hardness and Young's modulus are improved. The multilayer film is manufactured through the crystalline/amorphous stacking, the hardness and Young's modulus and wear resistance are superior than those of the single-layer film.

Keywords : HiPIMS, sputtering, TaN, multilayer

BP-ThP-5 Rotating Spokes in Reactive HiPIMS Process Measured by Spatially Resolved OES*, **Marta Šlapanská (slapanska@physics.muni.cz)**, M. Kroker, J. Hnilica, P. Klein, P. Vašina,* Masaryk University, Czechia

The rotating plasma patterns, also known as spokes, spontaneously appearing in E × B magnetised plasma discharges, such as Hall thruster and high power impulse magnetron sputtering (HiPIMS) discharge, have been thoroughly investigated mainly in the non-reactive atmosphere under many different experimental parameters. Among other things, it has been discovered that the presence of spokes enhanced the transport of sputtered species from the target to the substrate, leading to a much more energy-efficient HiPIMS process. Due to the reactive processes being widely used in industry, there is an effort to find out more information about spokes in reactive atmospheres and their effect on the deposition process and the transport of sputtered species at those conditions. The use of spatially resolved optical emission spectroscopy in a single-shot mode is one of the possibilities for a deeper understanding of the spokes.

In this contribution, the non-invasive spatial-resolved OES of the spoke was conducted in reactive HiPIMS discharge. The HiPIMS pulses were 100 µs long with a repetition rate of 5 Hz. The 3-inch titanium target, argon as working gas, and nitrogen as reactive gas were utilised. The constant total pressure was set to 1.0 Pa. Different reactive gas flows were applied to measure the properties of spokes in both metallic and poisoned modes.

The fast photodiode and the Langmuir probe were used to capture and determine the position of the passing spoke. The signals from the photodiode and the Langmuir probe were synchronised with the spectrometer and an ICCD camera. The ICCD camera possesses a dual-image-feature mode, which allows capturing two consecutive images with only a 1.5 µs delay between them. It enabled to determine the spoke propagation velocity. The single-shot measurements ensured that one waveform and one double image were acquired simultaneously from a single HiPIMS pulse for each spectrum. The spatial-resolved emissions of argon, nitrogen, and titanium atoms and ions spectral lines were investigated within the spoke passing by the probes.

BP-ThP-6 Sputtered Amorphous Carbon Interlayers for Homogeneous Lithium Plating and Stripping in Solid-State Batteries*, T. Amelal, M. Futscher, J. Patidar, A. Müller, A. Aribia, Y. Romanyuk, **Sebastian Siol (sebastian.siol@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Recently, it was shown that the introduction of an amorphous Ag-C composite into solid-state batteries can lead to increased long-term stability.[1] However, the reason why the interlayer shows this advantageous behavior is not well understood.

We deposit thin carbon interlayers between current collector and solid electrolyte by two physical vapor (PVD) deposition techniques. By using direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) the kinetic energy of the incident ions can be tuned over a wide range. This allows us to independently vary the density, conductivity, and microstructure of the carbon interlayers.

We show the influence of different material properties of the carbon interlayer on lithium plating and stripping using copper as the current collector and lithium phosphorus oxynitride (LiPON) as the solid electrolyte. We find that the amorphous carbon interlayer reduces the overpotential for lithium plating and increases the critical current density for lithium plating and stripping up to 8 mA/cm^2. We further show that the initial lithium loss due to interphase formation and the critical current density strongly depends on the morphology and the electrical conductivity of the carbon interlayers. Finally, we investigate the role of Ag by introducing different amounts of Ag into the amorphous carbon interlayers. Our results shed light on the key factors that enable homogeneous lithium plating and thus the use of lithium metal in solid-state batteries.

[1] Y.-G. Lee et al. High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes. Nat. Energy 5, 299–308 (2020)

BP-ThP-9 e-Poster Presentation: Effect of Precursor Interactions on Film Growth Rate and Properties in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Alloy Films*, **Kinsey Canova (kcanova2@illinois.edu)**, S. Shrivastav, C. Romnes, D. Yun, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign, USA

HfB_2 coatings impart excellent surface hardness and low sliding friction, but the service life in air at moderate temperatures is reduced by the formation of boron oxide, which is lost to evaporation.Addition of Al is one possible route towards oxidation resistance, if the surface can form an Al_2O_3 surface layer that impedes further oxygen transport. (We report oxidation studies elsewhere in this conference.)

We use low temperature chemical vapor deposition (CVD) to grow $Hf_{1-x}Al_xB_2$ alloy films from two precursors, $Hf(BH_4)_4$ and Me_3N-AlH_3 (TMAA).We show that TMAA flux accelerates the reaction rate of the $Hf(BH_4)_4$, but that a flux of the TMAA byproducts, including Me_3N, inhibits the growth rate of HfB_2. In the former case, we will present evidence towards which chemistry is involved in the growth acceleration, whether it be precursor-precursor interaction or another precursor-byproduct interaction; high byproduct pressures for these experiments can be sustained within a deep trench or under slow pumping.These results imply a feedback loop in the film growth rate, where the accelerated deposition due to TMAA is opposed by a progressive increase in the Me_3N inhibitor pressure, which may dampen the acceleration effect.

We uncouple these interactions using two distinct CVD chambers.The conventional CVD chamber is rapidly pumped, and the alloy growth rate is found to be a steady-state function of the precursor fluxes and substrate temperature (surface reaction rates).The other CVD chamber is unpumped (static), which allows the use of very high precursor pressures to amplify the effects of precursors and byproducts. We interpret these results in the context of accelerating and inhibiting interactions that we have measured in other chemistries, and we then show how the growth rate affects film stability, density, and composition.

BP-ThP-13 Biocompatibility Evaluation of nc-TiC/a-C:H Nanocomposite Diamond-like Carbon Coatings: Effect of Carbon Content*, B. Lou,* Chang Gung University, Taiwan*; Y. Hsiao, L. Chang,* Ming Chi University of Technology, Taiwan*; M. Ger,* National Defense University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

The nc-TiC/a-C:H nanocomposite diamond like carbon (DLC) coating has been studied due to its good mechanical properties, corrosion resistance and biocompatibility. In this work, four nc-TiC/a-C:H coatings with different carbon contents were grown by a superimposed high power impulse magnetron sputtering (HiPIMS) and medium frequency (MF) coating system utilizing a plasma emission monitoring feedback control. The target poisoning ratio ranging from 80% to 95% and the gas flow rate of acetylene were controlled by a plasma emission monitoring (PEM) system. The chemical composition, crystallinity, hardness, wear resistance, adhesion and surface roughness values of coatings were investigated. Furthermore, the in vitro biocompatibility of MG 63 human osteoblast-like cells and the migration ability of HaCaT keratinocyte cell on selected DLC coatings were also evaluated, respectively. The sensitization test of DLC coatings was conducted by the in vivo animal test using the subcutaneous implantation of DLC coated 316L SS disks on the back of SD rats. The pathological changes and inflammation of tissues after the subcutaneous implantation were explored.

In this work, the hardness and elastic modulus of four DLC coatings fabricated from 80% to 95% target poisoning ratios were higher than 14 GPa and 120 GPa, respectively. The wear rates of four DLC coatings were all lower than $10^{-6}mm^3/N/m$ with coefficient of friction values less than 0.25. Meanwhile, very good cell adhesion, free of toxicity, good cell migration (**Fig.1**) and proliferation ability, and free of sensitization in animal body were achieved for two nc-TiC/a-C:H DLC films (TiC80 and TiC90) deposited at 80% and 90% target poisoning ratios, which can be further deposited on the 3-dimensional surfaces of surgical instrument, such as surgical blades and xysters.

Keywords: nc-TiC/a-C:H nanocomposite diamond like carbon coating, HiPIMS, in vitro MG63 cell test, in vitro cell migration test, subcutaneous implantation in vivo animal test

BP-ThP-14 TiN/TaN Superlattice Films Improved by Interfacial Dopings*, Zecui Gao (zecui.gao@tuwien.ac.at), N. Koutná, J. Buchinger, T. Wojcika, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The superlattice architecture, characterized by different nanolayered materials that are alternatively and coherently stacked, allows to stabilize metastable phases and optimize typically antagonistic properties of ceramic coating materials, such as hardness and fracture toughness. As rocksalt-structured TiN and $Ta_{0.5}N$ (featuring metal vacancies) have significant elastic differences, they promise a pronounced superlattice (SL) effect. TiN/Ta_xN films were thus deposited with a ~5 nm bilayer period by DC reactive magnetron sputtering. As expected, the SLs show a higher hardness (32.9 GPa) than monolithic TaxN (30.1 GPa) and TiN (28.5 GPa), with an intermediate indentation modulus of 425.0 GPa ($Ta_{0.5}N$ 379.9 GPa and TiN 529.7 GPa).

As established by previous studies, the improved hardness is partly due to the hindrance of dislocation movement across interfaces. Thus, we implement atomic quantities of Si/C/B in between all layers of TiN/Ta_xN SLs to further enhance the interlayer boundaries. All of the doped superlattice coatings show exceptional hardness properties and improved epitaxial growth on MgO compared to the doping-free SL. Especially, the TiN/Si/Ta_xN film produced the highest hardness of ~40.7 GPa, and the TiN/B/Ta_xN film produced the highest fracture toughness of ~4.11 MPaÖm. Overall, they possess promising hardness and Fracture toughness compared favorably to their monolithic building blocks and TiN/Ta_xN SL.

BP-ThP-16 Fifty Shades of TiN: How Deposition Conditions Influence the Growth Morphology and Thereby Hardness and Especially Fracture Toughness*, Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at), R. Hahn, B. Hajas, A. Kirnbauer,* TU Wien, Austria

About fifty different TiN coatings were prepared by reactive and non-reactive magnetron sputtering, as well as by reactive cathodic arc evaporation. In addition to vary between these three individual deposition techniques, we also individually varied the substrate temperature, partial pressures, substrates (e.g., Si(100), MgO(100)(110)(111), sapphire), substrate-to-target distance, as well as bias potential. The fracture toughness of these individually prepared TiN coatings was evaluated from micromechanical bending tests (inside a FEGSEM) of free-standing cantilevers. The individual deposition techniques and conditions result in either pronounced columnar or rather dense growth morphologies, with open or compact column and grain boundary regions, or epitaxially grown single-crystals. Due to these variations in growth morphology, the hardness (obtained by nanoindentation) of TiN varied between 15.9 and 33.9 GPa and their fracture toughness between 0.6 and 2.9 MPa√m.

We will have a closer look on the overall correlation between growth morphologies, preferred orientation, residual stresses, and mechanical properties. But also, how a subsequent vacuum annealing treatment (to mimic application at elevated temperatures) influences these characteristics.

Functional Thin Films and Surfaces
Room Golden State Ballroom - Session CP

Functional Thin Films and Surfaces (Symposium C) Poster Session

CP-1 Cross-Linking Processes in Antimicrobial UV-Sol-Gel and Thermal-Sol-Gel Systems Initiated by Atmospheric Pressure Plasma Characterized by FTIR*, Simon Chwatal (Simon.Chwatal@joanneum.at), J. Lackner, W. Waldhauser,* Joanneum Research Forschungsgesellschaft GmbH, Austria*; M. Stummer,* INOCON Technologie GmbH, Austria*; H. Steiner,* Aerospace & Advanced Composites GmbH, Austria*; A. Coclite,* Graz University of Technology, Austria

The versatile adjustability of the sol-gel chemistry is a great technological advantage over other coating systems, especially due to the usability of organic and inorganic precursors as well as the variation of the reaction control and drying, curing, compaction. Alongside the many promising possibilities for producing functional coatings using the sol-gel process, challenges remain by (1) the temporal stability of sol-gel systems, (2) sensitivity of sol-gel systems to slight fluctuations in the ambient conditions during production but also processing, (3) crack formation caused by shrinkage during drying and curing, and (4) widely required curing temperatures of up to 180 °C for several minutes to hours. The last two challenges can be solved by very quick plasma curing instead of using UV or heat-based, long-lasting processes separately. Plasma combines both high and short UV and temperature impacts on the sol-gel system. INOCON Technologie GmbH has developed and patented a hot gas atmospheric pressure plasma source for exactly this purpose. In the current work, special attention is given to the atomic bonding and cross-linking processes initiated by the hot plasma and the occurring interactions. In order to better show the influence of both main plasma characteristics, a thermal and a rather new UV curing sol-gel system developed by Aerospace & Advanced Composites GmbH are used once. FTIR analyses are a base for evaluating and providing information about the intensity and position of the peaks. They also show the progress of the curing process. The hardness of the layer is an indicator of the degree of cross-linking. The harder the system, the better the atomic structures are linked together.

In addition to these studies, the antimicrobial effect of the sol-gel systems is also tested. The biocidal effect should be further enhanced by applying zinc or copper particles on the cured sol-gel layer within a subsequent process step. Alongside the experiment and optical spectroscopy, gas flow simulations, with the software ANSYS, are used to include information on the processes within the plasma, initiated by gases, flow rates, plasma jet power, and ad-mixed precursors. Therefore, INOCON Technologie GmbH carried out a CFD-simulation model. The temperature plays an important role here, must be estimated beforehand, since critical temperatures lead to discoloration or even decomposition in the layer, and thus renders the result unusable. For this purpose, a transient thermal simulation is conducted to take the influence of the curing speed into account.

CP-2 Crystallization and Vitrification Kinetics by Design: The Role of Chemical Bonding*, Matthias Wuttig (wuttig@physik.rwth-aachen.de),* RWTH Aachen University, Germany

Controlling a state of material between its crystalline and glassy phase has fostered many real-world applications. Nevertheless, design rules for crystallization and vitrification kinetics still lack predictive power. Here, we identify stoichiometry trends for these processes in phase change materials, i.e. along the GeTe-GeSe, GeTe-SnTe, and GeTe-Sb2Te3 pseudo-binary lines employing a pump-probe laser setup and calorimetry. We discover a clear stoichiometry dependence of crystallization speed along a line connecting regions characterized by two fundamental bonding types, metallic and covalent bonding. Increasing covalency slows down crystallization by six orders of magnitude and promotes vitrification. The stoichiometry dependence is correlated with material properties, such as the optical properties of the crystalline phase and a bond indicator, the number of electrons shared between adjacent atoms. A quantum-chemical map explains these trends and provides a blueprint to design crystallization kinetics.

C. Persch, M. Müller, A. Yadav, N. Honne, J. Pries, S. Wei, P. Fantini, E. Varesi, F. Pelizzer, M. Wuttig, *The Role of Chemical Bonding to Design Crystallization and Vitrification Kinetics*

Nature Communications 12, 4978 (2021)

CP-3 Theoretical and Experimental Study to Simplify AgZn Alloy IR Refractive Index Calculation*, **Daniel Lin (ding@labforinvention.com)**, T. Ding, G. Ding,* Labforinvention, USA

Abstract

The optical refractive index and electrical resistivities of Silver Zinc alloy were studied experimentally by a co-sputtering method. The theories on alloys refractive index currently are too complex, dependent on too many factors, so it can still only be a semi-practical prediction. In this study, a new method was developed to simplify the calculation of silver alloy IR refractive index by comparing silver refractive index at the same deposition condition, specifically: (1) theoretically, the refractive index ratio n_{alloy}/n_{Ag} between silver and its alloy at IR region is assumed to cancel out most factors so that it only depends on free electron density n_e and the film resistivity ρ; further, only dependent on alloy concentration and resistivity ρ; (2) Experimentally, this assumption was approximately met by: the deposition conditions between sputtering Ag and its alloy were identical except the alloy with an additional tiny Zinc co-sputtering power; (3) The experimental results agreed well with this simplified calculation. Further discussions are compared with the literature on how the zinc electrons contribute to the optical and electrical properties in low Zn concentration AgZn alloy (<10%) found in this study.

CP-6 Sputter Deposited Advanced Anode Functional Layers for Solid Oxide Fuel Cells*, K. Steier, **Justyna Kulczyk-Malecka (j.kulczyk-malecka@mmu.ac.uk)**, P. Kelly,* Manchester Metropolitan University, UK

Solid oxide fuel cells (SOFCs) convert the chemical energy stored in fuels, such as hydrogen and gaseous hydrocarbons, directly into electrical power and thermal energy through electrochemical reactions. State-of-the-art SOFC anodes consist of a cermet of nickel and yttria-stabilised zirconia (YSZ) to increase the reactive sites at the anode/electrolyte interface.

Nanostructured Ni-YSZ functional layers has been produced using reactive pulsed DC magnetron co-sputtering of metallic targets of zirconium-yttrium and nickel. Whilst recent studies show the deposited Ni-YSZ films from a single Ni-YSZ compound target, we present the co-deposition from decoupled Ni and Zr-Y targets, which allows the deposition of Ni-YSZ with a graded composition of nickel within the structure.

The sputtering process was performed in an oblique angle deposition mode, to deliberately generate columnar nanostructures, in mixed argon/oxygen atmospheres. Deposition parameters, such as deposition angle and deposition pressure have been studied to determine their influence on the structural and morphological properties in the context of their application as SOFC anode functional layers. The obtained films were characterised by SEM, EDS and XRD. We found that sputter deposited YSZ films led to a higher porosity within the YSZ scaffolds with increasing deposition angle and pressure. During the co-sputtering of Ni and Zr-Y, Ni was oxidised to NiO and then subsequently transformed to catalytically active nickel during the reduction in hydrogen, facilitating the required porosity for the gas transport.

Furthermore, two designs of Ni-YSZ anodes were deposited onto a spark plasma sintered YSZ electrolyte-supported button cell coupled with a commercial LSM cathode. The first design used a constant Ni composition and the second comprised of a graded Ni content within the structure. Finally, both configurations have been tested in fuel cell mode under hydrogen and air flows for anode and cathode, respectively, to characterise the performance of the functional layers.

CP-8 Unraveling the Bisignate and Broadband Chiroptical Response from All-Dielectric Distorted L-Shape Metamaterials*, **Ufuk Kilic (UFUKKILIC@UNL.EDU)**, M. Hilfiker, S. Wimer, A. Ruder, E. Schubert, C. Aryropoulos, M. Schubert,* University of Nebraska-Lincoln, USA

With a broad variety of nanofabrication technologies available, structures with different morphologies and subwavelength scale dimensions were proposed as strong candidates to manipulate light from visible to infrared spectral regions. [1,2]. Of particular interest, all-dielectric three-dimensional nanostructures have been frequently reported as prominent contestants which can tackle both the lossy nature of metals and the insufficient broadband chiral response of their planar thin film configurations [1,3].

Here, we propose a simplistic chiral nano-platform: all-dielectric distorted L-shape metamaterials so-called *nanoboomerangs*. Thanks to glancing angle deposition, a recently emerging bottom-up fabrication technique with precise sample stage manipulation ability, we successfully assembled achiral silicon columnar structures and fabricated three-dimensional, highly porous, superlattice-type, distorted L-shape metamaterial. Using Mueller matrix generalized spectroscopic ellipsometry technique, we performed the chiroptical characterization of the *nanoboomerangs which* exhibit extremely broadband, large, tunable, and bisignate chiroptical response. We believe that this new metamaterial platform can be a strong candidate for a myriad of next generation photonic integrated technological applications including but not limited to chiral sensors, drug-delivery systems , and chiral-topological insulators.

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CP-10 Microstructured Electrodeposition of Copper Templated by Photo-Induced Monolayer Patterning*, **David Sconyers (david.j.sconyers2.civ@army.mil)**, C. Longo, J. Maurer,* US Army DEVCOM AC, Benet Laboratories, USA

Materials presenting surfaces with antiviral or antibacterial properties represent a growing area of interest due to the threat of future global pandemics. Surface morphologies that are hostile to the adhesion and replication of microorganisms are a commonly employed defense system found in nature. Defined textures and patterns of this kind can be emulated artificially via directed electrodepositon of transition metals from aqueous solutions onto electrically conductive substrates relevant to human use. Here, we carry out the electrochemical generation of such surfaces, driven by the selective coating of self-assembled monolayers (SAMs) of alkylphosphonates and alkoxysilanes onto mild steel. Photo-induced monolayer patterning (PIMP) subsequently generates defect sites in these engineered coatings, characterized through Fourier-transform infrared spectroscopy (FTIR), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) and contact angle (CA) measurements. The exposed steel at these defect sites provide points of nucleation for the electrochemical reduction of copper, and have been shown to generate deposits that exhibit variable microstructure.

CP-12 Ag Segregation in Co-sputtered ZrCuAlNi:Ag Thin Films*, M. Steinhoff, D. Holzapfel, S. Karimi Aghda, D. Neuß, P. Pöllmann, M. Hans,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; J. Schneider, **Clio Azina (clioazina@gmail.com)**,* RWTH Aachen University, Germany

The development of nanocomposites opens the door for new functional materials which combine the properties of two or more constituents. Herein, we report on the formation of Ag-reinforced thin film metallic glass nanocomposites by a hybrid direct-current magnetron sputtering and high-power pulsed magnetron sputtering process. The effects of Ag-content, substrate temperature and substrate bias potential on the phase formation and morphology of the nanocomposites were investigated.

While applying a substrate bias potential did not strongly affect the morphological evolution of the nanocomposites, the Ag content dictated the size and distribution of Ag surface segregations, while the bulk of the film remained featureless. However, at higher substrate temperatures, increased Ag contents led to the formation of lamellar-shaped Ag segregations in the bulk and that of a polycrystalline Ag layer at the surface, both of which were due to thermally enhanced surface diffusion.

The electrical resistivity of the produced nanocomposites was strongly affected by the segregations as a significant decrease was observed for the dual-phase systems, supporting the combination of properties of the metallic glass matrix and metallic reinforcement.

Coatings for Biomedical and Healthcare Applications
Room Golden State Ballroom - Session DP-ThP

Coatings for Biomedical and Healthcare Applications (Symposium D) Poster Session

DP-ThP-3 Antimicrobial and Aging Properties of Ag-, Ag/Cu- and Ag Cluster-Doped Amorphous Carbon Coatings Produced by Magnetron Sputtering for Aerospace Application*, G. Sanzone, J. Yin, **Hailin Sun (hailin.sun@teercoatings.co.uk)**,* Teer Coatings Ltd, UK

Inside a spacecraft, the suitable temperature and humidity, designed for onboard human crew, also creates an ideal breeding environment for the proliferation of bacteria and fungi, which can present hazard for both the safety running of equipment and human health. To address this issue, it is proposed to coat the key parts and components with wear-resistant antimicrobial thin films prepared by magnetron sputtering. Silver and copper are among the most studied active bactericidal materials for a long history. In this work we investigate the antibacterial properties of silver doped, silver-copper doped, and silver cluster doped amorphous carbon coatings for aerospace applications and their longevity, which is heavily influenced by the metal diffusion rate to the coating surface. Samples have been prepared with different silver and copper volume fractions via co-sputtering, while Ag cluster samples are prepared using a cluster source to better control the metal particle size distribution in the amorphous carbon coating matrix. Antibacterial tests are performed under both terrestrial gravity and microgravity conditions, to simulate the condition in the space. Results show that silver doped coatings are very effective in terms of antimicrobial property but with a faster silver atom diffusion, while those silver-copper doped samples have generally a slightly lower antimicrobial activity, but no obvious metal diffusion observed. For the silver cluster doped samples, they show a high antimicrobial activity despite a much lower silver volume fraction, and a seemingly slow Ag metal diffusion rate.

DP-ThP-4 Structure and Mechanical Properties of Superelastic TiZrNb and TiSnZrNb Coatings for Biomedical Applications*, T. Choquet, A. Fillon,* Institut des Sciences Chimiques de Rennes, France*; A. Michel,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; M. Vayssade,* Université de technologie de Compiègne, France*; T. Gloriant,* Institut des Sciences Chimiques de Rennes, France*; **Gregory Abadias (gregory.abadias@univ-poitiers.fr)**,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Titanium alloys are propitious materials in biomedical implants for their mechanical properties and biocompatibility. Nitinol (Ni-Ti), especially, has been used because of its superelasticity (up to 12% recoverable strain) due to a reversible martensitic transition. Ni, however, has been proven allergenic and so in the past decade, research has focused on β-type titanium alloys with non-toxic and non-allergenic elements such as Nb, Sn, Ta or Zr with the aim of replacing Ni-Ti. In this study, novel coatings based on ternary and quaternary titanium alloys have been elaborated. Their properties have been studied for bulk materials; however, the structural and mechanical properties for their thin film counterpart remain to be elucidated, which is the aim of the present study.

Ti-Nb-Zr and Ti-Nb-Zr-Sn coatings have been elaborated at room temperature by magnetron sputtering at a working pressure of 0.26 Pa. By using different targets and by changing the power applied to them during deposition, different chemical compositions have been obtained, with Nb content ranging from 0 to 33 at.%. The focus has been on identifying the crystallographic structure and the mechanical properties of the films depending on their chemical composition. XRD, TEM and resistivity measurements were performed to study the phase formation with respect to the Nb content. The stress induced during film growth has been evaluated *in-situ* using wafer curvature measurements and the mechanical properties were evaluated using nano-indentation and tensile tests. To assess the biocompatibility of the films, early cell behavior (cell adhesion, spreading and morphology) will be characterized and standardized cytotoxicity assay will be conducted.

Using XRD θ/2θ scans, the films have been found to be highly textured: the main peaks are 002 α and 110 β. XRD, TEM and resistivity show that with increasing Nb and Zr content, the phase evolves from hexagonal α phase to orthorhombic α'' martensite and then to cubic β phase. The curvature measurements have shown that at low Nb content, the film first develops a compressive stress that evolves during continuing growth into tensile stress. At high Nb content, the stress remains compressive throughout deposition. Preliminary *in vitro* biocompatibility tests show that osteoblast cells well adhere on the quaternary coatings after 72 h and manifest cell functional activity.

DP-ThP-5 Development of Multilayer Hydroxyapatite (HA) - Silicon (Si) Coatings Deposited on Ti6Al4V by Magnetron Sputtering with Potential Biomedical Application*, **Julián Andrés Lenis Rodas (julian.lenis@udea.edu.co)**, K. Perez Zapata, F. Bolívar Osorio,* University of Antioquia, Colombia*; P. Rico, J. Gómez Ribelles,* University of Valencia, Spain

Titanium alloys, specifically Ti6Al4V, are widely used in the biomedical field because they have an adequate balance between mechanical properties, corrosion resistance and biocompatibility. However, when it is incorporated into the human body, unfavorable reactions can be obtained that do not allow adequate osseointegration, due to the formation of a fibrous and non-adherent layer between the biomaterial and the bone, which can trigger the failure or rejection of the implant. The purpose of this study was to evaluate the influence of the surface modification of Ti6Al4V with a Hydroxyapatite (HA) - Silicon (Si) coating on its in vitro biological response, also studying the effect of surface roughness. The deposition process was carried out by Magnetron Sputtering on Ti6Al4V surfaces with different roughness - RMS, 3.8 nm and 48.7 nm. The surface morphology of the coatings was observed by Scanning Electron Microscopy and Atomic Force Microscopy, the chemical composition was evaluated by means of EDS and micro-Raman spectroscopy. The biological response of the coatings was evaluated by MTT and cell adhesion assays, using mouse mesenchymal stem cells. The control in the process parameters allowed to obtain coatings with a good compositional balance (a Ca/P ratio close to 1.67 and characteristic vibrations of HA). RMS values of 27 ± 5 nm and 52 ± 6 nm were obtained for the coatings obtained on the Ti6Al4V with different roughness. The biological tests indicated a non-toxic behavior in the HA-Si coatings, in addition, the cellular adhesion of the Ti6Al4V was favored both by the incorporation of this system and by increasing its roughness.

DP-ThP-6 Effective Antiviral Copper Coatings onto Thermoplastic Against SARS-CoV-2*, C. Popescu,* IRCER, France*; M. Courant,* CHU Limoges, France*; E. Laborde,* IRCER, France*; S. Alain,* CHU Limoges, France*; V. Perin,* Kometa Technologies, France*; A. Castro,* CITRA, France*; L. Youssef,* IRCER, France*; T. Maerten,* Oerlikon-Balzers, France*; **Marjorie Cavarroc (marjorie.cavarroc@safrangroup.com)**,* Safran, France*; D. Alain, A. Vardelle,* IRCER, France

The actual viral outbreak continues to have a tremendous impact on human health, social relations, and the economic situation worldwide. Eengineered metallic coatings can mitigate the viral transmission from the thermoplastic surfaces (fomites) touch points in transports. This goal is achievable by functionalizing thermoplastic surfaces with metals through innovative designs that inhibit or destroy the microorganisms. The life span of these functionalized surfaces depends on their physical-chemical properties and external factors (e.g., humidity, temperature, cleaning agents, etc.) that can modify the engineered surface. The presented work focus on copper-based thermoplastic surfaces obtained by different deposition methods to observe the influence of the chemical composition of the surface, but also the importance of coating structure and texture, to increase the SARS-CoV-2 inactivation rate. The in-vitro antiviral tests are realized in agreement with normalized protocols to qualify the antiviral surfaces (ISO 21702:2019). The obtained results show that the deposition method has a strong influence on both the microstructure and the surface chemistry of the engineered Cu films. The coatings enhanced grain dislocations increase the Cu ions release and their participation in the reactive oxidative species processes influences the viral growth time.

DP-ThP-7 Antibacterial Graphene Coatings Electrophoretically Deposited on Nitinol Substrate*, **Madhusmita Mallick (madhusmita1509@gmail.com)**, K. Mitra, A. N,* Indian Institute of Technology (IIT) Madras, India

Graphene can be an effective antibacterial candidate owing to its bactericidal property. In this study, graphene coatings were prepared on Nitinol substrate through a cost-effective electrophoretic deposition method (EPD). The antibacterial activity of graphene-coated samples was investigated against two strains of gram-positive (S.Aureus) and gram-negative (E.Coli) bacterias by classic colony counting method, live/dead fluorescent microscopy and scanning electron microscopy (SEM) techniques. Here, bare nitinol substrate was chosen as a control sample.The results showed that the coatings exhibited stronger antibacterial activity against E. coli bacteria with thin membrane than S. aureus bacteria with thick membrane. Furthermore, the antibacterial test suggested that oxidative stress mechanism is the main factor of antibacterial activity of EPD prepared graphene coatings.

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Golden State Ballroom - Session EP-ThP

Tribology and Mechanical Behavior of Coatings and Engineered Surfaces (Symposium E) Poster Session

EP-ThP-2 Atmospheric Pressure Plasma Deposition of Low Friction Coatings on Engineering Thermoplastics: The Plasma-Process-Structure in the Versatile Spray Coating Technique as Basis of Commercial Applications, ***Dietmar Kopp (dietmar.kopp@joanneum.at)**, J. Lackner, R. Kaindl, W. Waldhauser,* Joanneum Research Forschungsgesellschaft GmbH, Austria*; M. Stummer,* INOCON, Austria*; A. Coclite,* Graz University of Technology, Austria

Deposition strategies to obtain low friction and wear resistant coatings on 3D-printed, rough polyamide 12 (PA, nylon) surfaces were developed by atmospheric pressure plasma deposition. Dry lubricants such as MoS_2 and graphite were fed as powder material to the DC plasma torch by INOCON Technologie GmbH, applying parameter sets that would not thermally damage the heat sensitive polymers. In general, microtribological characterization indicates that especially high influence on the coating performance is given by the coating composition and thickness. Pure MoS_2 coatings are quickly worn, especially on roughness tips (mean substrate roughness R_a up to 20 µm), exposing the substrate locally and leading to friction coefficients similar to PA12 and rather limited potential of wear protection. Compound coatings with graphite within a MoS_2 matrix provide huge potential for wear protection (>20 times less penetration depth) even in the case of exposing PA12 to roughness tips, due to the transfer of lubricating carbon into these exposed areas. If the thickness is sufficiently high, missing wear of tips results in low-friction behavior with friction coefficients <0.1 (thus, 4 times lower than for uncoated PA12).

EP-ThP-3 The Influence of Boron in Thick AlTiN and AlCrN Coatings Deposited by Bipolar HiPIMS to Control Residual Stress and Improve Tribomechanical Properties, ***Adrián Claver (adrian.claver@unavarra.es)**,* Institute for Advanced Materials and Mathematics (INAMAT2), Universidad Pública de Navarra (UPNA), Spain*; I. Fernandez,* Nano4Energy SL, Spain*; J. Endrino,* Nano4Energy SL, University Loyola, Sevilla (Spain), Spain*; J. Santiago ,* Nano4Energy SL, Spain*; J. Fernández Palacio,* Centre of Advanced Surface Engineering, AIN, Spain*; J. García,* Institute for Advanced Materials and Mathematics (INAMAT2), Universidad Pública de Navarra (UPNA), Spain

Thick PVD coatings provide wear protection, improving thermal and abrasion resistance during machining operations[1]. In order to improve tool life, multiple attempts have been made to increase the thickness beyond 5 um [2]. However, ion bombardment during film growth usually induces high compressive stress in thick films, resulting in adhesive failure of coated tools in tribological applications. In this work, we investigated how to reduce high stress levels in thick AlTiN- and AlCrN- based coatings [3] (up to 10 µm) by incorporating boron to the metal nitride structure. The composition and microstructure of the coatings were characterized using Glow Discharge Optical Emission Spectrometry (GDOES), Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The stress of the coatings was determined by curvature method and compared with the results derived from XRD analysis. Nano-hardness, scratch tests and pin-on-disk tests were carried out to study the tribological properties of the coatings. Machining tests were performed to validate in service performance of the coatings. The results show that standard AlTiN and AlCrN are hard and dense coatings but highly stressed. However, the incorporation of boron induces a nanocomposite type structure, formed by nanocrystalline domains and boron-rich amorphous regions. As a result, stress is reduced, while thermal stability, elasticity and fracture toughness are enhanced.

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EP-ThP-5 Optimized a-SiC_x:H Intermediate Layers for Well-adhered a-C:H Thin Films on Ferrous Alloys, *V. Piroli, J. Weber, M. Goldbeck,* UCS, Brazil*; F. Cemin,* UNICAMP, Brazil*; A. Michels,* UCS, Brazil*; F. Alvarez,* UNICAMP, Brazil***; Carlos Figueroa (cafiguer@ucs.br)**,* UCS, Brazil

Hydrogenated amorphous carbon (a-C:H) thin films have been gaining much attention among new technologies due to their low friction coefficients and high wear resistance. However, the low adhesion of the couple a-C:H thin film / ferrous alloy is still an ongoing challenge. The use of Si-containing interlayers not only minimizes residual stress and provides chemical affinity but also these intermediate layers can be obtained by cheap PECVD technologies. Nevertheless, high temperatures in the interlayer's deposition process, e.g., 300 °C [1], do not allow massive applications due to the degradation of previous substrate's heat treatment. This work aims to study the adhesion of a-C:H thin films on AISI 4140 steel, with an a-SiC_x:H interlayer, by using relatively low a-SiC_x:H deposition temperatures to enable the scale production of well-adhered a-C:H/a-SiC_x:H/steel structures.

Samples of AISI 4140 steel were treated in a low-cost pulsed-DC PECVD equipment with electrostatic confinement. The a-SiC_x:H interlayer was deposited for 10 min using a tetramethylsilane (TMS) / Ar vapor mixture. During the interlayer's deposition, the temperature varied between 85 °C and 200 °C, according to the process. The a-C:H film was deposited using an acetylene (C_2H_2) / Ar gas mixture for 60 min at 80 °C.

The thin films were characterized by FEG-SEM, optical microscopy, XPS and scratch test. Cross-section FEG-SEM allowed observing three well-defined regions in the sandwich structure: the a-C:H film (top layer), the a-SiC_x:H film (intermediate layer) and the steel (bottom layer). One can observe an exponential decay of the defects density by increasing the interlayer's deposition temperature. XPS determined the content of oxygen present in the a-C:H/a-SiC_x:H interface, which varied between 1.5% (for 85 °C) and 0.5% (for 200 °C). The critical scratch loads (Lc), obtained from the scratch test, varied from 4.3 N (for 85 °C) to 5.9 N (for 175 °C). To date, samples with Si-containing interlayers produced from hexamethyldisiloxane (HMDSO), TMS or tetraethoxysilane (TEOS) at 500 °C presented maximum a-C:H critical loads of 3.4 N, 0.4 N and 0.3 N, respectively [2]. Finally, the use of relatively low temperatures on the deposition of well-adhered, with minimum oxygen content a-C:H/a-SiC_x:H/steel structures represents a new finding. The results of this research could facilitate industrial production of coatings with a more affordable market price.

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EP-ThP-6 A Deep Neural Network for Pattern Optimization of Microtextured Surfaces in Lubricated Contacts, *A. Silva, **Veniero Lenzi (veniero.lenzi@fisica.uminho.pt)**, L. Marques,* University of Minho, Portugal

The reduction of friction between moving parts in contact in mechanical equipment is fundamental in order to reduce wear, increase equipment efficiency and reduce the use of lubricant. It is well-known that the treatment of surfaces through micro-texturing allows for an improvement of the tribological performance of the contact, however it is not clear how to find the optimal texturing pattern that provides the best friction reduction.

In this work, we designed a deep neural network (DNN) that can predict the Stribeck curve of a lubricated contact, starting solely from the knowledge of the initial texture. The DNN has been trained using a in-house developed finite elements method solver for the Reynolds equation that correctly treats the cavitation problem by using the iterative inexact Newton algorithm. The training set for the DNN consisted of randomly generated patterns of dimples with fixed depth and radius.

Our DNN is capable of calculating Stribeck curves in milliseconds with a mean square error lower than 0.5 % when compared to curves obtained with the direct solver. This enabled us to solve the inverse problem, that is finding the optimal texturing given a Stribeck curve, by means of a search within the solution space obtained using the DNN.

EP-ThP-7 e-Poster Presentation: Tribological Behavior of Lamellar Solid Lubricant Coatings in Low Viscosity Hydrocarbons*, Euan Cairns (euancairns@my.unt.edu)*, *A. Ayyagari,* University of North Texas, USA*; S. Berkebile,* US DEVCOM Army Research laboratory, USA*; D. Berman, S. Aouadi, A. Voevodin,* University of North Texas, USA

Transitioning to multi-fuel capability of modern combustion engines has generated need for new sources of effective lubrication inside fuel pump assemblies. Low-viscosity fuels pose a tribological challenge when used in fuel injection systems, as they provide lower lubricity when compared to conventional diesel fuels, leading to degradation of service life of fuel pump and injection system components. Lamellar solid lubricants (MoS_2, WS_2, graphite, h-BN) may become a good secondary source of lubrication when applied to such components as coatings. However, their tribological behavior in fuel environments is unknown. In this report, we compared sliding wear performance of lamellar solid lubricant coatings applied by burnishing onto the surface of yttria-stabilized zirconia (YSZ) coating and tested in ethanol and dodecane environments. The results showed that the tribological behavior of the solid lubricants depends on their composition and environment. MoS_2-based coatings provide the best performance when compared to hexagonal BN, graphite, and WS_2, when tested in a high-frequency reciprocating sliding against steel counterpart. The coefficient of friction of MoS_2 in dodecane is 0.08 for the first 5,000 cycles, while for other solid lubricants it is above 0.1. Possible lubrication mechanisms are discussed, where interactions between fuel molecules and the lamellar lubricant structure as well as oxidations processes may affect the lubrication mechanisms. The discussions of these mechanisms are supported with SEM/EDS and Raman spectroscopy analyses of the tribological contacts

EP-ThP-10 Mechanical Behaviour and Effects of Cu/Ni Nanolaminate Coatings on the Fatigue Properties of Welded Steel Specimen*, Jakob Brunow (jakob.brunow@tuhh.de)*, *M. Rutner,* Hamburg University of Technology, Institute for Metal and Composite Structures, Germany

Nanostructured metal multilayers have been known to possess exceptional material properties regarding strength, magnetism, radiation resistance, fatigue resistance, corrosion resistance and abrasion resistance. Since there are a lot of governing factors for the material properties of nanostructured metal multilayers (NMMs), i.e. global composition, local composition, used metals and interface strength, NMMs can be tailored to specific needs. [1]

Cu/Ni NMMs have seen special interest in the scientific community for the wide variety of possible applications and the possibility to synthesize with a single-bath electrodeposition process. [2]

Current research at the University of Hamburg is focusing on the strengthening of welded steel structures against fatigue, by coating the surface with a nanostructured Cu/Ni-metal laminate patch. [3] The findings are in accordance with other studies that studied the fatigue properties of Cu/Ni nanolaminate coatings. [4]

The surface roughness is measured with AFM before and after fatigue loading. The nanolaminate Cu/Ni coating on the fractured fatigue samples are examined with serial FIB cross sectioning. Subsequently a TEM-lamella is taken from the crack tip to investigate the crack initiation and assess the fracture mechanisms of the Cu/Ni NMM. The Cu-layers experience multi-crack formation and the initial multi-cracks are arrested at the interfaces. The Ni layers bridge those cracks and each layer ruptures individually, resulting in a distinctive crack pattern.
The lifetime enhancement of the welded sample are linked to the fracture mechanism of the NMM and can thus be attributed to the following five mechanisms: reduced surface roughness, micro-crack bridging, energy dissipation, crack arrest at interfaces and changes in surface tribology. [5]

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EP-ThP-11 Nanoindentation Spectrometry*, Esteban Broitman (esteban.daniel.broitman@skf.com)*, SKF B.V., Netherlands

The precise knowledge of material microstructures is of vital importance to understand their mechanical and tribological performance. Standard microstructural characterization, carried out by optical and electron microscopy together with X-ray diffraction, is usually correlated to the hardness determined by Rockwell or Vickers indentation at macro- and microscale, and nanoindentation at nanoscale.

In the first part of the presentation, the background of a novel statistical nanoindentation technique to measure hardness and Young's modulus of materials is described [1]. We indicate how experiments are designed, and how the distribution of the hardness and modulus of elasticity determined from the nanoindentation observations are deconvoluted to generate hardness histograms that reflect unique characteristics (fingerprints) of each coating or bulk material. We show how the statistical deconvolution analyses gives an estimate of the microstructural constituents, their volume fraction and corresponding plastic and elastic properties at nanoscale. In the second part, numerous examples on different kind of coatings and bulk materials are presented to illustrate the usefulness of the novel technique.

We demonstrate that, by using nanoindentation as a novel tool for static nanomechanical spectrometric analysis of coatings and bulk materials, a fundamental understanding of the relation between local microstructure (phases and their size) and local material response during elastic and plastic deformation can be obtained.

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New Horizons in Coatings and Thin Films
Room Golden State Ballroom - Session FP-ThP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-ThP-1 Analysis of (Al,Cr,Nb,Ta,Ti)-Nitride and Oxynitride Diffusion Barriers in Cu-Si Interconnects by 3D-Secondary Ion Mass Spectrometry*, Andreas Kretschmer (andreas.kretschmer@tuwien.ac.at)*, TU Wien, Institute of Materials Science and Technology, Austria*; F. Bohrn, H. Hutter,* TU Wien, Institute of Chemical Technologies and Analytics, Austria*; E. Pitthan, D. Primetzhofer,* Uppsala University, Department of Physics and Astronomy, Sweden*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

A number of different high-entropy sublattice nitrides have been investigated in the past as diffusion barriers between Cu and Si. These investigations were performed by depositing several nanometer thin barriers on single crystalline Si substrates, followed by a thick Cu layer on top, and subsequent vacuum annealing. In this work we report on the barrier performance of a nitride, and also three oxynitrides of the high-entropy alloy Al-Cr-Nb-Ta-Ti by depositing a reversed stacking sequence. 10 nm of (Al,Cr,Nb,Ta,Ti)-O-N (between 0.5 and 63.7 at% O, obtained by Elastic Recoil Detection Analysis) were deposited on polished polycrystalline Cu substrates by magnetron sputtering at room temperature with -100 V bias, followed by deposition of 200 nm Si. The samples were then vacuum annealed at 600, 700, 800 and 900 °C for 30 min. All four investigated coatings perform similar. While Secondary Ion Mass Spectrometry depth profiling in high-current-bunched (HCBU) mode with a high mass resolution (of >12.000 amu, lateral resolution ≈1 µm) shows breakthrough of Si even at 600 °C, 3D constructed images with Burst Alignment (BA, lateral resolution of ≈2 nm) depth profiles reveal that this failure is a highly localized phenomenon. The failure is likely related to recrystallization effects at the Cu grain boundaries, leading to punctuation of the diffusion barrier, as the diffusing Si stays confined in columnar regions within the Cu. Aside from this penetration, the majority of the area of each barrier coating retains its function. This in-depth analysis shows that the barrier function of the nitride and oxynitride coatings essentially stays intact up to 800 °C and fails completely at 900 °C.

FP-ThP-2 Maximum Achievable N Content in Amorphous Nitrides*, Jiri Houska (jhouska@kfy.zcu.cz)*, University of West Bohemia, Czechia

The contribution reports the latest results concerning the maximum achievable N content in amorphous nitrides prepared by atom-by-atom growth. Structures of amorphous CN_x, Si-C-N, B-C-N and Si-B-C-N are predicted by extensive ab-initio molecular-dynamics simulations (over 15 000 trajectories) in a wide range of compositions and densities [1-3]. When and only when the structures are allowed to include unbonded N_2 molecules, the predicted lowest-energy densities are in agreement with the experiment. The main attention is paid to the N_2 formation, with the aim to predict and explain the relationships between [Si]/[B]/[C] ratios and the maximum achievable content of N bonded in stable amorphous networks ($[N]_{network}$). The results reveal that N_2-free networks are characterized by maximum $[N]_{network}$ between 34% (CN_x) and 57% (SiN_x). Networks formed in parallel to the formation of unbonded N_2 molecules (which subsequently either diffuse out or stay trapped in the material) are characterized by maximum $[N]_{network}$ between 42% (CN_x) and 57% (SiN_x). The measured N contents in (Si)-(B)-C-N films prepared in our laboratory by reactive magnetron sputtering are in an excellent agreement with the prediction. Further analysis shows that while the N_2 formation takes place at a packing factor below the critical value of 0.28 which is valid in a wide range of compositions, the lowest-energy packing factor (sometimes below 0.28, sometimes above 0.28) depends on the composition. The presented methodology constitutes a new way how to support the experiment by ab-initio simulations. The results are important for the design of amorphous nitrides for various technological applications, prediction of their stability, design of pathways for their preparation, and identification of what may or may not be achieved in this field.

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FP-ThP-3 Bulk Diffusion of Impurities in TiN: An Ab Initio Study*, Ganesh Kumar Nayak (ganesh.nayak@unileoben.ac.at),*

Montanuniversität Leoben, Austria*; M. Popov,* Material Center Leoben, Austria*; D. Holec,* Montanuniversität Leoben, Austria

TiN-based materials are widely established as protective coatings for cutting tools. Grain interiors (single crystal regions) could serve as reservoirs for functional species, e.g. Al or V, which provide effective lubrication and wear protection at high temperatures by diffusing to the coating surface where they form a protective oxide scale (Al) or a lubricious oxide to reduce friction (V).

In this contribution, we will report on our recent work in addressing issues related to the atomistic modeling of mass transport. To do so we employ complementary computational investigations to determine elementary point-defect migration mechanisms in crystalline materials and subsequently their relative rates. The density functional theory (DFT) is used to describe interatomic forces, is the most reliable computational tool to calculate atomic jump rates as a function of temperature. Since TiN is a harmonic crystal it gives us access to temperature-based properties derived from the lattice vibration with harmonic and quasi-harmonic approximation. We will present the DFT-based "5-frequency model" allowing us to calculate the diffusion coefficient in the crystalline material. Moreover, the influence of TiN stoichiometry on its diffusion properties is taken into account through the change in the concentrations of the intrinsic point defects as a function of composition. These concentrations are obtained via a thermodynamic formalism based on the dilute solution model. We find that in stoichiometric TiN the vanadium impurity diffusion proceeds via the vacancy mechanism on the Ti sublattice. Furthermore, we also demonstrate that pressure has a notable impact on the diffusivity of V, Al, and Ti in TiN.

FP-ThP-5 Data-Driven Design Guidelines for Ceramic Superlattices With Enhanced Fracture Resistance*, Nikola Koutná (nikola.koutna@tuwien.ac.at), A. Brenner,*

TU Wien, Austria*; D. Holec,* Montanuniversitat Leoben, Austria*; P. Mayrhofer,* TU Wien, Austria

Superlattices—alternating coherently grown materials of nm thicknesses—showed a great potential for enhancing typically antagonistic properties of ceramics: strength and toughness. Selection of layer components, however, is far from trivial, as nanolaminated films do not combine mechanical properties of the layer materials in a simple manner. In this work, we employ high-throughput density functional theory calculations to develop design guidelines for superlattices based on cubic transition metal nitride and/or carbide ceramics. Out of 153 MX/M*X* superlattices (M, M* = Al, Ti, Zr, Hf, Nb, V, Ta, Mo, W, and X, X* = C, N) 145 are chemically and mechanically stable and most often contain vacancies on the non-metallic sublattice. Superior ductility together with moderate-to-high fracture toughness and interface strength (above that of the cubic TiN) narrow the set of the most perspective candidates. Key ingredients promoting the interface-induced enhancement of hardness and/or fracture toughness are lattices parameter and shear modulus mismatch of the layer constituents. Adding the requirement of phonon stability yields MoN/M*N, M*=Nb, Ta,Ti; TiN/WN (nitrides); HfC/M*N, M*=Mo, W; NbC/M*N, M* = Mo, W; TaC/M*N, M* = Mo,W; VC/M*N, M* = Hf, Ta, Zr (carbonitrides); as the top candidates for novel superlattice films.

FP-ThP-6 Preparation of Single and Multilayer Films of Boron Carbide, Titanium Diboride and Hexagonal Boron Nitride Using Pulsed Laser Deposition*, Falko Jahn (jahn@hs-mittweida.de), S. Weißmantel,*

Laserinstitut Hochschule Mittweida, Germany

Boron containing film materials provide outstanding mechanical, thermal and chemical properties which leads to growing interest in applying these materials in wear resistance coatings. Boron carbide, the third hardest known material after diamond and cubic boron nitride, shows indentation hardness values up to 49 GPa and a very high chemical and thermal stability. Titanium diboride's thermal properties exceed even those of boron carbide with a melting point over 3200°C and exceptional hardness at high temperatures (> 2000°C). Both materials are very well suited as wear resistance coatings, especially in very corrosive or hot environments. However, the brittleness of both materials may restrict their use regarding applicable loads

The presented approach to overcome these restrictions is to combine the material properties of boron carbide and titanium diboride with the properties of a less brittle but also very hard material by forming multilayer structures. Since this material should provide a similar thermal and chemical stability, we chose hexagonal boron nitride whose hardness can be varied between 10 GPa and 25 GPa depending on the process parameters.

The presented results contain both the produced single and multilayers using the pulsed laser deposition technology. The mechanical properties of the produced films of boron carbide, titanium diboride and hexagonal boron nitride are investigated in dependence of the process parameters such as ablation fluence and substrate temperature.

The obtained mechanical material properties are applied to simulations of various multilayer designs under certain load conditions in order to find suited multilayer parameter combinations such as thickness or mechanical property of the sublayers. Promising multilayer designs are produced and characterized. The mechanical properties of the presented thin films are measured using nanoindentation. The surface quality is characterized by scanning electron microscopy and the sublayer adhesion is estimated using instrumented scratch testing and a calotte-grinding method.

FP-ThP-7 Anisotropic Super-hardness of Hexagonal WB_{2-z} Thin Films*, Christoph Fuger (christoph.fuger@tuwien.ac.at), R. Hahn, L. Zauner, T. Wojcik,*

Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria*; M. Weiss, A. Limbeck,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien , Austria

Physical vapor deposited transition metal borides are an emerging class of materials. Their inherent promising properties range from ultra-low compressibility, highest thermal stability to chemical inertness, allowing an application as protective coating in quite harsh environments. Our recent ab initio calculations suggest an attractive combination of Poisson's ratio, bulk-, and shear modulus for α-structured WB_{2-z} (space group 191, AlB_2-prototype, P6/mmm). This leads to an interesting combination of high hardness while maintaining a sufficient fracture toughness. The stabilization of the α-structure over the intrinsically favored ω-structure (space group 194, W_2B_5-prototype, $P6_3$/mmc) is based on omnipresent growth defects (e.g. various types of 0-dimensional vacancies) throughout the PVD deposition. However, next to the stabilized phases (hence prevalent bonding nature) also the morphology, especially column size and grain boundary interior, has a huge impact on the mechanical response.

Here, we focus on the binary WB_2 material system in terms of its phase formation using DFT and further illustrate the impact of prevalent lattice orientations on the mechanical properties. We show, that the α-WB_{2-z} structure is preferentially stabilized by B vacancies, exhibiting its energetic minima at sub-stoichiometric compositions of about $WB_{1.5}$ – being also experimentally underlined.The mechanical properties show that α-WB_{2-z} coatings in 0001 orientation reveal super-hardness (H > 40 GPa) compared to their 10-11 oriented α-WB_{2-z} counterparts (H ~ 30 GPa). This is attributed to differences in the generalized stacking fault energies (GSFE) of basal and pyramidal slip systems in hexagonal diboride crystals. Our results show that the mechanical properties, in particular H, of PVD α -WB_{2-z} coatings can change significantly due to the crystallographic orientation, highlighting the feasibility of tuning mechanical properties by crystallographic orientation relations.

Keywords: WB_2; Physical Vapour Deposition; DFT; Structural defects; Anisotropy;

FP-ThP-10 Characterization of a Novel Ionic Liquid-Based Chromium Plating Formulation*, **Cameron Longo (cameron.m.longo.civ@army.mil)**, D. Sconyers,* US Army - DEVCOM AC - Benet Laboratories, USA*; M. Quiroz-Guzman, D. Morrison, T. Bush, M. Arsenault,* Trion Coatings, LLC, USA*; J. Maurer,* US Army - DEVCOM AC - Benet Laboratories, USA

Hexavalent chromium electroplating has come under severe scrutiny, with increasingly strict regulations and plans for complete removal from operations within the US within the next 10 years. Hexavalent chromium poses large risks, as it is a known carcinogen and presents severe occupational and environmental hazards in its use. However, chromium coatings offer many benefits, including excellent wear and corrosion resistance, and has good hardness and adhesion properties. As such, an effective chromium plating alternative for hexavalent-based processes is sorely needed.

Several systems which utilize trivalent chromium have been proposed, which offer highly reduced health and environmental risks, and could serve as appropriate replacements. An ionic liquid-based trivalent chromium process, dubbed SAFE Chrome, has been developed as an alternative to aqueous chemistries, and utilizes a charged organic species to bind to chromium ions to facilitate deposition. The analysis of weakly-bound organometallic complexes holds many unique challenges, the most salient of which is the desire to characterize the complex as it exists in solution. Mass spectrometry techniques are some of the most attractive options, as they afford highly robust and sensitive means of characterization. Traditional techniques, such as electrospray ionization (ESI) or matrix-assisted laser desorption/ionization (MALDI), have great potential to perform structural characterization of the components of these complexes using varying ionization approaches and tandem MS analyses, while more novel technique such as liquid injection field desorption/ionization (LIFDI) may offer unique insights into the bound form of the complex. Techniques such as infrared (IR) and ultraviolet-visible (UV-VIS) spectroscopy, as well as X-ray techniques like small-angle X-ray scattering (SAXS) can also offer insights into the structure or binding of the complex, while electrochemical analyses can inform on the electron transfer processes and valence of the metals. These data together help to form a deeper understanding of the chemistry occurring in solution during plating, and enable more intelligent design and better control of these emerging plating technologies.

Surface Engineering - Applied Research and Industrial Applications
Room Golden State Ballroom - Session GP-ThP

Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-ThP-1 Water and Oil Repellent Coating on Fabric Using Hollow Cathode PECVD*, R. Mbamkeu Chakounte,* Univ Appl Sci & Arts (HAWK), Göttingen, Germany*; J. Jolibois,* AGC Interpane, Germany*; O. Kappertz,* Univ Appl Sci & Arts, (HAWK), Göttingen, Germany*; **John Chambers (john.chambers@agc.com)**,* AGC Plasma Technology Solutions, USA*; H. Weis,* AGC Interpane, Germany*; H. Wiame,* AGC Plasma Technology Solutions, Belgium*; W. Viöl,* Univ Appl Sci & Arts (HAWK), Göttingen, Germany

Thin film deposition is a suitable process for textile finishing at a time when environmental protection is a global concern. Thin film technology textile treatments not only avoid the harmful chemistry and resulting hazardous waste of wet chemistry, but limit the use of chemicals, water, etc., and do not require a drying system, resulting in much lower energy consumption. Various PECVD processes have therefore been developed over the years for the textile industry to overcome wet processing's disadvantages.

Water and oil repellent finishes are amongst the most studied treatments for fabrics. With PECVD, surface modification is carried out through plasma polymerization, which produces polymers with a higher degree of cross-linkage than conventional polymers. Moreover, these plasma processes are room temperature methods, so heat-sensitive monomers can be used. Among the commercially available precursors, short perfluoroalkyls can thus be used to impart water and oil repellency to fabrics, avoiding long-chain perfluoroalkyls which endanger the environment, human and animal life through the release of PFOAs and PFOS.

Within thin film industry, hollow cathode plasma source (HC) technology is increasingly gaining attention for PECVD. The key advantages of this technology are a high deposition rate and a good uniformity over large areas. However, HC is a high-density plasma source, appropriate for the deposition of inorganic layers, typically SiO_2, but challenging for the deposition on fabrics without modifying their bulk properties or damaging their surface.

In this work, we demonstrate the successful use of HC technology to impart water and oil repellent properties on polyolefin textiles with fluorinated and silicone precursors. The effect of parameters such as power, pressure, gas composition and flow on water and oil repellency have been evaluated according to international standards, contact angle and the film composition analysed through FTIR measurements. Water contact angles greater than 150°, *i.e.* superhydrophobic surface, and oil repellency grade of 4 have been obtained.

Keywords: Low-pressure, hollow cathode, plasma polymerization, water and oil repellent

GP-ThP-2 Modification of Polymer 3d Printed Parts Through Vacuum Metallization*, **Andrew Miceli (n00928754@unf.edu)**, G. Bevill, S. Stagon,* University of North Florida, USA

Polymer three dimensionally (3D) printed parts have grown to become the most common prototypes for mechanical and functional design over the last decade. Like their classical injection molded counterparts, these polymer parts can benefit from surface metallization. For example, our group has metallized 3D printed polymer parts to increase mechanical performance, act as reflectors for telescopes, and protect the polymer from ultra-violet light damage. Unlike injection molded parts, the surfaces of 3D printed parts from the fused deposition modeling (FDM) method are naturally rough. Additionally, legacy wet-chemical metallization techniques for non-conductive polymers have fallen out of favor due to the use of caustic and toxic chemicals. In this presentation we demonstrate the metallization of poly-lactic-acid (PLA) 3D printed parts from the FDM method using magnetron sputtering. Prior to metallization, the parts surfaces are modified through low energy atmospheric plasma etching. Surface roughening is observed and characterized using scanning electron microscopy and laser scanning optical microscopy. Film adhesion is measured in accordance with ASTM D3359 and adhesion is shown to improve with the degree of plasma etching. Additionally, the electrical resistivity of the films is measured using four point probe. As an extension, smooth high-reflectivity surfaces are made to demonstrate the applicability of this method for the rapid prototyping of reflectors. Overall, it is shown that sputter deposition metallization of polymer 3D printed parts is a promising technique to improve the functionality of these rapidly prototyped parts.

GP-ThP-8 Reactive HiPIMS Deposition of AlO_x Interlayer for Pt Thermistors on SiN_x*, **Atasi Dan (atasi.dan@nist.gov)**, E. Antunes, C. Yung, N. Tomlin, M. Stephens,* Applied Physics Division, National Institute of Standards and Technology (NIST), Boulder, USA*; J. Lehman,* Applied Physics Division, National Institute of Standards and Technology (NIST), USA

Thin film thermistors with negative temperature coefficient of resistance (TCR), like Pt, are desirable for temperature-sensing applications. To achieve high sensitivity in detecting a small change in temperature, a high-quality interlayer of AlO_x is required between the SiN_x membrane and the Pt thermistor. High power impulse magnetron sputtering (HiPIMS) is known to produce high-quality thin films by generating high ionization of sputtered material which can significantly improve properties of the film over conventional sputtering techniques. In the case of reactive HiPIMS, it is important to monitor the reactive gas flow, peak current, growth rate, etc, to avoid instability in the process and control the growth of the poisoned layer on the target surface.

In this study, we investigate how target poisoning on the Al surface in the presence of oxygen can be influenced by a change in pulse length or frequency. We also show that an appropriate selection of deposition parameters can systematically provide an easier control in the reactive HiPIMS process to determine the performance of the film. The present results open the possibility of using a HiPIMS-based AlO_x interlayer in $Pt/AlO_x/SiN_x$ thermistors for achieving a high negative TCR. Additionally, we show the role of Pt target power in enhancing the TCR of $Pt/AlO_x/SiN_x$.

GP-ThP-9 Synthesis of Large Area ta-C Coating by Single-bend FCVA Source Using in-line PVD System*, HoeKun Kim (ndkim2@naver.com), K. Lee, S. Lee,* Korea Aerospace University, Korea (Republic of)*; J. Kim,* University of Incheon, Korea (Republic of)

Tetrahedral amorphous carbon (ta-C) coating is a hydrogen-free carbon coating with the remarkable properties comparable with those of diamond film, such as high hardness, optical transparency and chemical inertness. Moreover, ta-C coating can be synthesized through a relatively convenient method and has a much smoother surface, making the tribological performances of ta-C coating better than those of other diamond coatings. Among the various attempts used to prepare ta-C coatings, the filtered cathodic vacuum arc (FCVA) method is a particularly suitable technique for the mass-production of industrial ta-C coatings, and the performable properties make ta-C coatings suitable for potential commercially important components in applications such as automobile accessories, optical devices, and aerospace parts. In this study, large area ta-C coating on a 300x300mm STS plate was synthesized by single-bend filtered cathodic vacuum arc (FCVA) using in-line PVD system. Source and bend filter connecting 45° bent together were used to produce carbon plasma from a graphite target with a diameter of 50mm and a purity of 99.99%. Especially, raster magnet system was designed and constructed for large area synthesis in this source. The large area ta-C coatings with 1.8µm thickness were synthesized successfully, and thickness uniformity was showed as 92.4%. Raman spectroscopy analysis showed that the ta-C coatings had high sp3/sp2 fraction over 63%, and the hardness showed high values of 48.5 GPa. In addition, the ta-C coatings with 700nm in thickness, a sp3/sp2 fraction over 74%, and about 63 GPa hardness could be synthesized with a similar uniformity. Detailed experimental results will be presented.

Acknowledgement

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Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Golden State Ballroom - Session HP-ThP
Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

HP-ThP-1 e-Poster Presentation: Strategies for Increasing the Fracture Toughness of Hard Coatings Using CrN as a Role Model*, **Rainer Hahn (rainer.hahn@tuwien.ac.at)**, S. Rosenecker, D. Forstner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wojcik,* Institute of Materials Science and Technology, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Transition Metal Nitrides (TMN) are well known for their good mechanical stability, chemical inertness, as well as tribological properties. Hence, they successfully found application in the metal forming industry, and are in use as protective coatings in the automotive, aerospace, and energy industry. Besides TiN, CrN is one of the most applied and investigated hard coatings. A decisive disadvantage of these hard coatings, however, is their low fracture tolerance. Premature failure of the coating due to crack initiation and propagation leads to economic disadvantages or completely excludes an application for safety reasons.In recent years, micromechanical testing methods have made it possible to measure and specifically improve the fracture toughness of thin film materials [1]. This study focuses on microcantilever bending tests [2].

In this contribution we present three possible strategies for enhancing the fracture toughness of cathodic arc evaporated CrN coatings: toughening by grain refinement, multilayer toughening, and alloying approaches. While our first approach—grain refinement—did not lead to a significant toughness increase, we could observe an increase in fracture toughness and hardness for the other two strategies. Hereby, superlattice (multilayered) systems, CrN/TiN in our case, show the highest potential with an increase from 2.0 MPa·m$^{1/2}$ and 20 GPa for pure CrN up to 3.7 MPa·m$^{1/2}$ and 30 GPa respectively. Nonetheless, the alloying of Si (the maximum Si content was 10 at.%) to CrN as the second promising approach still yields an increase in toughness up to ~3.0 MPa·m$^{1/2}$ and 28 GPa. Besides the mechanical characterization of our samples, we also performed extensive X-ray diffraction studies and high-resolution TEM studies to describe the structure and morphology.

Keywords: Hard Coatings, Physical Vapor Deposition, Micromechanical Testing, Fracture Toughness

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HP-ThP-2 Insights on Fracture and Fatigue Mechanisms of Hard Protective Coatings*, **Lukas Zauner (lukas.zauner@tuwien.ac.at)**, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Tailoring the intrinsic fracture characteristics of hard protective coatings towards the fatigue properties of state-of-the-art bulk materials is paramount for the application of innovative coating materials extending the fatigue-life of high-performance components. Thus, an in-depth knowledge on the failure pathways of ceramic-based thin films – generally associated with lack in intrinsic ductility – but also coated components under long-term mechanical and/or thermal loading is essential to extend their lifetime. In consequence, understanding and implementing coating concepts that allow for a controlled, and hence predictable crack propagation throughout their operating spectrum are of major interest for various industrial applications. Despite recent advances [1], literature reports on the fatigue resistance of especially hard ceramic coatings, but also coated components in general, are relatively rare with a strong approach via macroscopic test facilities. Within this study we present a methodical approach to understand the failure behaviour on different length scales utilizing model systems (*i.e.*, Cr and Cr-based compounds) to consider the aspect of different bonding strengths and crystal structures, respectively. Using quasi-static and cyclic bending of pre-notched, unstrained micro-cantilever beams in conjunction with in-situ synchrotron X-ray diffraction the intrinsic fracture toughness (K_{IC}) as well as the critical failure aspects of thin films under various loading conditions are presented. Up to the high-cycle fatigue regime (*i.e.*, $N = 10^7$ cycles), the failure of monolithic sputter deposited PVD coatings is shown to be dominated by the inherent fracture resistance, irrespective of the bonding character. The recorded fatigue behaviour is further correlated with large-scale dynamic-mechanical analysis of coated Ti6Al4V platelets to step up in length scale and thus including residual stresses and changes in the elastic constants on the coating-substrate interface. The results are expected to provide key-insights into the underlying mechanisms promoting crack growth in PVD coated components.

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HP-ThP-5 Acoustic Monitoring of Nanoindentation Induced Nanofatigue*, **Jurgis Daugela (jdaugel1@jhu.edu)**,* Johns Hopkins University, USA*; A. Daugela,* Nanometronix LLC, USA

In the era of fast product development thin film engineers are looking for quick and efficient methods of characterization.Nanoindentation based multi-cycle loading offers an inside look into the real-time contact fracture dynamics [1]. A nanofatigue phenomenon can be observed on thin sub-micrometer films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves, where post-test imaging helps identify a materials' behavior [2, 3].In addition, classical Mason-Coffin and racheting fatigue models derived for the nanoscale contact can be utilized in predictions and correlate well with experimentally obtained nanofatigue cycles.

A newly developed ultrasonic nanoindentation tip operates in the hundreds of kHz; therefore, it induces milions of load cycles within seconds.The resulting nanofatigue induces different thin film fracture modes such as radial, sink-in, and produce unique acoustic signatures.The ultrasonic nanoindentation tip monitors associated waveforms, which can provide an additional inside into the nanofatigue process dynamics via advanced acoustic waveform analysis.Following our previous study [4], acoustic waveforms were processed using a combination of wavelet based signal decomposition and Deep Learning. The proposed Deep Learning technique yields a reliable classification of acoustic signatures obtained during the fracturing of sub-micrometer thick coatings.

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4. A. Daugela, *Materials Science & Engineering A*, **800** 140273 (2021)

HP-ThP-6 Spotting the CSM Plasticity Error during Nanoindentation with Continuous Stiffness Measurements*, B. Merle,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; **Hendrik Holz (hendrik.holz@fau.de)**,* University of Erlangen-Nuremberg (FAU), Germany

Dynamic nanoindentation is a popular method for continuously probing the mechanical properties of a coating as a function of depth. Here, it is shown that special caution must be exercised when testing materials with high modulus-to-hardness ratios (E/H) at fast loading rates, as the choice of harmonic parameters can result in a significant underestimation of the elastic modulus and overestimation of hardness.The errors are caused by the processing of elastic-plastic data by the lock-in amplifier in a technique initially designed to be applied to elastic deformation only. Intuitively, the higher the amount of plastic deformation within a cycle is, the larger the difference to the ideal condition is, and the higher the error is. The exact mechanisms leading to this error are discussed based on simulated CSM signals and experimental measurements.

HP-ThP-7 Advanced Characterisation in Amorphous Thin Films for Biomedical Applications*, M. Sebastiani,* ***Edoardo M. Rossi (edoardo.rossi@uniroma3.it)**,* Università degli studi Roma Tre, Italy

One of the main goals of tissue engineering is the preparation of multifunctional biomaterials showing good mechanical properties, biocompatibility, and antibacterial activity simultaneously. Multi-element thin films are a new class of nano-engineered materials showing an excellent combination of high-strength and biocompatibility. Additions of Au, Cu, Zn or Ag to Ti-based films can induce potential antibacterial behavior [1, 2]. In this framework, Ti-Cu and Ti-Cu-Ag thin films were deposited on silicon substrate by physical vapor deposition magnetron sputtering (MS-PVD), with the aim of obtaining concurrent biocompatibility and antibacterial properties with better mechanical properties. The produced films were characterized by X-ray diffraction (XRD), nanoindentation, atomic force microscopy (AFM), scratch adhesion and X-ray photoelectron spectroscopy (XPS), to investigate their structural, mechanical, and surface properties. The biocompatibility of thin films is investigated by fibroblasts MRC-5 cell lines. Finally, the antibacterial activity of these thin films against Pseudomonas aeruginosa (P. aeruginosa) and Staphylococcus aureus (S. aureus) is evaluated and correlated to the Ag contents. Ti-Cu thin films shows complete amorphous structure, but addition of silver changes the film structure to partially crystalline at 20% Ag and completely crystalline at 30% Ag. XPS spectroscopy shows titanium oxidized to Ti (IV), copper partially oxidized to Cu (II) and partially in metallic state while silver remains unoxidized. The observed surface chemistry can be a main explanation for the excellent combination between biocompatibility and antibacterial properties [3]. In fact, the formation of mixed copper and titanium oxide on the surface of Ti-Cu and Ti-Cu-Ag thin films induces high biocompatibility and remarkable antibacterial properties.

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[3] S. Rashid, et. al., Nanomaterials 2021, 11, 435.

HP-ThP-8 Capabilities of Time-of-Flight Low-Energy Ion Scattering Demonstrated on the Example of Surface Oxidation of Ti and Ti-Based Hard Coatings*, **Philipp M. Wolf (philipp.wolf@physics.uu.se)**,* Department of Physics and Astronomy, Uppsala University, Sweden*; D. Neuß,* Materials Chemistry, RWTH Aachen University, Germany*; T. Tran,* Department of Physics and Astronomy, Uppsala University, Sweden*; M. Hans, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden

Ion scattering methods, especially Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA), are well established methods allowing the study of composition and structure of materials with a nm resolution. Ever thinner films and the study of surfaces introduce the need for a sub-nm resolution, difficult to achieve with MeV ion methods like RBS and ERDA. Here, we present a time-of-flight low-energy ion scattering (ToF–LEIS) setup, offering resolutions down to a monolayer,[1] using the exemplary case of surface oxidation of pure Ti and Ti-based hard coatings like TiN and (Ti,Al)N. The employed ToF-LEIS setup, able of detecting both neutrals and ions, offers high surface sensitivity to study the structure and composition of the outermost atomic layers by using primary ions with energies of 1–10 keV.[2] A connected preparation chamber, including an ion sputter gun, a heating filament, a gas inlet system, an Auger electron spectrometer (AES), a low-energy electron diffraction setup and an e^-–beam evaporator enables the in situ preparation and study of surfaces exposed to stimuli like high temperatures or reactive gases. The possibility of studying initial modification steps at surfaces not only offers further insights into the behavior of the immediate surface region, but can also yield knowledge on the general behavior of material systems. Due to the low ion currents necessary, ToF-LEIS, like other ion scattering methods, can be considered as non-destructive.

We demonstrate the analytical power of our approach by studying the surface oxidation of in situ grown Ti as well as ex situ grown Ti, TiN and (Ti,Al)N prepared by sputter deposition. These systems were chosen to compare surfaces more prone to oxidation like pure Ti with surfaces that show a comparably increased stability towards oxidation like TiN and (Ti,Al)N. The films were exposed to O_2 at pressures of 1.0×10^{-6} and 1.0×10^{-5} mbar for up to 90 min with sample temperatures ranging from room temperature up to 850°C. As expected, the ex situ grown Ti-based hard coatings show a high resistance to further surface oxidation even at increased temperatures, while for pure Ti we were able to observe surface oxidation both in AES and ToF-LEIS measurements already when offering 1.0×10^{-6} mbar O_2 for 30 min at room temperature, further increasing with the amount of offered O_2. The presented results showcase the capability of our ToF-LEIS setup to study surfaces and ultrathin films and the effects external stimuli have on them.

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Topical Symposia
Room Golden State Ballroom - Session TS1P-ThP
Anti- and De-Icing Surface Engineering - TS1 Poster Session

TS1P-ThP-1 A Fracture Mechanics Approach to Ice-Shedding Surfaces*, **Michael Wood (michael.wood3@mail.mcgill.ca)**, P. Servio, A. Kietzig,* McGill University, Dept. Chemical Engineering, Canada

The adhesion of ice to external structures has been a persistent engineering challenge. This includes the accumulation of ice on metallic structures such as aircraft wings and power transmission equipment. There has therefore been considerable effort put into the development of passive ice-shedding surfaces in the past few decades. To-date there have broadly been two prevailing research paradigms for the engineering of low ice adhesion strength surfaces: (i) application of low surface energy chemical coatings / infusion of sacrificial lubricants; and (ii) limiting ice-substrate contact through superhydrophobic texturing. The results of these efforts have been overall mixed with coatings and lubricants needing continual reapplication and superhydrophobic texturing often leading to ice-substrate interlocking effects. We take a decidedly different approach to the design of low ice adhesion surfaces by choosing microstructures which induce interfacial cracking in combination with cohesive failure of ice within microstructure pores, an approach that allows for ice-shedding surfaces to be made of bare metal. Specifically, in this work we test the ice adhesion characteristics of an ultra-fine woven stainless-steel wire cloth, which we show has an extremely low ice adhesion strength of 12.5 kPa. Our testing shows that the low ice adhesion strength stems from the three-dimensional microstructural network formed by the woven stainless-steel wires which make up the cloth. Compared to a monolithic metal surface, the cloth structure possesses pores at each weaving point which induce the formation of micro-cracks during the ice freezing process. The cloth also possesses microstructural compliance of each woven wire segment which leads to facile opening of each of these micro-cracks. Rather than relying on few cracks which must open from edge-to-edge of the ice-substrate interface on monolithic materials, cracks at the interface with the woven wire cloth need only open from one weaving point to the next. Starting first with this fracture mechanics approach to ice-shedding surface engineering and only then tuning the surface chemistry, we may see new benchmarks set for low ice adhesion strength surfaces.

Topical Symposia
Room Golden State Ballroom - Session TS3P-ThP
Electrochemical Cells – Hydrogen and Batteries - TS3 Poster Session

TS3P-ThP-1 Ionic Conductive Polymer Electrolyte for High-Performance Flexible Solid-State Supercapacitors*, **Haylay Ghidey Redda (ghaylay12@gmail.com)**, W. Su, R. Chen, B. Hwang,* National Taiwan University of Science and Technology, Taiwan

In recent years, high-performance ionic conductive polymer electrolytes have emerged as a crucial research target within flexible solid-state supercapacitors (FSSC). In this study, a flexible ionic conductive gel polymer electrolyte is designed to enhance FSSC's electrochemical stability and effectiveness. The ionic conductive gel polymer electrolyte is manufactured from 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfony)imide as ionic liquid (IL), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) as host polymer and $Li_{1.5}Al_{0.33}Sc_{0.17}Ge_{1.5}(PO_4)_3$ (LASGP) as ceramic filler. The scanning electron microscope (SEM) image confirms that a homogeneous uniform phase with a smooth surface is achieved as the ionic liquid is added into the host polymer solution. The X-ray diffraction (XRD) patterns show that the PVdF-HFP blend has a semi-crystalline structure, and its amorphous nature extends with increasing IL and LASGP ceramic fillers. In light of this, the GPE film is used as the electrolyte and separator due to its high ionic conductivity 78 mS cm^{-1}), excellent thermal stability up to 346℃. Finally, the AC||LASGP/IL/PVdF-HFP||AC FSSC cell achieves a remarkable high specific capacitance of 115.45 F g^{-1}, and its corresponding specific energy density reaches 27.10 Wh kg^{-1} at 1 mA. These results suggest that GPE films with activated carbon electrodes are candidate materials for nanotechnology systems and FSSC applications.

Functional Thin Films and Surfaces
Room Town & Country C - Session C4-FrM

Photo- and Electrochemically Active Surfaces

Moderators: Peter Kelly, Manchester Metropolitan University, UK, **Carlos Tavares**, University of Minho, Portugal

9:00am **C4-FrM-4 Shedding Light on Implant Biointerfaces: Designing Innovative Photocatalytic Coatings Towards Cell-Assisting and Bacteria-Killing Functions on Titanium***, **Valentim Barão (vbarao@unicamp.br)**, B. Nagay, C. Dini, H. Pantaroto,* University of Campinas (UNICAMP), Brazil **INVITED**

A significant concern emerging from current Implant Dentistry is the increasing prevalence of peri-implant infections and the lack of consensus on the most effective therapeutic technique to treat such diseases. Therefore, new strategies for peri-implant biofilm control are urged to be developed to guarantee the long-term predictability of the implant treatment. Within the context of photochemical processes, the development of photocatalytic coatings and photofunctionalized surfaces can be alternatives for reducing the biofilm formed on and assisting cellular interactions with dental implants. Targeting these optimal biological functions, the outstanding concept of photofunctionalization and photocatalysis for environmental decontamination, using the well-known crystalline titanium dioxide (TiO_2) coating as a photocatalyst, have shed light on scientists to the use of this strategy for biomedical implant application. Nevertheless, the use of photocatalysis for implant rehabilitation is still in its infancy. The main challenge of using TiO_2 as a photocatalyst for biomedical purposes is that, because of its wide band gap, TiO_2 can only produce bactericidal reactive oxygen species by ultraviolet (UV) light, which is harmful to human health due to its fast absorption by DNA. To overcome this limitation, photocatalytic coatings consisting of visible light-responsive photocatalysts have been developed for using with implants therapy. For this, to reduce the band gap to a level compatible with visible light ($\lambda \geq 400$ nm), it is necessary to resort to alternative strategies, such as elemental doping with metals and anions. Therefore, this presentation aims to approach multifunctional coatings for biomedical implants using the concepts of photocatalysis under UV and visible lights and the antibacterial mechanisms of biocompatible metals. We will also discuss the UV photofunctionalization on pre-osteoblastic cell differentiation and mineralization potential. In addition, the modulation of key inflammatory markers by UV-modified surfaces will also be addressed. From a clinical perspective, the use of light might be an effective strategy to reduce biofilm-related diseases and accelerate the wound healing of dental implants.

9:40am **C4-FrM-6 Hematite and Titania Thin Films: Energy and Environmental Applications (Virtual Presentation)***, **Josef Krysa (Josef.Krysa@vscht.cz)**,* University of Chemistry and Technology, Czechia **INVITED**

Titania (TiO2) and hematite (α-Fe2O3) have potential applications as semiconducting photoanodes for either hydrogen production *via* photoassisted water electrolysis or photoelectrochemical (PEC) oxidation of water pollutants. The advantages of TiO2 are high stability, nontoxicity, and low price. However, it absorbs only a very small part of sunlight (3% of the total power). On the other hand, iron oxide (α-Fe2O3) has a favourable band gap (2.0 – 2.2 eV), which enables absorption of a substantial fraction of solar light, resulting in the theoretical maximum power conversion efficiency of 27 %. This has created much interest in the past, which has been rekindled by the advent of new thin film preparation and texturization methods. Limitations are the non-ideal position of the conduction band, *i.e.* too large an electron affinity for spontaneous water reduction, low minority carrier diffusion length, surface states that can mediate recombination, low stability in acidic media, and photocorrosion. We have recently fabricated Sn-doped hematite (Fe2O3) films by aerosol pyrolysis (AP) on fluorine doped tin oxide (FTO). Photosensitivity had an onset around 650 nm and maximum incident photon to electron conversion efficiency (IPCE) was 0.21 at 400 nm. The aim of the present work was to check whether the capping with TiO2 can be used for corrosion protection of such films.

AP hematite films on FTO were covered by titania films fabricated by spray-pyrolytic coating. Spray pyrolysis of TiO2 used as precursor a 0.2 M ethanolic solution of titanium di-isopropoxide bis-acetylacetonate. AP hematite layers coated with TiO2 show that with increasing thickness (increasing number of passes of the spray nozzle) of the TiO2 coating the photoelectrochemical response decreased. This is due to TiO2 increasingly taking part in the solid liquid interface. This is also reflected in the photocurrent onset shifting to more negative potentials. The Faradaic efficiency (f) of the photocorrosion reaction in 1 M sulphuric acid decreased from 0.47 % (for an unprotected hematite electrode) to 0.17 % for that covered with spray coated TiO2 layer (but decreased photoresponse).

10:20am **C4-FrM-8 Multifunctional Coatings for Maritime Applications***, **José Castro (uc2021120076@student.uc.pt)**,* University of Coimbra, Colombia*; M. Lima, I. Carvalho, M. Henriques,* University of Minho, Portugal*; S. Carvalho,* University of Coimbra, Portugal

The main transportation system in the world commerce are ships and their problems could be critical, affecting the world economy. Corrosion and biofouling are considered like common issues associated to maritime components and those must be prevented to avoid possible damage, pollution or functional performance losses and hence, economical and environmental drawbacks. In this context, some products have been applied to minimize dead times in maintenance in ships, and hence extend its productive time. Tributyltin (TBT) paint was the most used solution before 2008, however it was banned since then. With this lack, multifunctional coatings seem to be a good option to replace TBT. Zirconium (oxy)nitrides doped with Cu obtained by Magnetron Sputtering technology, could gather the desired properties in maritime applications. The films were sputtered over SS316L substrates, material used largely in the naval industry, among others. Cu_xO_y and Zr(O)N coatings were deposited as control samples, and these helped to disclose features and mechanisms in Cu-Zr(O)N films. The properties of films were assessed by SEM, EDS, XRD, AFM, and OCA measurements. Also, EIS and potentiodynamic polarization tests were performed in NaCl (3.5% wt.) solution for 24 h to simulate seawater exposure. XPS were done before and after corrosion test to establish the action of copper and its reactivity with artificial seawater. Also, copper ionic release was studied in seawater by ICP-OES. Bacterial inactivity, which is directly related with the antibiofouling surface potential, was evaluated by inhibition halo tests. The results revealed that Cu did not react with Zr(O)N directly during deposition process. This demonstrates the influence of Cu in Zr(O)N was promote gaps among film's columns boundaries, affecting other films properties such as surface energy, roughness, and wettability. Concerning corrosion tests, Cu deteriorates the Zr(O)N chemical strength against seawater. On the other hand, ZrON film exhibited an antibacterial action with the Cu inclusion, though after the chemical activation. The Zr(O)N films were unable to capture enough oxygen to oxides the copper during the deposition process. With the additional availability of oxygen from the chemical activation process, the Cu inside the ZrON film, can react to form CuO. The Cu^{2+} ions releasing had no influence on the antibacterial film action. The presence of CuO was vital to get an antibacterial comportment. The obtained results shown the first sight of the potential of Cu-Zr(O)N films to be applied as a unique coating to avoid biofouling and corrosion under seawater exposure and replace TBT paint in maritime components.

New Horizons in Coatings and Thin Films
Room Town & Country C - Session F3-FrM

2D Materials: Synthesis, Characterization, and Applications

Moderator: Suneel Kodambaka, University of California Los Angeles, USA

8:00am **F3-FrM-1 Tackling Scalability in the Synthesis of Two Dimensional Chalcogenide Semiconductors and their Heterostructures***, **Nicholas Glavin (nicholas.glavin.1@us.af.mil)**,* Air Force Research Laboratory, USA **INVITED**

The rapid development of 5G communications, wearables, sensors, and internet of things have pushed forward the need for all types of electronics and sensors requiring the exceptional properties of two-dimensional (2D) nanomaterials. Graphene and other 2D materials have become an increasingly interesting candidate in these systems due to the mechanical strength and flexibility at the ultimate materials scaling limit, unique transport characteristics, tunable optical properties, controllable surface sites and the potential for facile device fabrication. In this talk, challenges and opportunities to address scalability in 2D material transition metal dichalcogenides is presented. These techniques include low cost and customizable laser-manufacturing approaches and a two-step metal conversion process for direct synthesis of superlattices to allow material properties by design.

8:40am **F3-FrM-3 2D Nanosheets Exfoliation and Functionalization from Hexagonal Boron Nitride in Aqueous Phase for Ultrafast Solvent Transport of Molecular Solute Screening Film**, ***Degu Lere Keshebo (keshebos@gmail.com)***, *C. HU, J. Lai,* National Taiwan University of Science and Technology, Taiwan

Currently hexagonal boron nitride is promising materials for its solidity in different working conditions but preparation based on environmental friendly technique is challenging. In this study, aqueous phase exfoliation using tannic acid has demonstrated an easy, novel, green method used to prepare functionalized boron nitride nanosheets. Both microscopic techniques (TEM, SEM AFM) and spectroscopic techniques (XRD, XPS, FTIR, and Raman) were used to characterize the exfoliated nanosheets and synthesized membrane. Tannic acid is adsorbed on hexagonal boron nitride surface and gradually exfoliating in the form of a few layers of functionalized boron nitride nanosheets, it behaves as a green surfactant by weakening the interlayer interaction. Ultimately, the functionalized exfoliated nanosheets used to prepare membrane for environmental applications. Fascinatingly, the prepared membrane is an exceedingly stable in water and other organic solvents and shows good efficiency in transporting solvents with excellent screening of solutes with long-term antifouling. The synthesized membrane's rapid transport rate of solvents and good separation efficiency of solutes can be due to robust nanochannel and thin laminar networks of nanosheets, which afford beneficial properties for the membrane effective separation and purification processes.

Keywords: hexagonal boron nitride, 2D nanosheets, tannic acid, noncovalent functionalization, antifouling, molecular sieving

Topical Symposia
Room Town & Country B - Session TS1-FrM
Anti- and De-Icing Surface Engineering

Moderators: Kevin Golovin, University of Toronto, Canada, **Jolanta-Ewa Klemberg-Sapieha**, École Polytechnique de Montréal, Canada

8:00am **TS1-FrM-1 Penguin-Inspired Anti-Icing Surfaces**, ***Anne Kietzig (anne.kietzig@mcgill.ca)***, *M. Wood,* McGill University, Canada **INVITED**

Over the past decades considerable research efforts have been made to provide novel and ideally passive anti-icing strategies. Broadly these efforts have either started off from aiming at reducing the amount of water present for solidification on a given surface or at facilitating the dislodging of already grown ice. In our work, we have addressed both aspects by taking inspiration from the South American penguin *Spheniscus humboldti* which exhibits strategies to not only shed water but also already accreted ice. The biomimicry of the Penguin feather's functionality is achieved by using a compliant finely woven wire cloth to mimic the microstructure of the feather in combination with using laser-micromachining to further decorate the latter with nanogrooves. Laser-micromachining in combination with selective post-processing techniques further allowed us to render the surface chemistry of our biomimetic surface either hydrophilic or hydrophobic, which allowed us to selectively identify the role of surface chemistry on our anti-icing surface. Our results from this biomimetic surface not only highlight that different physical mechanisms are at play when considering water and ice shedding, but also emphasizes the role of the hierarchical surface structure. Laser-machined nanogrooves with hydrophobic surface chemistry clearly support water shedding. Whereas, the porosity and compliance of the microstructure favors a multitude of evenly spaced crack initiation locations with facile and short pathways for crack propagation, which accordingly leads to exceptionally low ice adhesion strengths. In conclusion, our biomimetic approach highlights that having learnt from a natural example and abstracting the relevant features and functionalities to engineering provided us with a framework that exploits fracture mechanics to design the ice-shedding property and wetting science to separately design the water-shedding property.

8:40am **TS1-FrM-3 Screening of Anti-Icing Strategies Against Aeronautic Secondary Icing**, ***Paloma García (garciagp@inta.es)***, *J. Mora, F. Carreño, M. González, A. Agüero Bruna,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Ice protection is an important issue in the aeronautic field, which has been traditionally faced by the use of active systems (systems that need energy support). In last decades, the use of several passive solutions, based on surface engineering strategies, has been explored to replace the active systems, or to decrease their energy consumption. However, so far the idea of completely avoiding ice accretion with a passive system seems utopic. In addition, ice accretion affects different sections of aircrafts, but to present, a single method efficient in all possible icing locations, has not been found. Thus different solutions must be designed for each specific application, and testing should be undertaken attending to the different location issues.

For instance, electrothermal active systems are widely used to protect sensible areas on aircrafts, i. e. leading edges. Those systems increase the surface temperature to avoid ice accretion or release or melt the ice once it has been accreted. As a result, icing in the downstream area of the wing's chord is caused by exposure to this ice-melted water droplets as well as to direct supercooled water. This is considered as secondary or runback icing resulting in an important challenge in aviation, and the use of anti-icing solutions can perhaps contribute to avoid or reduce this issue.

In this work, 12 materials and references, attending to 5 different anti-icing strategies have been tested using a common methodology. These include Slippery Liquid Infused Porous Surfaces (SLIPS), elastomer coatings, superhydrophobic surfaces and low surface energy materials. The test methodology includes the evaluation of ice adhesion after impact icing in an icing wind tunnel (IWT) as well as ice accretion through direct impinging of supercooled droplets and after melting or heating in an active system in the IWT.

Among the studied materials, several coatings showed ice accretion reduction and some of them also significantly reduced ice adhesion. In general, 2 strategies showed more promising results in terms of anti-icing features: SLIPS and elastomeric coatings. In addition, low roughness, low surface energy and high water droplet mobility (low contact angle hysteresis) were correlated with anti-icing behaviour. These are easy to measure properties which do not require complex equipment that can be considered as indicators of potentially good anti icing and de-icing performance. Results also showed that superhydrophobic solutions reduced runback icing as a result of a reduced interaction of the melted ice droplets with the surface.

9:00am **TS1-FrM-4 Influence of Organosilicon Based Modification on Ice Adhesion and Wettability of Unsaturated Polyester Gelcoats Surfaces**, ***Rafal Kozera (rafal.kozera@pw.edu.pl)***, *B. Przybyszewski, K. Zolynska,* Warsaw University of Technology, Materials Science and Engineering, Poland; *B. Sztorch, R. Przekop,* Adam Mickiewicz University of Poznan, Poland; *A. Boczkowska,* Warsaw University of Technology, Materials Science and Engineering, Poland

In recent years, the world of science and industry has paid a lot of attention to coatings as a functional materials.Used as the outer layer on an composite elements, they fulfill a number of extremely important functions.Starting with protection against weather conditions, through improving mechanical properties, and ending with decorative functions. One of the significant problem in many industries is accumulation and build-up of ice and snow what is a negative and unwanted phenomenon. Ice formation and accretion present serious, sometimes catastrophic, safety issues for all kinds of industry where application of the composites components has already become common e.g. wind turbines blades, aircrafts, electric and telecommunication infrastructure as well as other composite constructions exposed to supercooled water droplets both on the ground and in the air. In example, ice on wind turbine blades or aircrafts disrupts airflow by altering the shape of the wing surface, which leads to increased drag and decreased efficiency of the systems what cause necessity for more often servicing and utilization of energy consuming systems.

In the present work, composite materials based on unsaturated polyester resin and authors' chemical modifications were prepared and characterized in order to find compromise between hydrophobic and icephobic properties. Studies were conducted by means of goniometer to investigate contact angle, hysteresis and roll of angle, ice adhesion tester in order to find correlation between modified surface and ice and profilometer for roughness characterization.

Presented work is conducted in the frame of the project entitled"ICEphobic SURfaces for components based on polymER composites- IceSurfer" (no. LIDER/16/0068/L-9/17/NCBR/2018) under the LIDER program of the National Center for Research and Development, Poland.

9:20am **TS1-FrM-5 Quasicrystalline Coatings Exhibit Durable Low Interfacial Toughness with Ice***, Kevin Golovin (kevin.golovin@utoronto.ca),* University of Toronto, Canada

Ice accretion can adversely impact many engineering structures in commercial and residential sectors. Although there are many reports of low-ice-adhesion-strength materials, a scalable and durable deicing solution remains elusive, as ice detachment is dominated by interfacial toughness for large interfaces. In this work, two durable quasicrystalline coatings (QC1 and QC2) were applied on aluminum substrates using HVOF thermal spray. XRD confirmed the quasicrystalline phases. Except for the roughest QC2 sample (root-mean-squared roughness ≈ 7 µm), a toughness-mediated regime of fracture was observed when detaching longer lengths of ice from the quasicrystalline coatings. The interfacial toughness was calculated to be 0.9 J/ m^2 for the smoothest QC1 sample (root-mean-squared roughness ≈ 1.5 µm) and 1.1 J/m^2 for the smoothest QC2 sample (root-mean-squared roughness ≈ 0.3 µm), demonstrating that low-interfacial toughness coatings are possible to fabricate from metallic materials. Apparent shear strengths as low as 30 and 80 kPa at an ice length of 20 cm were observed for QC1 and QC2, respectively. A small imposed deflection could also dislodge 20 cm-long pieces of accreted ice adhesively. Interfacial toughness increased with surface roughness in line with the concept of a shielding factor that hinders crack propagation. Finally, the mechanical durability of the smoothest QC1 and QC2 samples was confirmed using abrasion, UV irradiation, pencil scratching, elevated temperature, and chemical contamination. Overall, thin quasicrystalline coatings exhibit the unique combination of low interfacial toughness and high durability, leading to long-lasting ice protection applicable to many different surfaces.

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