

Hard Coatings and Vapor Deposition Technologies

Room Golden West - Session B5-1

Hard and Multifunctional Nanostructured Coatings

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

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

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

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

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

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

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

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

temperatures. The results document pronounced changes in the mechanical properties, thermal stability, residual stresses and wear resistance in the dependence of the coating architecture, which contributes to a general understanding of the structure-stress relationships in multi-layered films with various architectures and material combinations.

10:40am **B5-1-3 Plasma Tailoring for Controlled Compositional and Microstructural Evolution of TiB₂ Coatings from Magnetron Sputtering Techniques and DC Vacuum Arc**, *Johanna Rosen*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *N Nedfors*, *I Zhirkov*, Linköping University, IFM, Thin Film Physics Division, Sweden

INVITED

Titanium diboride (TiB₂) is a versatile (hard) material of high potential for various thin film applications due to its combination of, e.g., high strength, high melting temperature, and high conductivity. This presentation will show paths for controlled synthesis of TiB₂ through choice of synthesis technique and drastically different (inherent) plasma properties. Starting with magnetron sputtering of TiB, films from a TiB₂ target, it often result in highly overstoichiometric films due to differences in kinetic energy, ejection angle, and gas-phase scattering of sputtered Ti and B species. We show that the B/Ti atomic ratio can be reduced from 2.7 to 2.1 by increasing the Ar pressure from 5 mTorr to 20 mTorr, while also changing to stronger magnets in the magnetron to retain dense films of high crystal quality. High power impulse magnetron sputtering (HiPIMS) have a higher fraction of ionized sputtered species compared to regular dc magnetron sputtering, and it is possible to control the flux of ionized species by varying the pulse frequency, and hence duty cycle. This allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant. We show that the additional energy supplied during film growth in the HiPIMS process results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to \geq 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Applying a pulsed bias in synchronous with the HiPIMS pulse, the relative fractions of B⁺, Ti⁺ and Ar⁺ within the flux of bombarding ions can be varied. This makes it possible to tune and lower the residual stress compared to coatings deposited under bombardment of mainly Ar⁺ ions. Finally, we also present results from TiB₂ synthesis based on DC vacuum arc, and a new design of cathode - anode assembly allowing a stable, reproducible, and close to fully ionized plasma flux of Ti and B. The arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

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

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

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

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

Hard Coatings and Vapor Deposition Technologies

Room Golden West - Session B5-2

Hard and Multifunctional Nanostructured Coatings

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

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

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

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

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

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

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

In hot forging of steels, the severe mechanical impact and thermal cycling caused by the intermittent contact with the hot ingot, combined with a high abrasive wear, require coatings of good thermal resistance, high thickness, and sufficient energy-absorbing properties. Such coatings were deposited using the high-capacity industrial coating unit π^{1512} , equipped with a combination of cylindrical rotating and planar arc cathodes. An advanced multilayer concept, consisting of alternating nanostructured AlCrTiN- and CrN-based sublayers has been developed, where metallic nanoclusters were embedded into the CrN-based matrix. While the thick Al-rich AlCrTiN sublayers provide good high-temperature anti-wear properties and do act as a thermal barrier, the energy-absorbing CrN-metal composite sublayers reduce the intrinsic coating stress and improve coating compliance, thus allowing for the use of a thick coatings even for this high impact stress application.

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

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

2:10pm **B5-2-3 New Insights in High Temperature Properties and Oxidation Behaviour of AlCrSi₃N Coatings**, *Nikolaus Jäger, S Klima, M Meindlhumer*, Montanuniversität Leoben, Austria; *H Hruby*, eifeler-Vacotec GmbH, Germany; *C Mitterer, J Keckes, R Daniel*, Montanuniversität Leoben, Austria

Hard protective coatings are widely used to protect tools for numerous machining and forming applications. The requirements on the coating properties permanently rise due to the demand of their use under extreme conditions, such as for high-speed machining and dry cutting of hard-to-cut materials. Increasing loads and temperatures in the contact area between tool and work piece create severe challenges with respect to thermal stability and oxidation resistance, claiming for advanced hard coatings suitable for operation temperatures exceeding 1000°C. A solid understanding of the diffusional mechanisms resulting in oxidation and phase transformation of metastable phases is thus the basis to establish strategies for improved high-temperature behaviour of the protective coatings. In order to understand these mechanisms, thermogravimetry and differential scanning calorimetry were used to study the thermal stability and oxidation mechanism during annealing of arc evaporated AlCrSiN coatings with varying Si-content. Furthermore, synchrotron X-ray diffraction in Ar atmosphere was used for in-situ investigation of the high-temperature behaviour at temperatures up to 1100 °C. The results reveal the microstructural evolution, phase transformations and development of residual stresses during thermal loading, and show the positive impact of the Si-content. Additionally, a position resolved synchrotron X-ray nano-diffraction experiment was performed to study the formation of an oxide scale and the development of the microstructure and residual stresses of the Al₆₃Cr₂₇Si₁₀N coating across its thickness. Based on the results of this study, strategies to ensure an increased high-temperature stability and enhanced oxidation resistance of the coatings will be proposed to improve operation performance of the coated tool.

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

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

Hf-B-Si-X-C-N films were deposited onto Si(100), SiC and glass substrates using pulsed magnetron co-sputtering of a single B₄C-Hf-Si-X target (at a fixed 15% Hf fraction and a varying Si + X fraction in the target erosion area) in Ar + N₂ gas mixtures at the N₂ fraction of 15% and 25%. A planar unbalanced magnetron (127 × 254 mm² target) was driven by a pulsed dc power supply operating at a repetition frequency of 10 kHz with a fixed voltage pulse length of 50 μs (duty cycle of 50%). The total pressure was 0.5 Pa and the substrate temperature was adjusted to 450 °C during the deposition on the substrates at a floating potential.

All Hf-B-Si-X-C-N films possessed a sufficiently high hardness (close to 20 GPa), low compressive stress, high elastic recovery and high oxidation resistance in air at elevated temperatures (above 1000 °C). Addition of Y and Ho into the Hf-B-Si-C-N films prepared at the 25% N₂ fraction in the gas mixture resulted in enhancement of the optical transparency. Addition of Mo into the Hf-B-Si-C-N films prepared at the 15% N₂ fraction in the gas mixture led to an increase in the electrical conductivity.

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

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

INVITED

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

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

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

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

We achieved a dramatic increase in film growth rate from 4.8 to 8.4 $\mu\text{m}/\text{h}$ when sputtering a $\text{Ti}_{0.49}\text{Al}_{0.49}(\text{LaB}_6)_{0.02}$ instead of a $\text{Ti}_{0.50}\text{Al}_{0.50}$ target, while keeping all other deposition parameters unchanged. Due to the different poisoning behavior of Ti and Al, the Al-fractions of our coatings ($\text{Ti}_{0.42}\text{Al}_{0.58}\text{N}$ and $\text{Ti}_{0.42}\text{Al}_{0.56}\text{La}_{0.02}\text{B-N}$) is higher as that of the respective target. Furthermore, the hardness increased from 34 to 40 GPa, the maximum annealing temperature (before a significant hardness reduction sets in) increased from 800 to 1100 °C, and also the oxidation resistance was significantly improved. After exposure to ambient air at 950 °C for 1 h the oxide scale thickness is only 0.50 μm on our Ti Al La -B-N coatings, whereas the Ti Al N coatings were already fully oxidized. The results obtained even outperform the already excellent properties of Ce-alloyed Ti-Al-N.

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

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

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

In this talk, we will show the thermal evolution of nanometallic multilayers (NMMs) with the goal of elucidating on the microstructural transitions that occur during annealing; in turn, these findings will allow for a better understating of possible paths that could aid thermal stabilization. NMMs are nanostructured thin films that can be tailored to control the grain size and the local composition. Thus, NMMs configurations that favor selected kinetic paths were selected to resolve microstructures during thermal transitions. In this study, Hf-Ti and Mo-Au NMMs, deposited by magnetron

sputtering, were annealed at critical temperatures identified using DSC scans. The heat-treated samples were characterized by TEM and EDS techniques. The results provide insight into the mechanisms controlling the thermal evolution of nanocrystalline thin films.

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

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

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

Cr_2AlC MAX phase has aroused worldwide concern these years as the ternary nano-laminate structure enabled them with combined properties of both metal and ceramic. In the present work, in order to study influence of Al content on coatings property, coatings with different Al content were prepared by a post heat treatment of pre-deposited Cr-Al-C coatings. Rietveld refinement of XRD was used to quantitatively analyse the phase composition. Results showed that the coatings were composed of Cr_2AlC , Al_6Cr_5 and Cr_7C_3 with different percentage. The hardness of Cr_2AlC coating varied from 10.17 to 19.00 GPa, the modulus changed from 198.43 to 267.62 GPa. The relationship between phase composition and electrochemical corrosion behavior were also studied.

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

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

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

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

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

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

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

Hard Coatings and Vapor Deposition Technologies

Room Golden West - Session B1-1

PVD Coatings and Technologies

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

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

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

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

As examples of metastable transition metal oxides, the (Cr,Zr)₂O_{3+x} coatings deposited using reactive ion beam sputtering and the thin films of (Zr,Ta)O_{2+x} deposited using radiofrequency magnetron sputtering will be addressed. For the first system, the solubility of zirconia in chromia driven by the microstructure defects and in particular the mechanisms of the incorporation of zirconium into the crystal structure of Cr₂O₃ will be discussed. For the second system, the deposition of oversaturated (Zr,Ta)O_{2+x} having an orthorhombic crystal structure will be reported. For both oxide systems, it will also be shown, how the formation of nanocomposites and the presence of internal interfaces influence the thin films properties.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

CVD Coatings and Technologies

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

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

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

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

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

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

References:

[1] L. Chen, J. Paulitsch, Y. Du, et P. H. Mayrhofer, « Thermal stability and oxidation resistance of Ti–Al–N coatings », *Surf. Coat. Technol.*, vol. 206, n° 11–12, p. 2954–2960, févr. 2012.

[2] J. Todt *et al.*, « Superior oxidation resistance, mechanical properties and residual stresses of an Al-rich nanolamellar Ti_{0.05}Al_{0.95}N coating prepared by CVD », *Surf. Coat. Technol.*, vol. 258, p. 1119–1127, nov. 2014.

[3] J. Todt *et al.*, « Al-rich cubic Al_{0.8}Ti_{0.2}N coating with self-organized nano-lamellar microstructure: Thermal and mechanical properties », *Surf. Coat. Technol.*, vol. 291, p. 89–93, avr. 2016.

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

INVITED

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

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

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

TiAlN is today a common choice for wear-resistant coatings on cutting tools used for metal machining due to its high hardness and excellent oxidation resistance. For long, physical vapour deposition (PVD) has been the standard method for producing commercial available TiAlN coatings. Using PVD it has been impossible to reach Ti_(1-x)Al_xN coatings with a higher Al content than $x = 0.65$. A few years ago however a new low pressure chemical vapour deposition (CVD) technique was developed that makes it possible to deposit Ti_(1-x)Al_xN coatings with a very high Al content, $x = 0.9$. These high Al content TiAlN coatings show improved hardness compared to other TiAlN coatings and commercially available CVD grown TiAlN coatings are just reaching the market. However, wear-resistant coatings often combine layers of different materials to improve properties, where one common candidate is alumina. It is thus of interest to investigate if CVD grown TiAlN can be combined with other materials in multilayered coatings. In this work, the focus has been on investigating the possibility of growing kappa alumina on CVD grown TiAlN. TiAlN multilayer coatings were produced on standard WC/Co cemented carbide substrates, where

kappa alumina layers were grown on top of TiAlN layers with different texture. The coatings were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy (STEM and TEM), and energy dispersive X-ray analysis (EDX). Focus were on how the microstructure of the different textured TiAlN layers, which are metastable, changed when exposed to temperatures necessary for growing kappa alumina, and the texture of the grown kappa alumina. The results show that hexagonal AlN and cubic TiN can be found precipitated along grain boundaries in the TiAlN layers. The orientation relationships between TiAlN and kappa alumina layers were also described and a model for how the kappa alumina grains are growing on the TiAlN grains suggested.

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

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

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

10:00am B2-1-7 Some Guidelines for the Determination of Texture Coefficients in CVD α -Al₂O₃ Coatings, Rafael Stylianou, M Tkadletz, Montanuniversität Leoben, Austria; M Penoy, CERATIZIT Luxembourg S.à r.l., Luxembourg; C Czettl, CERATIZIT Austria GmbH, Austria; C Mitterer, Montanuniversität Leoben, Austria

α -Al₂O₃ coatings deposited onto cemented carbide tools by chemical vapor deposition (CVD) are widely employed in cutting applications due to their excellent wear resistance, thermal stability and chemical inertness. Recent advances have allowed the control of their crystallographic texture, enabling α -Al₂O₃ coatings to benefit from the anisotropy in wear resistance across various orientations. Within this study, a comprehensive microstructure characterization of CVD α -Al₂O₃ coatings is presented, with the goal to provide useful guidelines for the determination of their crystallographic texture in the growth direction using texture coefficients determined by X-ray diffraction, as well as pole figures derived from X-ray diffraction and electron back-scatter diffraction. Texture coefficient calculations require the X-ray diffraction intensities from a $\theta/2\theta$ scan of texturized coatings and non-texturized powder standards. Within this work, texturized coating intensities were determined for a representative sample (i.e. a CVD α -Al₂O₃ coating). Non-texturized intensities were retrieved, firstly from an equivalent coating turned into powder by chemically etching the substrate with HNO₃, and secondly from a corundum standard sample provided by NIST. Synchrotron intensity measurements have been performed for the non-texturized powder samples, and are used as a reference. In a next step, intensity data has been collected from four different X-ray diffractometers in parallel beam and Bragg-Brentano configurations, for both coating and powder samples. The calculated texture coefficients indicate a (001) growth texture, which was confirmed by pole figure measurements of the α -Al₂O₃ coating surface. Based on the results obtained, a simple set of guidelines is advised for the determination of texture coefficients: (a) X-ray intensity acquisition only for symmetric $\theta/2\theta$ scans, (b) removal of X-ray background intensity, (c) introduce intensity corrections, that take into account the irradiated α -Al₂O₃ volume, corresponding to each diffraction angle value, (d) use of reflections that have a high peak to background X-ray intensity ratio, (e) exclusion of second order reflections at the presence of first order reflections, (f) texture coefficients provided should be accompanied by the respective

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

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

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

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Hard Coatings and Vapor Deposition Technologies

Room Golden West - Session B1-2

PVD Coatings and Technologies

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

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

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

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

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

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

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

INVITED

Due to its high chemical stability, excellent biocompatibility, and refractory nature, metallic Tantalum (Ta) has been used in many areas, including microelectronics (e.g. in capacitors), biomedical implants, surgical instruments, masks in X-ray lithography, and structural applications at high-temperatures. Metallic Ta can have three different crystal structures: body-

centered cubic (alpha phase), tetragonal (beta phase), and face-centered cubic (FCC). Bulk Ta generally exists as alpha phase, which is relatively ductile and soft whereas Ta thin films obtained by vapor deposition are usually a mixture of alpha and beta phases. The beta phase, hard and brittle, is metastable and converts to the alpha phase upon heating to 750–775 °C. FCC Ta has only previously been reported as dispersed nano-grains embedded in alpha or beta phased ultrathin films or highly deformed bulk Ta. In this presentation, we report on the controlled synthesis of Ta thin films of a few micrometers on both Co-Cr-Mo alloy and Si substrates with the three different crystal structures, including single-phased alpha Ta, single-phased beta Ta, a mixture of alpha and beta Ta, single-phased FCC Ta, by magnetron sputtering. X-ray diffraction pattern of FCC Ta and the accurate determination of its lattice parameter are reported for the first time. Based on the results, a multilayered gradient Ta thin film, $\beta\text{-Ta}/\beta\text{-Ta}+\alpha\text{-Ta}/\alpha\text{-Ta}$, with high adhesion has been obtained on biomedical CoCrMo alloy sheets.

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

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

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

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

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

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

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

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

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

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

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

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

CVD Coatings and Technologies

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

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

Low reflective films containing CoO are processed by chemical vapor deposition from direct liquid injected solutions of $\text{Co}_2(\text{CO})_8$ in heptane, in the presence of oxygen. The films are deposited on silicon and epoxy resin – carbon fiber composite coupons in a cold wall reactor operated at 5 Torr between 50 °C and 160 °C. Those processed at 50 °C, 125 °C and 160 °C present a cauliflower-type nodular morphology, with distinct nodules grown on a relatively smooth background, with similar microstructure but on a finer scale. XRD and FTIR analysis reveal that low temperature processed films are composed of CoO, while those processed at 125 °C and above also contain the spinel structure Co_3O_4 . All films contain significant concentration of amorphous, aliphatic carbon. The optical reflectivity in the visible region stems from 1 to 14% depending on deposition temperature. The combination of specific microstructural features of the coatings, namely a fractal “cauliflower” morphology and a grainsize distribution more or less covering the near UV and IR wavelength ranges enhance light scattering and gives rise to a low reflectivity. In addition, the columnar morphology results in a density gradient in the vertical direction that we interpret as a refractive index gradient lowering reflectivity further down. The coating formed at 125°C shows the lowest reflectivity (1 %) in the range 400 – 750 nm and presents an interesting deep black diffuse aspect. It can thus be applied as antireflective coating in startracking instruments used for spacecrafts navigation.

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

SiC/SiC composites are of great interest for high temperature structural applications such as jet engines. The SiC matrix is usually deposited by chemical vapor deposition (or infiltration: CVD/CVI) using a mixture of methyltrichlorosilane (MTS, CH_3SiCl_3) and hydrogen. If not handled carefully, this process can lead to silicon co-deposition and inhomogeneous infiltration of the fiber fabrics. In this context, we have studied vinyltrichlorosilane (VTS, $\text{C}_2\text{H}_3\text{SiCl}_3$) as an alternative precursor for SiC. The low-pressure CVD reactor was associated to a microbalance and an FTIR spectrometer to record the deposition rate and the gas concentrations as a function of the deposition temperature, pressure, $\alpha = (P_{\text{VTS}}/P_{\text{H}_2})_{\text{initial}}$ and total flow rate. Model porous substrates were also submitted to CVD/CVI, to evaluate the homogeneity of infiltration in a few selected conditions. This approach allowed proposing a basic mechanism for the CVD using VTS/ H_2 and, besides, identifying proper conditions for the growth of pure and crystalline SiC. The Arrhenius plots of the deposition rate show three distinct kinetic domains. Free carbon is co-deposited within the low-temperature kinetically-controlled regime CRR1, while VTS is only partially decomposed. Such a carbon excess results from the formation of highly reactive carbon-bearing species, e.g. C_2H_3^* , in contrast with the silicon-bearing species. Changes in the heterogeneous reactions are responsible for a transient regime CRR2 characterized by a particularly high apparent activation energy and a hysteresis phenomenon. The higher temperature CRR3 domain, of lower activation energy, is more favorable to deposit pure SiC. In the gas phase, H_2 seems to play a role in the homogeneous decomposition of VTS. In the solid, the replacement of H_2 by Ar leads to carbon-rich coatings, as observed in the CRR1 domain. Low deposition temperatures are usually beneficial to the homogeneity of infiltration for the CVI process. The lowest thickness gradient between the surface and the core of porous substrates is indeed observed in the CRR1 domain. A carbon-rich coating is deposited at the entrance of the model channel pore but the composition sharply turns to pure SiC deeper in the channel. The influence of residence time τ_r and the depletion of the reactive carbon precursors in the gas phase is likely responsible for such a change in the nature of the deposit. By following the VTS concentration as a function of τ_r , the apparent activation energy of the homogeneous decomposition of the precursor could be evaluated at about 290 kJ/mol. A simple homogeneous and heterogeneous mechanism was constructed based on the previous investigations.

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

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

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

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

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

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

3:10pm **B2-2-6 Dense, Uniform, Transparent SiO₂/TiO₂ Coatings Derived from a Single Precursor Source of Tetrabutyl Titanate Modified Perhydropolysilazane**, *Zongbo Zhang*, Institute of Chemistry, Chinese Academy of Science, China; *D Wang*, University of Chinese Academy of Sciences, China; *Y Luo, C Xu*, Institute of Chemistry, Chinese Academy of Sciences, China

SiO₂/TiO₂ thin or multilayers of SiO₂ and TiO₂ coatings have been widely investigated and applied in the fields of optical waveguiding, antireflection coatings, thermal protection systems, self-cleaning coatings, and semiconductor devices, for their excellent optical, photocatalytic, superhydrophilic, electrical, and mechanical properties. Various methods have been adopted to prepare SiO₂/TiO₂ coatings, such as electron-beam evaporation, chemical vapor deposition (CVD), and sol-gel process. Among these methods, the sol-gel method is simple and inexpensive, especially suitable for preparation of coatings on components with complex surface or big dimensions. However, due to the faster hydrolysis rate of Ti precursor, co-hydrolysis of alkoxysilane and tetra-alkyl orthotitanate usually achieve inhomogeneous dispersion of SiO₂ and TiO₂ sol, which results in aggregates, cavities, rough surface in the formed SiO₂-TiO₂ coating.

In this work, dense, uniform, transparent, robust SiO₂/TiO₂ composite coatings have been successfully prepared by hydrolysis and subsequent thermal treatment of tetrabutyl titanate-modified perhydropolysilazane. The composition analysis revealed that Ti element was uniformly distributed in the composite coatings. The anatase TiO₂ formed initially in the coating when the heat-treatment temperature reached 700°C. The as-prepared coatings have their thickness in range of 100 to 142 nm, and transmittance over 90% in the visible region. The refractive index, surface hardness, and elastic modulus of coatings enhanced continuously with the increasing pyrolytic temperature. Besides, the obtained coating possesses excellent hydrophilicity with contact angle below 40° and low roughness with Sa below 3.5nm.

3:30pm **B2-2-7 Emerging Photoluminescence in Chemical Vapor Deposition Grown MoSe₂/h-BN Van der Waals Heterostructure**, *Pramoda K. Nayak*, Indian Institute of Technology Madras, India; *S Ahn, C Hyun, K Ma, H Shin*, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Atomically thin transition metal dichalcogenides (TMDCs) with chemical formula MX₂ (M = W, Mo and so on, and X = S, Se, or Te) have attracted considerable interest today owing to their sizable band gap in a technologically interesting range 1–3 eV [1], which paves the way to consider these materials for new generation field-effect transistors, sensors and optoelectronic devices. In parallel, hexagonal boron nitride (h-BN) have also gained a great deal of attention in the last few years with the emergence of two-dimensional atomic crystals and its unique electronic properties including wide band gap, low dielectric constant, high thermal conductivity and chemical inertness [2]. Van der Waals heterostructures made up of TMDCs and h-BN are supposed to exhibit improved materials properties which are different from that of individual counterparts [3]. Mechanical transfer process is the most preferred way to prepare TMDCs/h-BN HS, which includes a deposition of polymers and a solution-based washing process [4], that degrades the quality of sample. Therefore, it is very necessary to develop a simple, fast, and scalable direct growth process to avoid any material deterioration that arises during wet-chemical assisted transfer processes.

In this work, we report direct growth of MoSe₂ onto high-quality multilayer h-BN using chemical vapor deposition. Interestingly, we observed emerging photoluminescence in MoSe₂/h-BN HS, *i.e.* the PL intensity of monolayer MoSe₂ increases by one order of magnitude with reduced FWHM of 45 meV, implying high crystallinity of MoSe₂ while prepared on h-BN substrate. This is attributed due to the good interlayer coupling, cleaner and sharper interfaces, smaller lattice strain, and lower doping of the underlying h-BN substrate [5]. Our work allows fabrication of a variety of TMDCs/h-BN heterostructures and paves new direction to consider these materials for next-generation optoelectronics devices including solar cells, LEDs, Laser diodes and so on.

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[2] G. Cassabois, P. Valvin, B. Gil, *Nature Photonics* 10, 262–266 (2016).

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

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

[5] S. Wang, X. Wang, J. H. Warner, *ACS Nano* 9, 5246–5254 (2015).

3:50pm **B2-2-8 Innovative Concepts for Advanced CVD Carbide Coatings Grown by Direct Liquid Injection of Metalorganic Precursors**, *Francis Maury*, CIRIMAT, CNRS - University of Toulouse, France; *A Michau, CEA Saclay, France; G Boisselier*, CIRIMAT, France; *F Schuster*, CEA Saclay, France DLI-MOCVD is an emerging CVD process that combines the use of metalorganic precursors (MO) and direct liquid injection (DLI) of the reactive sources. The main advantages are a significant reduction of the deposition temperatures and the feeding of the reactor by high vapor flow rates. Even if the process can operate at atmospheric pressure, *e.g.* for continuous scrolling treatment, it is under moderately reduced pressures (0.1-5 kPa) that application prospects are greatest due to the diversity of coatings that can be deposited for surface engineering.

Initially DLI technology has been developed and has grown rapidly for the deposition of functional oxide thin films for optical and electronic devices. In that case, oxygen-containing precursors can be selected due to their good volatility, stability and solubility in organic solvents. A solution of precursor is injected and O₂ flow rate is frequently added to prevent the film contamination by carbon originating both from the solvent and the precursor since it can be consumed by combustion in the reactor. Oxidation of the film is not a problem since it is an oxide that is deposited.

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

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

Tuesday Afternoon, April 24, 2018

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

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

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

In the present work, the CVD process for (Ti,Si)_x(C,N)_y coating in the vertical hot-wall reactor was studied through the Computational Fluid Dynamics (CFD) simulation method. By means of ANSYS Fluent software, the reactor model was established and meshed. The CVD process of (Ti,Si)_x(C,N)_y coating from TiCl₄-SiCl₄-CH₃CN-NH₃-H₂ gas mixture was investigated under different deposition conditions. The thermal and hydrodynamic characteristics inside the reactor were simulated. The influence of concentration of gas species on the growth rate of (Ti,Si)_x(C,N)_y coating deposited on specimens, which were located at different position of the reactor, was predicted. The computational predictions of the growth rate were in reasonable agreement with the experimental measurements. The CFD method is of great importance to optimize the process parameters and provide theoretical guidance for improving the coating uniformity in thermal CVD process.

4:30pm **B2-2-10 Tribological Evaluation and Behavior of DLC Coatings on Steel in PE-CVD System with TiO₂ Over Layer using ALD Technique**, *Marco A. Ramirez R.*, Univap, Brazil; *E Saito*, Federal University of São Paulo, Brazil; *N Fukumasu*, University of São Paulo, Brazil

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

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

PVD Coatings and Technologies

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

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

The highest quality oxides such as SiO₂, Al₂O₃ and Indium Tin Oxide (ITO) require high temperature processing either during the growth of the film or annealing post-growth. Thermal SiO₂ is grown at ≈1000 °C, ALD Al₂O₃ is deposited at ≈300 °C, and magnetron-sputtered ITO must be annealed above 350 °C in order to turn the film conductive. These elevated temperature requirements are not compatible with polymer substrates used for flexible electronics.

We have deposited dense and pinhole-free thin films of SiO₂, Al₂O₃ and ITO at room temperature via ion beam sputtering. The deposition system consists of a 3-grid 14 cm RF ion gun directed at 200 mm targets of SiO₂, Al and ITO. All three processes require a small flow of O₂ to achieve stoichiometry. Typical conditions were: argon flow rate 3.3x10⁻⁷ m³/s, beam voltage 600 V, beam current 220 mA and acceleration voltage 150 V. The substrate wafers were kept at 20 °C. The base vacuum prior to deposition was 2.6x10⁻⁶ Pa.

The SiO₂ films were 100 nm thick and measured by the mercury probe technique to obtain the C-V and I-V characteristics. The films were found to be of similar quality as thermal oxide with a resistivity of 10¹⁴ Ω·m, breakdown field in excess of 7x10⁸ V/m, and pinhole-free with an etch rate in 6:1 Buffered Oxide Etch (BOE) of 1.6 nm/s.

The Al₂O₃ films were part of a Pt-Al₂O₃-Pt vertical tunnel junction and were kept extremely thin, from 3 nm to 4 nm. The current-voltage characteristics of these junctions indicated a breakdown field roughly twice that achieved by ALD films for the same structure. This breakdown voltage was found to be independent of junction area, strongly suggesting the absence of pinholes in the film.

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

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

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

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

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

TiO_xN_y-based decorative coatings were deposited using a reactive DC magnetron sputter deposition method. The substrates included Al, stainless steel, and Ti. Optical properties of single-layered and double-layered TiO_xN_y coatings were both investigated. The color of the coating was controlled by manipulating the sputter deposition conditions, including gas pressure and composition, DC power, electrode distance, and substrate type. Selected coatings were also deposited with an anti-reflective layer.

The resulting coatings were characterized using SEM, XRD, XPS, TEM, UV-vis spectroscopy, a-step, ellipsometry, and colorimetry. We show that at least 6 different colors were obtained on each type of the substrate, either single- or double-layered.

9:40am B1-3-6 SiO₂/Sc_{0.31}Al_{0.69}N/LiNbO₃ Multilayer Structure for SAW Device Applications, Chun-Ting Shen, National Cheng Kung University, Taiwan; *S Wu,* Tung-Fang Design University, Taiwan; *J Huang,* National Cheng Kung University, Taiwan

We report a temperature compensated surface acoustic wave (SAW) device on a SiO₂/Sc_{0.31}Al_{0.69}N/LiNbO₃ structure. The Sc_xAl_{1-x}N films (x=0.23, 0.24, 0.26, 0.29, 0.31, 0.34, 0.39) are deposited on lithium niobate substrate by reactive magnetron co-sputtering using Al and Sc as targets. The films have (002) texture and different degree of lattice strain caused by Sc atoms replacing specific Al sites. The highest piezoelectric coefficient (d₃₃) value 22.2 pm/V is achieved at x=0.31, which corresponds to the largest lattice distortion presented in 2D-XRD data. The electromechanical coupling coefficient (K²) and temperature coefficient of frequency (TCF) of SAW devices with different SiO₂ thickness on Sc_{0.31}Al_{0.69}N/LiNbO₃ are compared. The SiO₂/Sc_{0.31}Al_{0.69}N/LiNbO₃ structure have a great potential in high bandwidth, high temperature stability SAW device application.

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

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

Wednesday Morning, April 25, 2018

Hard Coatings and Vapor Deposition Technologies

Room California - Session B6

Coating Design and Architectures

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

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

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

Boride-, or diboride thin films in particular, show promising results when considering their use as hard protective coatings. Their drawback in ductility for binary systems calls for improvement via further alloying elements. Instead of trial and error, when designing novel ternary coating systems, we use a semi-automated High Throughput Search (HTS) calculating the basic properties (e.g., lattice parameters, bulk moduli, elastic constants, etc.) of all different TMB₂s' in two stable/metastable hexagonal structures (space group 191 with prototype AlB₂ vs space group 194 with prototype W₂B_{5-x}) via density functional theory (DFT).

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

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

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

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

Improved toughness is one of the central goals in the development of wear-resistant coatings. Extensive theoretical and experimental work has revealed that single-crystal NaCl-structure VMoN ceramics possess inherently enhanced ductility, as well as high hardness (≈20 GPa) [Kindlund et al. APL Mat 2013]. These surprising findings demonstrate that VMoN-

based materials are very promising candidates for replacing other ceramics in hard, refractory protective-coating applications. However, during applications, hard coatings inevitably oxidize which can compromise material properties. Herein, we use density functional theory to evaluate the mechanical properties, as well as the thermodynamical stability, of V_{0.5}Mo_{0.5}N_{1-x}O_x, with x approximately equal to 0.05, 0.1, and 0.5. We study cubic V_{0.5}Mo_{0.5}N_{1-x}O_x solid solutions characterized by both high and low short-range cation/anion ordering. V_{0.5}Mo_{0.5}N_{1-x}O_x is predicted to be thermodynamically stable for x < 0.1, although higher oxygen ratios can possibly be achieved with non-equilibrium growth techniques such as physical vapor deposition. Our results show that oxygen concentrations x = 5% and 10% have little effect on the mechanical properties of random V_{0.5}Mo_{0.5}N_{1-x}O_x alloys, which retain both hardness and ductility. At x = 50%, bulk, elastic, and shear moduli, as well as Cauchy pressure, are reduced by ~25%, but the material is still predicted to remain ductile. For ordered V_{0.5}Mo_{0.5}N_{1-x}O_x, x = 6% already results in a drastic change in mechanical properties, likely due to disruption of the cubic symmetry. A further increase in the oxygen content yields significant reductions in Cauchy pressures, indicating reduced ductility. However, the Cauchy pressure remains positive for all oxygen concentrations, suggesting that none of the investigated alloys are brittle according to the Pugh and Pettifor criteria.

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

The Al-Si-O-N material system allows for the creation of various hard, transparent thin films by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS). Combinations of the possible binary materials AlN, Al₂O₃, Si₃N₄ and SiO₂ lead on to ternary materials such as Al-O-N and Al-Si-N, and combining the latter two yields quaternary Al-Si-O-N. As long as the films are fully nitrated and / or oxidized, they are transparent and thus interesting for optical applications.

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

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

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

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

Wednesday Morning, April 25, 2018

10:00am **B6-7 The Effect of Hybrid PVD Process on the Mechanical and Antistatic Properties of TiO₂ Based Nanocomposite Thin Film**, *Ding-Shiang Wang, M Leu, T Chen, H Lai, J Chang, J Shih*, Industrial Technology Research Institute, Taiwan

In this paper, mechanical and antistatic properties of magnetron sputtered, filtered arc ion plating (FAIP) and a hybrid PVD process (magnetron sputtered+FAIP) prepared TiO₂ based nanocomposite thin film were investigated. Both of the antistatic properties of different thin films were analysis by measuring resistance values and decay times. The results showed that for magnetron sputtered and hybrid process prepared TiO₂ based nanocomposite thin film showed resistance around 10⁶~10⁸ W/sq and a short decay time. But for the FAIP process, the resistance uniformity is at about 80 %. In terms of mechanical properties, the FAIP and hybrid process nanocomposite thin film showed adhesion and hardness at around 15 N , 14 N and 15 GPa, 12GPa. For the nanocomposite thin film prepared by magnetron sputtered the adhesion and hardness are only about 9 N and 10 GPa. Thus for a high quality of antistatic tin film the hybrid PVD process was recommend due to the excellent mechanical and antistatic properties.

10:20am **B6-8 Optical, Electrical and Structural Characteristics of Mg-doped CuCrO₂ Transparent Conductive Thin Films**, *Ruei-Sung Yu, C Chu*, Asia University, Taiwan

CuCrO₂ is a transparent conductive oxide with a wide bandgap greater than 3.0 eV. The oxide is a p-type semiconductor that the main carrier is hole. CuCrO₂ can be used in various transparent optoelectronic p-n diodes. This study is focused on the features of magnesium (Mg) doping on the improvements of optical and electrical properties for the CuCrO₂ films. It is anticipated that the p-type CuCrO₂ with high conductivity, which is conducive to the developments of transparent p-n devices. We prepared CuCrO₂ films by using sol-gel method and the annealing under controlled argon atmosphere, with the attempt to identify the chemical composition, crystal structure, cross-section microstructure, surface morphology, and optoelectronic properties. The modulation of sol-gel process, the precursor solutions used were copper acetate, chromium acetate, magnesium acetate, triethanolamine, and anhydrous ethanol. The annealing temperature was 600°C for 120 minutes. XPS, XRD, FESEM, AFM, UV-Vis, and Hall effect measurements were employed to analyze the material properties. This study has established to decrease resistivity of p-type CuCrO₂ film by doping magnesium. The CuCrO₂ films with Mg were increased gradually from 0.20 at.% to 2.17 at.%. These compositions deviated from the stoichiometric proportion of 25, 25, and 50 at.% of Cu, Cr, and O, respectively. In the films, Cu and Cr were insufficient quantity. The oxygen was higher than the set proportion. The Mg were introduced in the delafossite CuCrO₂ films without any impurity phase. With the increase of the Mg doping, the surface root mean square roughness values of the CuCrO₂ decreased from 23.4 nm to 16.6 nm, and the direct bandgaps of the thin films increased from 3.09 eV to 3.13 eV. The proper contents of Mg doping in the CuCrO₂ can improve transmittance, and the films possess a higher absorption ability for ultraviolet light. The magnesium (Mg²⁺) replaced chromium (Cr³⁺) in the lattice sites of CuCrO₂, which can form carrier and increase the concentration. The resistivities of the undoped and optimal Mg-doped CuCrO₂ films were respectively 41.09 Ωcm and 0.64 Ωcm.

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

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

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

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

Zr and ZrC_x thin films are deposited on single-crystalline Al₂O₃(0001) and MgO(001) substrates at temperatures T_s between 723 K and 1323 K using pure Ar and Ar/C₂H₄ gas mixtures, respectively. The as-deposited film surface structure and composition are characterized *in situ* using low-energy electron diffraction and Auger electron spectroscopy. The bulk crystallinity, microstructure, and composition of the films are determined using a combination of x-ray diffraction, transmission electron microscopy, energy dispersive x-ray spectroscopy and x-ray photoelectron spectroscopy measurements. Using pure Ar discharges, we obtain single-crystalline hexagonal close-packed (hcp) Zr(0001)/Al₂O₃(0001) layers at 873 K ≤ T_s ≤ 973 K and {0001}-textured Zr layers at higher T_s. We attribute these results to the formation of Zr-Al intermetallic compounds at the Zr-Al₂O₃(0001) interfaces at higher T_s. With the introduction of C₂H₄, at low partial pressures of 2 × 10⁻⁷ Torr (with Ar pressure ~ 10 mTorr), we obtain smooth, hcp-Zr(0001):C layers. With increasing fraction of C₂H₄, we obtain increasingly C-rich ZrC_x layers whose crystallinity and composition vary sensitively with T_s. We expect that our results provide previously unknown information concerning the growth-related aspects of reactively sputter-deposited ZrC_x thin films.

Hard Coatings and Vapor Deposition Technologies

Room Golden West - Session B1-4

PVD Coatings and Technologies

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

2:10pm **B1-4-3 Particles in PVD-Coatings: Imperfection or Functional Add-on Feature?**, *Uwe Beck, J Baier, M Sahre, M Weise, G Hidde*, BAM Berlin, Germany

The application of PVD-coatings ranges from mechanical engineering, i.e. thicker tribological coatings, to precision optics, i.e. thinner optical coatings. For physical vapor deposition (PVD) technologies such as evaporation, sputtering, ion beam assisted/driven deposition, vacuum is a prerequisite for two reasons: at first process-related ones (evaporation source, plasma discharge, and mean free path) and at second coating-related ones (pure, perfect, and dense films). Usually, the goal is a homogenous coating of defined stoichiometry and micro-structure without any imperfection.

However, the implementation of micro- or nano-particles may occur accidentally or deliberately. Independent of the particle origin, there are two fundamental rules regarding coating functionality: at first, the larger the particle diameter to coating thickness ratio the more affected the functionality of the coating, and at second, the larger the material contrast in terms of the functional feature of interest the more affected the coating performance. Hence, embedded particles have to be avoided for the majority of thin films by all means. The unintended implementation of particles usually results in a malfunction of the coating from the beginning or is at least considered as a weak point of the coating creating a time-dependent defect under service conditions. The intended implementation of particles on surfaces and in coatings may create add-on features, topographic ones and functional ones, however, the facts mentioned hold true.

Examples of particle-initiated coating defects are demonstrated in dependence on the origin and the field of application. Strategies for deliberate attachment/embedding of particles on surfaces/in coatings are discussed regarding process compatibility and coating integrity. For industrial applications, both the validation of process compatibility of particle injection and the plasma resistance of particles under vacuum and plasma conditions have to be confirmed. Further points of interest are the homogeneity of particle distribution and the avoidance of particle agglomeration which is still a crucial point for dry dispersed particles. So far, technical applications are limited to PVD hybrid coatings, plasma dispersion coatings are still a challenge except for applications where homogeneity is not required as in case of product authentication.

2:30pm **B1-4-4 Gradient Coating for NIF Double Shell Targets**, *Hongwei Xu*, General Atomics, USA

Double shell provides an alternative implosion platform for National ignition facilities (NIF). Double shell inner shell incorporates density graded layer to suppress Rayleigh-Taylor instability during implosion caused by inhomogeneity. We will report our efforts of fabricating density graded layers for double shell inner shell using magnetron sputtering and characterization of graded layers. The cold welding was observed for a lot of metals when deposited on a spherical mandrel, which seems correlated with material ductility. W-Be gradient layer was fabricated for double shell inner shell because of their large density difference and microstructure changes were revealed with varying composition. A W-Be amorphous phase was also discovered.

2:50pm **B1-4-5 Growth Morphology and Piezoelectric Properties of AlN Thin Films Deposited by Reactive DC Magnetron Sputtering**, *Mathis Trant, M Fischer, K Thorwarth, H Hug*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The piezoelectric properties of aluminum nitride (AlN) make it a good candidate for many applications in microelectronics, electroacoustic and optoelectronics. Magnetron sputtering is widely used to prepare AlN thin films so that they can easily be integrated into, for example, MEMS devices. However, controlling the microstructure and microchemistry, especially at low deposition temperatures, is crucial for a good performance. Ions impacting on the growing film can be used advantageously in magnetron sputtering to address these needs. We investigate the effect of low energy

ion bombardment on the AlN thin film growth morphology and its correlation to piezoelectric properties.

An electromagnetic coil is used to generate a variable magnetic field that allows varying the ratio of ions and neutrals impacting on the growing film by more than one order of magnitude. With an increasing ion flux, the residual stress of AlN thin films changes from tensile to compressive. This evolution is compatible with a change in the growth morphology from open grain boundaries towards dense films. The piezoelectric properties of AlN thin films in the different growth regimes are discussed and possible applications for scanning probe microscopy are presented.

3:10pm **B1-4-6 Plasma Generation and Coating Composition from Ti-C, Ti-Al, and Ti-W Cathodes used in DC Vacuum Arc**, *Igor Zhirkov*, Linköping University, Sweden; *P Polcik, S Kolozsvári*, Plansee Composite Materials GmbH, Germany; *J Rosen*, Linköping University, Sweden

Arc deposition from composite cathodes is a common method for synthesis of a wide range of functional coatings. A commonly used cathode element is Ti, which combined with different elements can deliver properties of coatings requiring in various applications. To understand the plasma generation from these cathodes is of importance for controlling the structural and compositional evolution of the coating of interest. In this work, we present the correlation between cathode, plasma and film composition for Ti-C, Ti-Al, and Ti-W composite cathodes of various stoichiometry used for DC vacuum arc depositions. The generated plasmas are characterized with respect to plasma chemistry and charge-state-resolved ion energy, and the intensity of the macroparticle flux is evaluated. The obtained results are compared to corresponding evaluation of elemental Ti, Al, C and W cathodes. We show that the plasma and film composition are in good agreement for the Ti-Al and the Ti-W cathodes, while for the Ti-C cathodes, there is a significant loss (~ 50%) of the light element. We also show, that the kinetic energies of ions from the Ti-Al and Ti-W cathodes are slightly different from those from the elemental cathodes, while the difference between the Ti-C and Ti cathode is more pronounced (Ti³⁺ average ion energy; ~ 90 eV and ~ 50 eV, respectively). The ion charge states are also found to be sensitive to cathode composition. The overall observations are explained by the cohesive energies and melting temperatures of the phases present at the cathode surface during arcing, while also considering transportation of ions of different mass within the generated plasmas. The systematic evaluation of general trends in properties of the generated material fluxes accompanying the addition of elements of different masses and chemical reactivity (C, Al, W) to a Ti cathode, contributes to an increased understanding of plasma generation from a two element cathode, which in turn may provide guidance for selection of cathodes and experimental conditions for other material systems.

3:30pm **B1-4-7 Improved Adhesion Strength of the Gradient Zn-Mg Coating on TRIP Steel**, *Myeongkyu Song, J La, H Kim, S Lee*, Korea Aerospace University, Republic of Korea

The high-strength steels (HSS) such as dual phase (DP) steel, transformation-induced plasticity (TRIP) steel, and twinning-induced plasticity (TWIP) steel have been used extensively in automotive industries to reduce the weight and to improve the safety of automobiles. To ensure the corrosion resistance of HSS, advanced coating material and process to replace conventional galvanizing coating and process are necessary. Zn-Mg coating is a strong candidate for the corrosion protective coating of HSS, and physical vapor deposition (PVD) process is a promising process for deposition of Zn-Mg coating on HSS. As reported in previous works, however, the Zn-Mg coating showed the insufficient adhesion strength compared to Zn coating due to the high brittleness of the Zn-Mg coating.

In this study, to improve the adhesion strength of the Zn-Mg coating, the Zn-Mg/Zn coatings were synthesized on TRIP steel substrate using evaporation deposition process, and the annealing heat treatment at 200°C in vacuum led to the gradient Mg content along the cross-section of Zn-Mg coatings. Microstructure, chemical composition depth profile, and adhesion strength of gradient Zn-Mg coatings were investigated by field emission scanning electron microscopy (FE-SEM), glow discharge optical emission spectroscopy (GDOES), and punch test, respectively. The gradient Zn-Mg coating was synthesized successfully by heat treatment of Zn-Mg/Zn coating. The gradient Zn-Mg coatings showed an improved adhesion of the coatings during adhesion test, and this indicated that the adhesion strength of Zn-Mg coating could be improved by the gradient Mg content. Detailed experimental results will be presented.

Acknowledgement

Wednesday Afternoon, April 25, 2018

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Hard Coatings and Vapor Deposition Technologies Room California - Session B3

Deposition Technologies and Applications for Diamond-like Coatings

Moderators: Frank Papa, Gencoa, Konrad Fadenberger, Robert Bosch GmbH

1:30pm B3-1 Tribology of Diamondlike Carbons in Various Application Environments, *Gary Doll*, University of Akron, USA **INVITED**

Hydrogen free and hydrogen containing amorphous carbon materials are commonly referred to as diamondlike carbons. Due to the hardness and the ability to deposit coatings at temperatures compatible with most engineering materials, diamondlike carbons have become widely used as tribological coatings for addressing friction and wear in mechanical components. There are few if any intrinsic properties of these synthetic materials since their mechanical, structural, and compositional properties are strongly dependent upon the deposition process conditions. Furthermore, a high level of fundamental knowledge on how material properties relate to the tribological performances of diamondlike carbon coatings in various application environments has not been achieved. Application environments can be categorized by the type of tribological contact (rolling, sliding, mixed mode), lubrication condition, temperature, atmosphere, loading, and other items. This presentation shall discuss several examples where subtle differences in the deposition processes of diamondlike carbon coatings were responsible for transitioning unacceptable tribological performances in specific application environments to acceptable ones.

2:10pm B3-3 Synthesis and Comparison of Highly Tetrahedral Amorphous Carbon by Arc-mixed HiPIMS and Arc-free HiPIMS Modes, *H Hug, Rajesh Ganesan, K Thorwarth*, EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *M Tucker, N Marks*, Curtin University, Australia; *M Stüber, S Ulrich*, Karlsruhe Institute of Technology (KIT), Germany; *D McKenzie, M Bilek*, The University of Sydney, Australia; *S Guimond, M Arndt*, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Tetrahedral amorphous carbon films with high sp^3 content have been synthesized by high power impulse magnetron sputtering (HiPIMS) operated in an arc-free sputtering mode and in a mixed sputtering/arc mode. The properties of the films deposited in these both modes have been compared. In the mixed-mode, the presence of macroparticles in the deposited films were observed, though the amount and size of macroparticles are less than that of the ones in the films deposited by filtered cathodic arc vapour deposition. The short-lived cathode spots form in the magnetic racetrack and produce large numbers of carbon ions in the mixed-mode HiPIMS. In the arc-free HiPIMS, the macroparticle content in the films have been significantly reduced, however the deposition process has to be tuned for high degree of carbon ion production in order to compensate the loss of arc-facilitated carbon ion generation.

2:30pm B3-4 Evaluation of Superhard ta-C Coatings for the Machining of Synthetic Materials, *Frank Kaulfuss*, Fraunhofer Institute for Material and Beam Technology (IWS), Germany; *D Hoesel*, Fraunhofer Institute for Machine Tools and Forming Technology (IWU), Germany; *V Weihnacht, A Leson*, Fraunhofer Institute for Material and Beam Technology (IWS), Germany

The superhard ta-C carbon coatings are outstandingly suited as friction-reducing protective coatings for lubricated and non-lubricated application conditions. They can be deposited on all kinds of tools and components with very good adhesion over a wide coating thickness range. The coating is applied with the Laser-Arc technology, particularly developed for ta-C coatings. In order to obtain a high ta-C coating quality with low defect densities, a plasma filtering technique is used. With hardness of up to 70 GPa, ta-C coatings nearly reach the hardness of nanocrystalline diamond coatings. This results in an unusually high resistance to abrasive wear, above all in the machining of challenging composite materials. At the same time, the carbon surface reduces adhesion of material and causes very low friction between the tool edge and the cutting chips. The combination of

hardness and low friction provides ta-C coatings with a special advantage for the processing of composite materials.

2:50pm B3-5 Selection of DLC Coatings for Application in Wrist-watch Mechanisms, *Steve Franklin*, Steve Franklin Consultancy, Netherlands

Traditionally, watch manufacturers use liquid lubricants, sometimes applied to up to 100 individual lubrication points, to achieve the required low and stable friction behaviour between components and sufficient lifetime performance. Despite the careful treatment of parts and use of specific (often customized) lubricants, after a few years, the effectiveness of the lubricants degrades through evaporation, (wear) particle contamination, etc., and as a consequence watches break down or do not perform as required. In addition, some lubrication points are very difficult to access.

The goal of this study was to evaluate whether, for certain watch components, solid-lubricating coatings can be used to replace liquid lubricants.

Eight different types of Diamond Like Carbon (DLC) coatings and a titanium-stabilized MoS_2 coating (all commercially available, different suppliers), which had been preselected from a wider range of possibilities, were evaluated in laboratory tribological tests. The tests were carried out in air under reciprocating sliding conditions using an uncoated steel ball (4.5 mm diameter) sliding on a coated steel plate at 2N load, 10 mm/s sliding speed and at two levels of humidity, 30% and 70% RH. These conditions were chosen in order to simulate the actual use conditions as closely as possible. All tests were carried out three times to gain insight into the repeatability of the results.

The friction force was recorded continuously as a function of sliding distance up to 720m, corresponding to a test duration of 20 hrs. The average wear rate of the coating was determined at the end of the test, based on surface profilometry. Scanning Electron Microscopy (SEM) was used to examine the coatings and associated steel balls after testing.

Clear differences were observed in the friction and wear behaviour of the different coatings but this did not correlate well with coating hardness. Transfer layer formation from the coating onto the steel ball was observed in all cases and it is hypothesized that the formation of this layer is related to the running-in behaviour, i.e. the sliding distance needed in order to achieve a stable friction force. The characteristic appearance of the transfer layer, as observed using SEM, varied considerably between the coatings tested. Increasing the humidity from 30% to 70% had relatively small effects on the friction and wear behaviour.

Three coatings, Ti-MoS₂, a-C:H and Si-doped DLC, were found to exhibit the best performance in terms of tribological criteria specific to the application. These coatings were selected for further testing using actual watch components.

3:10pm B3-6 The Role of HiPIMS and Discharges with a Positive Voltage Reversal on Coating Properties in Industrial Applications such as Hard Coatings and DLC, *Ivan Fernandez, A Wennberg, F Papa*, Nano4energy SL, Spain; *G Eichenhofer*, HiP-V, Germany

HiPIMS (High Power Impulse Magnetron Sputtering) is a magnetron sputtering technology devoted to produce thin film coatings with enhanced properties. The technology offers advantages such as denser coatings, higher hardness values and smoother surfaces. This paper presents studies of the role the HiPIMS discharge, as well as an added positive voltage reversal pulse right after the negative HiPIMS pulse, have on coating properties and productivity in industrial applications.

The instant advantage is that the magnetron surface will be immediately discharged, which will reduce the tendency to arcing. However, there are several other effects observed during the performance of reactive sputtering, such as enhanced high energetic positive ion bombardment towards the substrate. Due to raise of the plasma potential, higher incorporation of reactive species into the depositing film, enhanced deposition rates and elastic hardness values, as well as crystallinity will be affected.

Measurements of the deposition rate, coating hardness and crystallinity have been performed for different metallic coatings (Ti, Al) as well as nitrides (TiN) and oxides (TiO₂) deposited in reactive mode and more recently the effects that HiPIMS and positive voltage reversal plays on DLC coatings, in terms of adhesion as well as the functional layer.

Wednesday Afternoon, April 25, 2018

3:30pm **B3-7 Towards New Horizon for DLC Coating Technology for Automotive Components, Tetsuya Takahashi**, Kobe Steel, Ltd., Japan
INVITED

Minimization of energy loss due to friction of sliding parts in automotive components becomes increasingly important to increase overall energy efficiency of vehicle. Surface engineering through application of DLC coating is effective to lead to enhancement of wear resistance and sliding property, and hence widely used in recent automotive industry. A product range of DLC coatings in automotive components includes, for instance, fuel injection system, valve lifter, rocker arm, piston ring, gears. Items for application have been expanding more and more in recent years. Depending on its application, suitable deposition techniques shall be selected and the process parameters including design of adhesion layer are optimized accordingly. In addition to conventional hydrogen containing DLC coatings, hydrogen free DLC having a high sp³/sp² ratio, also referred to as ta-C (tetrahedral amorphous carbon), draws a great practical attention due to its unique features of high hardness >40 GPa and a possible superlubrication effect in a particular lubricating condition. Deposition of ta-C with the controlled property and ensured adhesion is of practical significance. A productivity of coating process, i.e., throughput, is equally important especially for an industrial mass production scale.

In this work we compare systematically various DLC coatings deposited by various industrial vacuum coating technologies of, for instance, unbalanced magnetron sputtering, cathodic arc, also referred to as arc ion plating, and plasma enhanced CVD process. These are presented with respect to the coating properties, applications, and productivity. Our particular interest is also placed on ta-C coatings deposited by cathodic arc. We have developed a round-bar type target specially designed for ta-C coatings for industrial scale. The target was a pure graphite with a typical diameter of 20 mm. A stable arc discharge was sustained at a target surface either in vacuum or in inert gas atmosphere. The coatings were characterized as a low hydrogen content of <1%, high sp³ fraction of >80%, and high hardness of up to 70 GPa. Also the coatings exhibited a relatively low surface roughness in as deposited condition, implying a less emission of macroparticles without any mechanical and/or magnetic filter. For better understanding of intrinsic mechanical properties of coatings, Micro Slurry Erosion (MSE) test was performed where erosion rate of material against blasting was quantitatively evaluated and served as a representative material parameter. The results of MSE of some selected coatings are discussed in relation to the material properties and respective coating parameters.

4:10pm **B3-9 DC/Pulsed Cathodic Arc Discharge for Deposition of ta-C Coatings, Xiubo Tian, P Wan, H Liu, C Gong**, State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, China

The ta-C films have gained more interest in industrial applications due to excellent properties including good chemical stability, high hardness and wear resistance, good biocompatibility. Vacuum arc is an effective tool to deposit Ta-C films. To achieve better microstructure and surface properties, we have developed new power supply and system. The cathodic carbon arc may be driven by the specially designed power supply to produce required plasmas. With the assistance of external magnetic field, the plasmas near the samples may be optimized. In order to improve the adhesion between the film and substrate, the bottom layer and support layer were deposited. The processing parameters have to be optimized for the top ta-C coatings (thin and thick). A proper coil current (external magnetic field) was needed to achieve better adhesion of the films. A larger arc current was not favorable for better microstructure and surface properties. With the DC arc, the ta-C film possessed the nanohardness of 33.5GPa with a coil current of 0.1A. With the pulse work mode of arc power supply, a hardness of 45GPa was obtained with average current of 80A. The ta-C films have been utilized on surgical knives and cutting tools. The discharge of pulsed carbon arc, microstructure and surface properties of ta-c films will be presented.

4:30pm **B3-10 A General Engineering Applicable Superlubricity: Hydrogenated Amorphous Carbon Film Containing Nano Diamond Particles, Junyan Zhang, Z Cao**, State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

Designing promising mechanical systems with ultra-low friction performance and establishing superlubricity regimes are desirable not only to greatly save energy but also to reduce hazardous waste emissions. However, very few macroscale superlubricity regimes for engineering applications have been reported. Here, we demonstrate that sustained superlubricity can be achieved at engineering scale when the contact pressure is higher than 2 GPa. Such engineering superlubricity originates

from the *in situ* formation of curved graphene ribbons or onion carbon tribo-films at the sliding interface. Experimental data also demonstrate the wear of the amorphous carbon film containing some nano-diamond particles against Al₂O₃ ball is consistent with atomic attrition. A feasible two-stage mechanism is proposed to explain the friction and wear behaviors. This finding in amorphous carbon films will not only enrich the understanding of superlubricity behavior, but also be helpful to establish more superlubricity regime for more engineering applications.

Hard Coatings and Vapor Deposition Technologies Room Golden West - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-1-1 Contact Fatigue Performance of Cobalt Boride Coatings**, *A Meneses-Amador, D Sandoval-Juárez, G Rodríguez-Castro, D Fernández-Valdés, I Campos-Silva*, IPN, Mexico; *A Mouftiez*, ICAM Lille, Matériaux, France; *JoséLuis Arciniega-Martínez*, IPN, Mexico

In this work, an experimental and numerical study of the contact fatigue test on cobalt boride (CoB/Co₂B) coatings is presented. The boride layers were formed at the surface of Co-Cr-Mo alloy using the powder-pack boriding process at temperatures of 1123 K for 3 h and 1223 for 1 and 5 h of exposure times in order to obtain three different thicknesses. From the set of experimental conditions of the boriding process, contact fatigue tests were performed with a servo-hydraulic universal testing machine by repetitive impact of a sphere on the layer-substrate system. The methodology of the contact fatigue test consisted of two main stages. First a static critical load was determined, where radial cracks were considered as the failure criterion afterward fatigue conditions were conducted in low-cycle ($n < 100,000$) using sub-critical loads with a frequency of 6 Hz. The test results indicate that the thinner coating exhibited improved resistance to fatigue. In order to evaluate the stress field generated in the boride coating during the application of static and dynamic loads, a numerical simulations based in the finite element method was developed.

8:20am **B4-1-2 Revisiting the Nanocomposite Structure of Sputtered TiSiN Films**, *F Fernandes*, University of Coimbra, Portugal; *S Calderon, P Ferreira*, International Iberian Nanotechnology Laboratory, Portugal; *Albano Cavaleiro*, University of Coimbra, Portugal

TiSiN coatings with nanocomposite structure have been one of the most studied systems in the field of hard coatings with a large application in advanced machining and other high temperature cases due to their excellent mechanical, thermal and tribological properties. In a recent publication (F. Fernandes et al., SCT 264(2014)140), the authors have shown that the nanocomposite structure of these films can be easily achieved and tailored by changing relevant parameters during the deposition using the emergent HiPIMS technology (high power impulse magnetron sputtering), without requiring heating of the substrate. Here, we evaluate the effect of increasing the peak power on the nanocomposite structure of the TiSiN films and its correlation with their mechanical properties. For comparison purposes a TiSiN film deposited by direct current magnetron sputtering (DCMS) was also deposited, without substrate heating. The structure of the films was fully characterized by transmission electron microscopy (TEM) and X-ray diffraction. High-resolution plan-view and cross-sectional TEM, electron SAED patterns and EELS / EDS chemical analyses were performed to understand the elemental distribution and the phases presented in the films. The results revealed that, independently of the deposition process and deposition conditions, Si segregation was always observed. However, the coatings deposited by DCMS, or HiPIMS with low peak power, showed much more Si content in solid solution in the TiN lattice than the films deposited with higher adatom mobility (HiPIMS with high peak power). In the former, an extremely high number of dislocations are forming a network inside TiN grains that seems to be related to Si segregation. This distribution could evolve to a tenuous nanocomposite structure, which is clearly visible in the last ones, as usually encountered in high adatom mobility depositions of this system, TiN grains surrounded by a Si-N amorphous layer. The high number of dislocations can justify the hardness improvement of the coatings in relation to single TiN.

8:40am **B4-1-3 Nanostructured Functional Coatings – From Process Diagnostics in High Power Pulsed Plasmas to Coating Properties and Performance**, *Tobias Brögelmann, K Bobzin, N Kruppe, M Arghavani, M Engels*, Surface Engineering Institute - RWTH Aachen University, Germany

INVITED

The sustainable conservation of resources, the protection of environment, and the demand for increased productivity in manufacturing processes are the key drivers behind the design of physical vapor deposition (PVD) functional coatings that combine a low coefficient of friction and a low

wear rate over a wide range of working environments. This applies in particular to industrial applications like forging and metal cutting. The measures to increase productivity and sustainability of machining, such as high speed cutting, high performance cutting, and dry machining sharpen the demands on cutting tools. As a result of advanced cutting parameters in combination with the continuous development of new workpiece materials, nanostructured PVD coatings reach a 15 % share of the world market of hard and super-hard cutting materials in 2013, and will acquire an even stronger role in future tool development. Nanostructured functional coatings based on a nanocrystalline, -laminate, or -composite structure open a new path to the design of coatings with tailor made properties. High performance plasmas, such as high power pulsed magnetron sputtering (HPPMS) provide a complex deposition parameter set to control the structure on a nanometer scale and adjust the coating properties. However, reaching the full potential of the process technology and the nanostructured coating requires fundamental understanding and full control of the deposition process, in particular when using an industrial scale coating unit with a multi-fold rotating substrate holder.

In this talk, highlights of research and development at Surface Engineering Institute of RWTH Aachen University on nitride based nanolaminate and -composite PVD coatings for use in forming and machining processes will be presented. The plasma in reactive HPPMS and dcMS/HPPMS hybrid processes is investigated by space- and time-resolved plasma diagnostics. Further investigations are focusing on the relationship among pulse parameters and coatings properties, such as chemical composition, intrinsic stress and elastic-plastic behavior. Correlations between the plasma properties, the pulse parameters, such as pulse length, frequency, and pulse power, and the coating properties are the basis for process and coating adjustment to the demands in forging and machining. Due to highly non-linear or multidimensional cause-effect relations artificial neural networks (ANN) are trained with extensive data sets to link the process parameters to the coating properties. This comprehension-oriented approach will contribute to overcome the empirical approach on the synthesis path of nanostructured coatings in high performance plasmas.

9:20am **B4-1-5 Mechanical and Tribological Properties of Gradient and Multilayered CrVN/CrMoN Coatings**, *Y Chang, Chih-Cheng Chuang*, National Formosa University, Taiwan

Transition metal nitride coatings have been used as a protection of cutting and forming tools for several decades. To extend the lifetimes of these protective nitride coatings, numerous efforts have been made on enhancing hardness and oxidation resistance by incorporating elements such as Al, Mo, V and Si etc. into CrN and TiN to form gradient and multilayered coatings. Vanadium nitride (VN) is easily oxidized to form vanadium oxides and becomes lubricious under stress. In this study, gradient and multilayered CrVN/CrMoN coatings were synthesized by cathodic-arc evaporation. During the coating process of CrVN/CrMoN, CrN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. By controlling the different negative bias voltages and cathode currents, the CrVN/CrMoN possessed different microstructures and mechanical properties. The microstructure of the deposited coatings were investigated by field emission scanning electron microscope (FE-SEM) and field emission gun high resolution transmission electron microscope (FEG-HRTEM), equipped with an energy-dispersive X-ray analysis spectrometer (EDS). Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the films. The hardness of coatings was evaluated using nanoindentation and Vickers hardness measurement. Ball-on-disc wear tests were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. To evaluate the impact fracture resistance of the coatings, an impact fatigue test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. The combination of CrMoN and CrVN provides an alternative for a hard and lubricious coating. The design of gradient and multilayered CrVN/CrMoN coatings is anticipated to be advantageous in applications to enhance the machining quality of the cutting tools and life of mechanical parts.

9:40am **B4-1-6 Synthesis and Characterization of Multilayered Coatings in the Ti-Al-N System by a Reactive Gas Pulsing Process**, *Ahmed El Moutassim, M Pac, P Henry, LPMT, France; C Rousselot, FEMTO-ST, France; C Tromas, F Pailloux, T Cabioch, SP2MI, France*

Nanostructured coatings of metallic nitrides are commonly used in the industry as protecting coatings for cutting tools due to an excellent combination of properties including a high hardness, improved wear properties and oxidation resistance. To improve their functionality towards

various applications, it is necessary to test new deposition techniques beyond the conventional PVD techniques such as magnetron sputtering. The coatings here studied are synthesized by using a "Reactive Gas Pulsing Process" (RGPP) which is a promising new technique allowing one to obtain multilayer compositionally modulated coatings with potential excellent mechanical properties.

$Ti_xAl_{1-x}N/Ti_yAl_{1-y}N_y$ ($x \approx y \approx 0.5$; $0 \leq y \leq 0.8$) multilayers were synthesized, cyclical variations of the nitrogen flux being imposed during the deposition process to obtain a stacking of bilayers (thickness in the range 12-36 nm) for a total thickness varying from 400 nm to 2 mm. The coatings were characterized by using mechanical testing (friction test, scratch test, nanoindentation) and structural characterization techniques (X-Ray Diffraction (XRD), Scanning and Transmission Electron Microscopy (SEM, TEM), Electron Energy Loss Spectroscopy (EELS),...

Very different mechanical properties were obtained for coatings made of ceramic/ceramic bilayers ($y > 0.4$) and those with ceramic/metal bilayers ($y > 0.4$) and those with ceramic/metal bilayers ($y = 0$), the latter being softer with very poor tribological properties due to the presence of the TiAl phase. Very different internal stresses were also found for ceramic/ceramic and metal/ceramic multilayers. Observations in a TEM (HR, HAADF, SAED,...) combined with EELS experiments allowed to discuss the evolution of the microstructure and of the stoichiometry of the multilayer during the growth process. Complex phenomena like nitrogen interdiffusion and poisoning effect of the target during the deposition process have to be taken into account to discuss nitrogen amount and environment.

10:00am B4-1-7 Tribological Behavior of Transition Metal Nitride Films with Crystalline and Noncrystalline Tailored Multilayer Structure, Z Lin, Fan-Bean Wu, National United University, Taiwan

The transition metal nitride, TMN, films, including TaN, HfN, and MoN, were fabricated by RF magnetron sputtering with various microstructure features through input power and gas flow ratio control. With Ar/N₂ gas ratios and RF input powers from 8/12 to 18/2 and 75 to 300 W, respectively, the TMN nitride films evolved from crystalline, nanocrystalline to amorphous features. The multilayer films were further produced through tailoring of thin layers of above mentioned structural features to enhance the tribological behavior as protective coatings. Scratch and linear reciprocated pin-on-disc wear tests were practiced on singlelayer and multilayer TMN films to evaluate the adhesion strength and failure behavior. Severe cracking and chipping were found for the singlelayer TMN films with crystalline structure. Limited adhesive failure was observed for the multilayer coatings with alternate stacking of layers with different microstructures. Lower coefficient of friction for the crystalline/noncrystalline tailored multilayer TMN films during wear activities was also evident for their superior protective characteristics.

10:20am B4-1-8 Investigation of Microstructure and Properties of Magnetron Sputtered Zr-Si-N Thin Films with Different Si Content, Daniel Fernandez, Universidade Federal de Sergipe, Brazil; F Freitas, Universidade Federal de Sergipe, Brazil; L Félix, A Terto, Universidade Federal de Sergipe, Brazil; A Junior, Universidade Federal do Rio Grande do Sul, Brazil; F Mendes, Instituto Nacional de Tecnologia, Brazil; E Tentardini, Universidade Federal de Sergipe, Brazil, Brasil

The incorporation of silicon into zirconium nitride (ZrN) thin films is a known alternative to effectively refine their grains and improve mechanical properties and oxidation resistance. However, it is not well clarified in literature information regarding the structure formation mechanism and the influence of Si content in the chemical and physical properties of Zr-Si-N thin films. Thus, the aim of this work is to investigate the influence of varying Si concentration in the microstructure, morphology, mechanical properties and oxidation resistance of ZrN films. Pure ZrN and Zr-Si-N thin films were deposited by reactive magnetron sputtering technique, with Si content set between 3 and 15%. Characterizations were carried out using GAXRD, TEM, XPS, and high temperature oxidation tests. It was identified amorphous and crystalline areas along the films microstructure, consisting in crystalline grains embedded in an amorphous phase, which were characterized by EDS as Zr and Si rich areas, respectively. GAXRD results indicate peak intensity reduction and broadening increase due silicon nitride segregation to grain boundaries, which is responsible for grain size reduction, reaching magnitudes lower than 10 nm, calculated by Scherrer. GAXRD peaks shift are observed for all samples and it can be explained due formation of a solid solution in which Si replaces Zr atoms in ZrN crystal lattice and due a strong interface between crystalline phase and amorphous one. XPS confirmed the presence of compounds like ZrN and Si₃N₄ and it is also possible to infer the formation of a solid solution of Si in

ZrN lattice. Oxidation tests were performed at temperatures in the range of 773 K to 1373 K. ZrN film is almost fully oxidized at 773 K, while films with high silicon content maintain ZrN grains stable at 973 K. When oxidized, ZrN films form monoclinic ZrO₂ phase, but, in films with silicon addition, the stable phase is the tetragonal one. This happens due ZrN grain size reduction, because tetragonal phase has the lowest surface energy. Oxidation tests results confirm that there is a mechanism acting as diffusion barrier in films, preventing grains coalescence and oxygen diffusion into film structure. This mechanism is a direct consequence of silicon segregation process to grain boundaries, which ensures the formation of a nanostructure composed of ZrN grains embedded by an amorphous Si₃N₄ layer (nc-ZrN/a-Si₃N₄), allowing oxidation resistance improvement in at least 473 K.

10:40am B4-1-9 Low Temperature Surface Modification on Selected Thin Films Using HIPIMS for Antibacterial and Bio Applications, Wan-Yu Wu, Da-Yeh University, Taiwan

INVITED

In recent years, high power impulse magnetron sputtering (HIPIMS) has drawn a lot of attentions due to its high ionization of the working gas and the target atoms, and its ability to improve the quality of the resulting films, for example, better adhesion, higher density, and reduced surface roughness. Also, HIPIMS process allows the use of temperature-sensitive materials as the substrates. This feature opens a new window of applications. In this study, Ti-Cu, Cu-Ag, and TiN thin films were deposited using HIPIMS under various the target currents. The characteristics of these thin films, including microstructure, morphology, composition, adhesion to the substrate, and chemical bonding state are reported and discussed. Furthermore, the antibacterial activity, the corrosion resistance in simulated bodily fluid, the wear resistance against to the Al₂O₃ ball, and the biocompatibility test to MG63/3T3 were also presented.

11:20am B4-1-11 Using Nano-impact Method to Predict Erosion Performance of Advanced DLC Coating Systems, Samuel McMaster, T Liskiewicz, A Neville, University of Leeds, UK; B Beake, Micro Materials Ltd, UK

Diamond-like carbon is a metastable form of amorphous carbon with varying ratios of sp²/sp³ bonding. These coatings possess attractive mechanical, optical, chemical and tribological properties [1]. DLC coatings are becoming increasingly popular in the automotive and aerospace industry due to their high hardness, resistance to wear and low friction coefficient [2]. They can suffer from poor adhesion at high loads and impact stresses [3].

Well characterised coatings will enable the relationship between mechanical properties and impact behaviour to be studied. Impact and erosion testing has been used as part of a comparative study equating the energies dispersed in the substrate surface and characterising the wear scars produced by each method. DLC impact fatigue resistance requires improvement for more demanding applications [4].

Mechanical properties have been measured by nanoindentation using a partial loading technique. Variations in hardness and elastic modulus have been mapped through the multilayer coating structure. Macro-scale coating adhesion has been tested through scratch testing.

The DLC coating systems have been varied in this study by changing the composition (a-C:H, Si-doped and W-doped), coating thickness (1 micron and 3 microns), substrate material (316L stainless steel and hardened M2 Tool Steel) and substrate roughness (0.01 microns and 0.08 microns). All DLC coatings in this study have a gradient interlayer present.

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Thursday Morning, April 26, 2018

11:40am **B4-1-12 A Novel Methodology for Damage Characterization in Thin Hard Coatings Submitted to Extreme Loadings**, *Antonios Choleridis*, Ecole Nationale Supérieure des Mines de St-Etienne, France; *C Héau, M Leroy*, Institut de Recherche en Ingénierie des Surfaces, Groupe HEF, France; *S Sao-Joao, G Kermouche*, Ecole Nationale Supérieure des Mines de St-Etienne, France; *C Donnet*, Université de Lyon, Université Jean Monnet, France; *H Klöcker*, Ecole Nationale Supérieure des Mines de St-Etienne, France

Cost efficient PECVD deposited DLC is especially used in the automotive industry. While DLC coated components exhibit very little wear having a reduced friction coefficient [1], under severe conditions blistering driven in service delamination can sometimes be observed.

Perfectly adherent DLC coatings with high compressive process induced residual stresses were deposited on a M2 steel substrate and a thin under layer. Residual stresses, quantified on FIB milled micro-beams and by FE analysis [2,3,4] vary between 1 GPa and 2 GPa for the thinnest and thickest DLC coating respectively.

The samples were tested in severe loading conditions in a novel friction test facility. This test consists of a rotating ring rubbing against the surface of the DLC coated sample in an oil bath at 100°C. At the same time, an oscillating in-plane movement of the specimen takes place. The damage induced by the extreme loading conditions has been characterized by post mortem SEM and FIB observations.

FIB cross sections on blisters reveal the substrate microstructure, the interface and the different layers of the coating. To analyze the damage mechanism a novel characterization methodology was applied.

Successive FIB cross sections allow analyzing blister nucleation. Blistering occurs close to the underlayer/steel interface inside steel. The steel thickness is maximal in the center of the blister and decreases moving to its borders. For these reasons the blister was withdrawn in order to analyze this supplementary layer by EDS. The quantity of iron (Fe) detected by EDX analyses through several zones of this film confirmed the previous SEM observations.

Cracks initiate inside the M2 steel substrate, several nanometers beneath the (M2)-(under-layer) interface. The cracks then propagate towards this interface and propagation ends with interfacial failure. Carbides lead to local crack kinking.

The new methodology for analyzing damage of thin hard coatings presented here gives the necessary inputs for modelling coating delamination at a scale defined by the substrate microstructure.

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Hard Coatings and Vapor Deposition Technologies Room Golden West - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

1:30pm **B4-2-1 Target Race Track Chemistry is Different to What you Think: XPS Findings from Reactive dc and High Power Impulse Magnetron Sputtering Experiments**, *Grzegorz Greczynski*, Linköping University, IFM, Thin Film Physics Division, Sweden; *S Mráz*, RWTH Aachen University, Germany; *L Hultman*, Linköping University, IFM, Thin Film Physics Division, Sweden; *J Schneider*, RWTH Aachen University, Germany

It is demonstrated, that high power impulse magnetron sputtering (HIPIMS) of Ti target in Ar/N₂ atmosphere results in the formation of a nitride layer in the center portion of the race track, which is much thicker than during conventional dc process. Evidence comes from XPS *ex-situ* analyses of native Ti target surface chemistry [1][2] as well as from complementary sputter depth profiles, which reveal that, under identical process conditions and with N partial pressure optimized to yield stoichiometric TiN films, the compound layer is a factor of 2.5× thicker during HIPIMS. Even at values too low to yield stoichiometric TiN films on the substrate, the ~ 50 Å thick surface region of the HIPIMS operated target is severely nitrated (N/Ti ≥ 0.9), which is in stark contrast to dc magnetron sputtering where stoichiometric layers can be grown while avoiding target poisoning.[3] TRIDYN simulations of ion/target interactions reveal that such deep N implantation is only possible if N⁺ dominates the ion flux to the target during HIPIMS. These results are crucial for an understanding of reactive HIPIMS sputtering processes and finding robust working points necessary to grow high quality functional coatings at acceptable deposition rates.

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1:50pm **B4-2-2 Measurement of Residual Stress on TiN/Ti Bilayer Thin Films using Average X-ray Strain (AXS) Combined with Nanoindentation Methods**, *JiaHong Huang*, *S Lei*, National Tsing Hua University, Taiwan; *H Chen*, National Chiao Tung University, Taiwan

Pure metal interlayers are commonly applied in the hard and protective coatings to relieve residual stress and enhance adhesion on substrate materials. Although extensive studies have been performed in the past two decades, the effect of stress relief by a pure metal interlayer has not been fully understood, mainly due to the difficulty in accurately measuring residual stress in the individual layer of a bilayer coating. Recently we proposed a method combining average X-ray strain (AXS) and the elastic constant determined by nanoindentation (E_{NI}) to accurately measure the residual stress of hard coatings with an uncertainty < 10% [1,2], which provided an effective tool to respectively measure the layer stress in a bilayer coating. Since TiN/Ti is one of the most popular bilayer combinations, TiN/Ti coating was chosen as the model system in this study. The objective of this study was to accurately determine the residual stress in the individual layer of the TiN/Ti bilayer specimens by the newly proposed method. TiN specimens with three different Ti interlayer thicknesses, 50, 100 and 150 nm, were deposited on Si substrate using unbalanced magnetron sputtering. The residual stresses in TiN top layer and Ti interlayer were separately determined by combining AXS and E_{NI} , where AXS was measured using both lab X-ray and synchrotron X-ray sources. The overall stress of the entire TiN/Ti specimen was measured by laser curvature technique. The results showed that the Ti interlayer with thickness larger than 100 nm could relieve residual stress of the bilayer specimen. However, when the interlayer thickness was insufficient (50 nm), the stress of the entire specimen may increase instead of decrease even the interlayer was added. It was found that the Ti interlayer with thickness of 50 nm was subjected to a compressive stress, while interlayers with thickness of 100 nm and above were under a tensile stress. A physical model was developed to describe the stress variation with the interlayer thickness, which could delineate the experimental findings where a switch

of stress state from tension to compression occurred in the interlayer at a critical interlayer thickness. In addition, the switch of stress state in the interlayer may be also associated with the stress in the top layer. As the stress in the top layer increases, the interlayer thickness where the transition of stress state occurs will increase.

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2:10pm **B4-2-3 Challenges and Recent Progress in the Development of Arc Evaporated (Al_{1-x}Cr_x)₂O₃ Coatings**, *Christian Koller*, *A Kirnbauer*, *V Dalbauer*, *R Raab*, CDL-AOS at TU Wien, Austria; *S Kolozsvári*, Plansee Composite Materials GmbH, Germany; *J Ramm*, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Mayrhofer*, TU Wien, Institute of Materials Science and Technology, Austria

INVITED

Ceramic Al₂O₃-based coatings have been utilised for technical and functional purpose for decades. Their popularity with respect to protective applicability is based on the excellent combination of mechanical integrity, thermal stability, and chemical resistance. Physical vapor deposition (PVD) belongs to synthesis techniques of choice for industry, as process conditions allow for the utilisation of temperature sensitive substrate materials. Crystalline Al₂O₃ films can be grown at 600 °C and below, but the phase composition is in many cases dominated by metastable Al₂O₃ polymorphs and not the more favourable thermodynamically-stable corundum (α) structure. Among different alloying elements investigated with respect to their ability to stabilise the α-phase, Cr appears to be the most promising candidate. Only recently studies on (Al_{1-x}Cr_x)₂O₃ films were extended to cathodic arc evaporation. In order to develop protective coatings with an optimised property spectrum it is imperative to have a comprehensive knowledge of interdependencies of the synthesis procedure. This in first place includes process parameters and structure-property relationships, but it also implies a profound understanding of arc-induced modifications at the cathode surface and the ability to link these to the coating performance. We therefore study on the structural evolution of Al_{1-x}Cr_x-based coatings grown in intermetallic state and their transition to stoichiometric oxides, both as a function of the Cr content and oxygen flow rate, and in further consequence examine cathodes and macroparticles with different compositions. Monolithically-grown and gradient-structured (for which the oxygen flow-rate was gradually increased during the synthesis), coatings were prepared by Al_{0.75}Cr_{0.25}, Al_{0.70}Cr_{0.30}, Al_{0.50}Cr_{0.50}, or Al_{0.25}Cr_{0.75} cathodes and investigated with respect to their mechanical properties, thermal stability and oxidation behaviour. By the example of stoichiometric Al_{0.70}Cr_{0.30}-based oxides, the impact of alloying elements on either a promotion of the hexagonal corundum structure the stabilisation of transient phases is discussed and the significance of an optimised microstructure is demonstrated by multilayer architectures containing α-structured (Cr,Al)₂O₃ seed layers.

By taking different aspects of the cathodic arc evaporation process into account—i.e., cathode surfaces, droplets, oxide phase formation during synthesis—we could provide a further understanding towards the controlled synthesis of Al_{1-x}Cr_x-based coatings and thus introduce new concepts for their industrial application.

2:50pm **B4-2-5 Steel Doctor Blade Deposited by HIPIMS-CrN for Protection Purpose**, *Jia-Hong Zhou*, *Y Liou*, *Y Chen*, *J He*, Feng Chia University, Taiwan

Doctor blade has long been used for printing, tape casting process, thin sheet formation, etc, where corrosion and wear environments are encountered. Relatively few study work is revealed for improving the performance of the blade edge to resist wear and corrosion attack. In addition to the wet processes having been considered for protection purposes, this study focuses on CrN coating by using high power impulse magnetron sputtering (HIPIMS), which provide dense and strong film adhesion. It is anticipated that with this layer, it would be possible to provide improved corrosion and wear resistance for steel doctor blade. Substrate fixturing technique is developed. The microstructure of the obtained HIPIMS-CrN is examined. Results of field test are compared with the laboratory test for the blading performances.

3:10pm **B4-2-6 In-Line HIPIMS-TiNxOy to Produce Colorful Decorative Coatings**, *Yu-De Liou*, *Y Chen*, *J He*, Feng Chia University, Taiwan

Many study works based on batch-type PVDs (physical vapor deposition) have been commercialized, as an alternative to wet processes, due to their environment-friendly and color adjustable characteristics, as well as many

other features. However, it will be more feasible to use in-line PVD system to produce decorative coatings by taking the advantages of cost-effectiveness, small-piece handling capability and high through-put production.

In the present study, the decorative coatings based on TiN_xO_y are produced on motorcycle chain plates by using in-line system, where high power impulse magnetron sputtering (HIPIMS) technique is powered. It is found that the obtained coatings are strongly adhered with their color adjustable over a large range (blue, orange, peach red, ocean blue, gem green, champagne gold, violet purple and rosy gold, etc). The color can be controlled by the repeated entering of the tray (substrate holder) into deposition zone as well as the flow ratio of oxygen to argon during deposition. As a whole, the in-line HIPIMS system is feasible for producing high-quality decorative coatings.

3:30pm B4-2-7 Property of AIP Deposited Thick TiAlN Coating and Application to Actual Steam Turbine for Solid Particle Erosion Protection, Kenji Yamamoto, J Munemasa, Kobe Steel Ltd., Japan; Y Liang, National Cheng Kung University, Taiwan; T Abe, Toshiba Corporation, Japan; S Takada, T Takazawa, Y Iwai, University of Fukui, Japan

Erosion by high velocity solid particle (SPE) can produce a significant damage to high speed-moving aerodynamic objects such as blades for steam turbine or jet engine. SPE can cause a dimensional change and the result is compromising in aerodynamic integrity. Commonly these parts are made of ferrous alloy or light weight Ti alloy and erosion resistance of these metallic materials are not satisfactory. In case of steam turbine blade, mainly magnetite (Fe_3O_4) particles with relatively large diameter up to 150 μm are generated due to the oxidation of inner side of boiler tube and transferred by high velocity steam to the turbine.

High temperature diffusion layer such as boronizing or thermal sprayed metal carbide is commonly used for preventing SPE. But recently, more SPE resistant PVD deposited hard nitride compounds such as TiN [1], $TiSiN$ [2] or $TiAlN$ [3] are in consideration. As the particle diameter becomes larger, it is increasingly difficult to obtain enough SPE resistance with thin coating and at least coating with more than 10 μm of thickness, preferably more, is necessary. PVD deposited nitride, however, is in large compressive stress and difficult to deposit thick coating particularly on complex shaped parts.

Kobe Steel developed a new magnetically steered cathodic arc source "SFC" which is characterized by a variable control of residual stress of coating. With this new arc source, low-stress and thick TiAlN coatings were deposited and structural and mechanical properties were investigated. TiAlN coatings with different Al compositions were deposited by SFC and erosion resistance was evaluated by MSE method [4] using 50 μm alumina particle. It was found that best erosion resistance is obtained at Al composition between around 50 at%. The erosion rate of AIP-TiAlN is more than one order of magnitude smaller compared with conventional surface treatments such as boronizing or CrC thermal spray coating. Thick TiAlN coatings were also applied to fatigue and creep specimens made of 12 mass% Cr steel blade material and effect of coating on fatigue and creep resistance was investigated. The result showed that these properties remained unchanged by TiAlN coating. And finally, the thick TiAlN coating is applied to blades of an operating steam turbine in Japan and now they are in evaluation until the next overhaul.

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3:50pm B4-2-8 Stress Evolution during Cr_2AlC Film Growth, Andrius Subacius, A Matthews, University of Manchester, UK; M Hans, S Mráz, J Schneider, RWTH Aachen University, Germany

Cr_2AlC is a compound which belongs to the family of materials known as MAX phase. The general formula that describes this kind of compound can be expressed as $M_{1+n}AX_n$, where M is a transition metal, A is an A group element, and X is either carbon or nitrogen. MAX phase compounds are regarded as promising for certain applications due to some distinctive characteristics, such as being machinable, having good electrical and thermal conductivity and being resistant to thermal shock.

Residual stress in any film can be a major problem affecting the film properties and limiting the thickness to which they can be grown, due to the risk of debonding. Therefore, it is important not only to evaluate the

stress value after the film deposition but it is also beneficial to observe the stress evolution during the growth of the film. In this work, we observed the stress evolution of Cr_2AlC films during their growth. The films were deposited by DC magnetron sputtering from 2 or 4 compound targets at an average power density of 5 W/cm^2 each. Depositions were carried on in argon atmosphere at constant pressure of 3 mTorr (0.4 Pa). Substrate temperature was kept constant at 600 °C. Film thicknesses produced were between 2 mm and more than 8 mm. The in situ stress measurements were performed using a Multi-beam Optical Sensor (MOS) system by monitoring the curvature of the substrate and film with an array of parallel laser beams and a CCD detector. Stress values were calculated using Stoney's formula.

The residual stress of Cr_2AlC films was compressive ranging from about -1000 MPa to -200 MPa during the single film deposition process. In the early stages of the film growth the compressive stress is dominant reaching a peak value. As the film grows thicker the compressive stress decreases and becomes nearly constant.

4:10pm B4-2-9 Composition and Temperature Influence on ZrAlN/TiN Multilayer Structure: In-situ X-ray Scattering during Growth, and Transmission Electron Microscopy Studies, Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., Sweden; H Wang, Linköping Univ., IFM, Thin Film Physics Div. and Max-Planck-Institut für Eisenforschung GmbH, Sweden; J Muhammad, L Rogström, J Schroeder, Linköping Univ., IFM, Thin Film Physics Div., Sweden; D Ostach, N Schell, Helmholtz-Zentrum Geesthacht, Germany; J Birch, Linköping Univ., IFM, Thin Film Physics Div., Sweden

A massive industrial sector uses hard ware resistance thin films for applications involving extreme temperatures and pressures, and to reform energy and cost-efficiency they constantly call for novel and/or improved materials and coating designs. Over the last 8 years [1-5], we have investigated self-organised ZrAlN nanocomposites and related nanolaminated structures for such applications. We have shown that high immiscibility of ZrAlN alloys and sufficient mobility during growth lead to formation of nanostructures which possess high mechanical and thermal stability. The composite formation vary upon varying structural design and composition-temperature window and these parameter-space is a focus in this work.

Here, we present in-situ high-energy synchrotron wide angle X-ray scattering (WAXS) during growth of magnetron sputtered $Zr_{0.75}Al_{0.25}N/TiN$ and $Zr_{0.5}Al_{0.5}N/TiN$ multilayers complemented with structural characterization using cross-sectional transmission electron microscopy of as-deposited films[6]. The films are grown on MgO (001) substrates in Ar/N_2 mixture at substrate temperatures between 350 °C- 950 °C. In situ characterization revealed epitaxial multilayer growth simultaneous to complete segregation of cubic-ZrN and wurtzite-AlN in $Zr_{0.5}Al_{0.5}N/TiN$ deposited at 950 °C. When deposited at 350 °C, a preferential 002 texture evolve in these high Al containing films with two phase structure in nanocomposite layer with c-ZrAlN and h-AlN-rich phases. Low Al content in $Zr_{0.75}Al_{0.25}N/TiN$ results in single phase c-ZrAlN layers with 111 texture when deposited between 350 °C- 675 °C, and dual phase c-ZrN and w-AlN evolve at 825 °C. The composition-temperature windows for dense smooth films and for the formation of advantageous TiZrN phase at the interfaces are determined. In general, 1D-WAXS obtained in post analysis are consistent with the result of lab-scale XRD and 2D-WAXS patterns resembles SAED patterns for all the $Zr_{1-x}Al_xN/TiN$ multilayers studied in this work.

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4:30pm B4-2-10 Self-toughening in the TiAlN System, Matthias Bartosik, TU Wien, Institute of Materials Science and Technology, Austria; C Rumeau, R Hahn, TU Wien, Austria; Z Zhang, Austrian Academy of Sciences, Austria; P Mayrhofer, TU Wien, Austria

Titanium aluminum nitride has evolved to one of the most well established hard coating systems over the last decades. Its industrial success is mainly based on the superior oxidation and wear resistance as compared to titanium nitride as well as its age hardening ability. Though Ti-Al-N is

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among the most widely studied thin film materials, up to now scarcely any attention has been paid to its fracture toughness. Here we report on the evolution of the fracture toughness of Ti-Al-N upon ex-situ vacuum annealing [1]. We found that Ti-Al-N ceramic coatings become harder and tougher simultaneously - two material properties which are often mutually exclusive. The exceptional properties are attributed to the formation of a self-organized nanostructure and precipitation of severely distorted B4 AlN with multiple stacking faults and indications of nano-twins that evolve upon annealing. The fracture toughness was evaluated by performing single cantilever bending tests on free-standing, 2 µm thick, sputtered Ti-Al-N coatings. Additionally, cube corner experiments were conducted on coated Al₂O₃ substrates.

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4:50pm **B4-2-11 Load Sensing Characterization of Silicon Oxide Coatings**, **Tomasz Liskiewicz**, Leeds University, UK; *I Kolev*, Hauzer Techno Coating, Netherlands; *E McNulty, A Neville*, Leeds University, UK

Due to their high transparency, hardness, flexibility, barrier properties and hydrophilic properties [1,2], silicon oxide (SiO_x) coatings have been employed in a variety of industries including pharmaceutical, food packaging, corrosion protection as well as optical and electronic manufacturing [3,4].

In this work, SiO_x coatings were deposited on stainless steel substrates using the PECVD method with hexamethyldisiloxane (HMDSO) as a silicon precursor and oxygen (O₂) as the process gas. The HMDSO/O₂ ratio was varied between 1:1 and 1:36 in order to create coatings with different stoichiometry, and deposition time was varied to produce coatings with a total thickness ranging from 0.46 to 6.44µm. Coatings were characterised for their scratch resistance, nano-indentation hardness and elastic modulus, chemical composition (EDX) and crystallographic structure (X-Ray diffraction).

A dedicated test setup was developed in this study allowing measurement of coatings' insulating properties under mechanical stresses by simultaneous application of direct voltage through electrodes system, and mechanical compressive stress through varied normal load. The results obtained under constant normal load indicated that SiO_x coatings are efficient insulators, characterised by electrical resistivity ranging from 1.62 to 9.72 GΩ-cm, sheet resistance from 15.10 to 38.12 TΩ/square and conductivity from 0.10 to 0.62 (GΩ-cm)⁻¹. Moreover, coatings' insulating properties were characterised under ramped normal load, allowing to tune their load sensing capability by correlating applied mechanical stress with electrical response.

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5:10pm **B4-2-12 The Mechanical and Tribological Properties of TiZrNbN and TiZrNbN-Cu Films**, **Ihsan Efeoglu**, Atatürk University, Turkey; *H Aghdam, A Keles*, Ataturk University, Turkey; *O Baran*, Erzincan University, Turkey; *Y Totik*, Atatürk University, Turkey

">Due to improve friction and wear properties of cutting tools, various films are deposited on high speed tool steel. Transition metal nitride films are common used films for cutting tools. But with the developing technology, transition metal nitride films are inadequate. Therefore, soft metal such as Cu is used to improve the mechanical and tribological properties of transition metal nitrides. So, in this study, TiZrNbN and TiZrNbN-Cu films were deposited under two different working pressure (0.26 Pa and 0.33 Pa) on M2 high speed steel substrate with closed field unbalanced magnetron sputtering (CFUBMS). The microstructure and thickness values were examined with SEM. The chemical composition was determined by EDAX. The crystal phase orientation, grain size and texture coefficient were evaluated by XRD. The mechanical properties and critical load values of the films were obtained by microhardness test and scratch tester, respectively. Tribological properties of films were analyzed with a pin-on-disc tribometer. The hardness values and grain sizes were calculated ranging from 9.5-30 GPa and 17-45 nm, respectively. The atomic contents of Cu were 0.99% and 7.5% at 0.26 and 0.33 Pa working pressures, respectively. The grain size increased with decreasing hardness value and increasing Cu content. The maximum critical load was obtained in the softest film as 75 N. TiZrNbN-Cu films have better mechanical and

tribological properties than TiZrNbN films under the same working pressures.

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Hard Coatings and Vapor Deposition Technologies

Room Grand Hall - Session BP

Symposium B Poster Session

BP-1 Electrical and Reliability Characteristics of Dielectric Stack with Low Dielectric Constant SiCOH and Capping SiCNH Films, *C Lee*, National Chi-Nan University, Taiwan; *W Hung, Yi-Lung Cheng*, National Chi Nan University, Taiwan

The electrical characteristics and reliability of a dielectric stack with a low-k SiCOH film and a capping SiCNH film were investigated in this study. Two different low-k SiCOH films without and with the porosity (called dense and porous low-k) were used to identify the role of the porosity. The deposition of the capping dielectric film on both the dense and porous low-k films increased the overall dielectric constant. A higher increase in the dielectric constant was detected for the porous low-k film due to more serious plasma damage during a capping film deposition. With a capping SiCNH film, O₂ plasma damage and Cu diffusion were greatly retarded for both low-k SiCOH films. Larger improvements on TDDB and electromigration lifetimes were detected on the porous low-k film.

BP-3 Adhesion And Durability Of Multi-Interlayered Diamond-Like Carbon Film Deposited On An Aluminum Alloy, *Hidenobu Maruno*, *A Nishimoto*, Kansai University, Japan

Aluminum alloys are light and have good workability; however, they have drawbacks such as low hardness and poor wear resistance. These drawbacks limit their wide application in the automotive field. The deposition of a diamond-like carbon (DLC) film, which has high hardness and good wear resistance, on the substrate surface can improve these drawbacks. Because aluminum alloys and DLC films have poor affinity, the adhesion between them is poor. However, the usage of an interlayer can improve the adhesion between them. In this study, to investigate the effect of multi-interlayers on the adhesion and durability, a DLC film with an interlayer of Ti, Si-DLC, or Ti/Si-DLC was deposited on the EN AW-2024 Al alloy substrate via plasma enhanced chemical vapor deposition. Argon bombardment treatment was conducted to clean the substrate surface before deposition, the Ti interlayer was deposited via sputtering for 15 min, the Si-DLC interlayer was deposited using gas mixture of tetramethylsilane and methane for 15 min, and DLC was deposited using methane gas for 90 min. The nano-hardness of the Ti/Si-DLC multi-interlayered sample reached 21 GPa, which is nearly 4 GPa more when compared with single interlayered samples. A ball-on-disc test showed that the wear volumes of the ball and the multi-interlayered sample were smaller compared with the single interlayered samples. In addition, the durability distance of the Ti/Si-DLC multi-interlayered sample was 3300 m, increasing more than 1500 m than the single interlayered samples.

BP-4 The Effect of Cu on Fatigue Properties of TiZrNbN Coatings, *H Aghdam*, *A Keles*, Ataturk University, Turkey; *O Baran*, Erzincan University, Turkey; *Y Totik*, Atatürk University, Turkey; *Ihsan Efeoglu*, Ataturk University, Turkey

The fatigue properties are very important for cutting tools due to service life. Due to improve fatigue properties of cutting tools, transition metal nitrides with soft metal (Cu, Ni etc.) are coated on cutting tool materials. To investigate Cu effect on fatigue properties of transition metal nitride coatings, TiZrNbN and Cu doped TiZrNbN coatings were deposited on M2 high speed steel using reactive closed field unbalanced magnetron sputtering (CFUBMS) in bias voltage of -80V, coating pressure of 0.26 Pa and Cu target current of 0.6 A. Microstructure properties of the coatings were determined by XRD, SEM and EDAX. Mechanical properties of the coatings were examined with microhardness test. Fatigue properties of the films were examined using multipass scratch tester. According to the results, the mechanical properties of TiZrNbN doped Cu is better than TiZrNbN.

BP-5 Thermal Stability of Ni-B/ La₂O₃ Coatings by Electro-brush Plating Technique, *Dan Zhang*, *X Cui*, *G Jin*, *Z Cai*, *M Dong*, Harbin Engineering University, China

The metastable materials have gained a great deal of attraction due to their promising physicochemical properties, but the thermal stability limits their practical application. In this paper, Ni-B/La₂O₃ amorphous/nanocrystalline composite coatings were prepared on AISI 1045 steel substrate by electro-brush plating technique. The surface morphology, component and the phase structure of coatings were

observed by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD), respectively. The coatings were further analysis by Transmission Electron Microscope (TEM). Then the thermal stabilities of coatings with different content of La₂O₃ were also analyzed under different annealing temperature. It was found that the coating had a unique microstructure consisting of amorphous and nanocrystalline structures. The addition of La₂O₃ does improve the thermal stability of metastable Ni-B coatings when the annealing temperature is over 355°C. In addition, the thermal stability of the amorphous/nanocrystalline coatings depends on the percentage of amorphous phase, grain sizes and textures.

Acknowledgements

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BP-6 Properties of CrN_x Thin Films Deposited in Plasma Activated Polymers by Reactive Magnetron Sputtering, *M Rodrigues*, *P Pedrosa*, *Minho University*, Portugal; *A Ferreira*, *L Godinho*, *M Amaral*, *PRIREV*, Portugal; *M Neto*, *F Oliveira*, *R Silva*, Universidade de Aveiro, Portugal; *J Borges*, *Filipe Vaz*, *Minho University*, Portugal

Polymers are replacing traditional metallic materials, particularly in the automobile, electronic and decorative industries. Their low density, flexibility, design versatility and low cost production, combined with the properties of a shining, highly reflective and conductive metallic coating, gives them a huge advantage over common metals. One of the most used metallization process in the last decades has been chrome plating using highly toxic hexavalent chromium. However, following all the enacted legislation during the last years against the use of hexavalent chromium solutions, new chrome plating alternatives have emerged and include chemical, physical, and mixed approaches. One of such techniques is magnetron sputtering, which can be used on a wide range of available polymers and has a reduced environmental impact, unlike chrome plating.

In this work, magnetron sputtered CrN_x thin films were deposited on several polymers, including ABS, PA and PP. Two sets of thin films were obtained by varying the N₂ flow inside the vacuum chamber (series 1) and the deposition time (series 2). The polymers were also subjected to plasma treatment in Ar prior to the CrN_x thin films' deposition in order to enhance the adhesion. The fundamental microstructural, chemical and physical properties, as well as the quality and adhesion of the CrN_x thin films, were accessed by SEM, XRD, 3D profilometry, colorimetry, electrical resistivity measurements and scratch test. Main results show that high-quality, dense CrN_x films with enhanced adhesion and low percentage of defects were obtained. Magnetron sputtering is thus a promising alternative to the hazardous chrome plating for an effective metallization of different polymers.

BP-9 Influence of Ti on the Phase Stability of Magnetron Sputtered Mo-Si-B Thin Films, *Elias Aschauer*, *H Riedl*, CDL-AOS at TU Wien, Austria; *H Bolvardi*, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Polcik*, Plansee Composite Materials GmbH, Germany; *P Mayrhofer*, Institute of Materials Science and Technology, TU Wien, Austria

In terms of fuel and cost efficiency, the replacement of high-density Ni-based super alloys in aerospace industries came into the focus of research. A promising candidate are Mo-Si-B alloys, since they offer a high creep resistance, phase stability in a very broad range as well as excellent oxidation resistant. This broad field of mechanical and chemical properties is achieved by taking advantage of different phase combinations within the ternary phase diagram, leading to a multicomponent material. As it is well known in literature, molybdenum offers a poor oxidation resistance due to the formation of volatile oxides already above 400 °C – so called pesting phenomena. Alloying silicon and boron to refractory metals like molybdenum promotes the formation of glassy-like borosilicate oxide scales and inhibits the volatilisation of MoO₃. Nevertheless, retarded oxidation kinetics in a wide temperature field is strongly linked to the proper Si to B ratio. The molybdenum rich corner, known as Berczik triangle, offers a phase combination of Mo (A2), c-Mo₃Si (A15), and T₂-Mo₅SiB₂ (D8₁), next to the so-called Akinc triangle including c-Mo₃Si (A15), T₂-Mo₅SiB₂ (D8₁), as well as T₁-Mo₅Si₃ (D8_m). Especially, the T₁ and T₂ phases provide the ideal ratio of boron and silica to form either B-rich SiO₂ or even pure SiO₂ at low and high temperatures, respectively.

In order to access this highly interesting material characteristics, physical vapour deposition (PVD) can be used to make this promising material system accessible to many other applications and extend the field of operation. However, the most common deposition temperatures of about 500 °C do not lead to the desired phase combination, but rather to

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homogeneous, X-ray amorphous thin films. Alloying titanium to the ternary system is known to stabilise the T₂ phase, by substituting the Mo atoms within the tetragonal crystal structure up to concentrations of 40 % - also reducing the density significantly.

Therefore, the focus of the provided study is on the fundamental understanding of the phase evolution of magnetron sputtered Mo–Ti–Si–B thin films varying deposition parameters such as total pressure, bias voltage, and deposition temperature. Furthermore, the phase stability after thermal treatments in different atmospheres (vacuum, inert gas, and oxygen) is investigated up to temperatures of

1500 °C by using X-ray diffraction analysis as well as various (high-resolution) electron microscopy techniques and differential scanning calorimetry (DSC). The mechanical properties were investigated by nano-indentation of the as deposited and annealed state.

BP-10 Carbide Layer Coating on Titanium by Spark Plasma Sintering Technique, Akio Nishimoto, C Nishi, Kansai University, Japan

Titanium materials are widely used in aerospace, automotive and biomaterial engineering fields due to high specific strength, superior fatigue and corrosion resistance as well as excellent biocompatibility. However, titanium exhibits low hardness and poor wear resistance. Therefore, the development of a suitable surface modification technology is necessary to expand the use of titanium materials. In order to improve hardness and wear resistance of materials, there is the method to form the hard ceramics layer on the matrix surface. In this study, carburizing method was applied. The carburizing method can form the carbide layer which is superior in adhesion with the matrix compared with PVD or CVD method. However, in conventional carburizing methods, the deterioration of the mechanical properties of the matrix as a result of long-term and high-temperature processing is problematic. Therefore, spark plasma sintering technique, which features short processing times, was applied to form a carbide layer in this study. The purpose of this research is to form a TiC layer on commercially pure Ti (CP-Ti) and evaluate its properties. CP-Ti was used as the substrate, and graphite powder was used as the carburizing source. XRD analyses indicated that a TiC layer was formed on the substrates. Corrosion tests indicated that the corrosion resistance of the carburized samples was remarkably improved compared to that of CP-Ti. Wear tests revealed that the carburized samples exhibited low friction coefficients and improved tribological properties.

BP-13 Growth Kinetics of Boride Coatings on AISI W2 Steel, MarcoAntonio Doñu Ruiz, Universidad Politécnica del Valle de Mexico, Mexico; N Lopez Perrusquia, Universidad Politécnica Del Valle De Mexico, Mexico; V Serna Lara, V Cortés Suárez, Universidad Politécnica del Valle de Mexico, Mexico

The present work evaluate the growth of the boride coatings formed in the surface AISI W2 steel by powder pack boriding. This process was carried out in the temperature range of 1173–1273 K with the exposure times ranging from 2 h to 8 h. The presence of borides Fe₂B formed on the surface of steel substrate was confirmed by optical microscopy and X-ray diffraction. The distribution of alloy elements from the surface to the interior was confirmed by energy dispersive X-ray spectroscopy.

The morphology presented the boride layer Fe₂B showed smooth and compact, with range thickness average from 9.96 ± 2.61 μm to 45.86 ± 4.13 μm. A mathematical model of the growth kinetics of the Fe₂B coatings on AISI W2 was proposed for the powder-pack boriding. The boron diffusion coefficient (D_{Fe_2B}) was determined by mass balance equation of the (Fe₂B/substrate) interface, the kinetic model was set for the Fe₂B coatings, assuming that the growth of boride layers follows a parabolic growth law. In addition, a contour diagram describing the evolution of Fe₂B coatings as a function of time and temperature parameters was proposed to be used in practical application. Finally, the boron activation energy for the AISI W2 steel is estimated as 183.44 kJ mol⁻¹ and this value of energy was compared with the literature data.

BP-15 Study on Steels Boronizing Immersed in Diesel, Noe Lopez Perrusquia, M Doñu Ruiz, G Perez Mendoza, Universidad Politécnica Del Valle De Mexico, Mexico; V Cortés Suárez, Universidad Autónoma Metropolitana- Azcapotzalco, Mexico; C Torres San Miguel, Instituto Politécnico Nacional - ESIME, Mexico

This work shows the effect of diesel on a surface coating of boron in Microalloyed Steels. The steels are boronizing at 1273 K, with permanence of 6 h; the medium boriding by boron paste dehydrated; the medium boriding by boron paste dehydrated in solid box; the immersion of the steels Microalloyed boriding for 1 year in diesel at temperature ambient. The first phase consisted in the characterization and analysis of FeB/Fe₂B

obtained by paste dehydrated of boron, using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and microhardness (Hv). The second phase is the immersion of the boriding specimens in diesel, after the permanence time, were evaluated by the tensile test and analyzed the mechanical properties. This work presents the formation of boron coating, with the purpose of showing an alternative for the manufacturing industries; which generate containers for storage of liquids, biofuels and fuels

BP-17 Deposition of Nanodiamond Coatings on Steel Implant Materials with CrN/Al Interlayer, Y Li, F Ye, C Zhang, M Taheri, J Corona, Qiaoqin Yang, University of Saskatchewan, Canada

Integration of smooth nanocrystalline diamond coatings on steel substrates for biomedical implant applications has great application potentials due to their extraordinary wear/corrosion resistance and biocompatibility. However, CVD deposition of adherent and continuous diamond coating on steel substrates has met technical barrier of easy delamination. We will report on our recent progress on enhancing the adhesion of diamond coatings on steel substrates by using CrN/Al interlayer. The morphology, microstructure, composition and adhesion of the formed surface products are comprehensively characterized by SEM, TEM, XRD, Raman and synchrotron XAS as well as indentation test. The fundamental mechanism of enhanced interfacial adhesion is discussed.

BP-18 MoN/TaN Superlattices: from a Computer Design to a Realization, N Koutna, TU Wien, Institute of Materials Science and Technology, Austria; R Hahn, CDL-AOS at TU Wien, Austria; J Zalesak, Montanuniversität Leoben, Austria; M Friak, IPM, Academy of Science, Czech Republic; M Bartosik, TU Wien, Institute of Materials Science and Technology, Austria; M Sob, Masaryk University, Czech Republic; J Keckes, Montanuniversität Leoben, Austria; P Mayrhofer, TU Wien, Institute of Materials Science and Technology, Austria; David Holec, Montanuniversität Leoben, Austria

Nitrides are fascinating class of materials constantly revealing new and unexpected features, often related to metastable phases accessible via, e.g., non-equilibrium physical vapour depositions. Cubic MoN and TaN have been recently shown to strongly favour vacancies.

First principles calculations of undefected MoN/TaN superlattices suggest an interface-induced structural transformation from cubic to tetragonal phases (ζ-TaN, ζ-MoN). An analysis of their elastic constants reveals that the TaN volume fraction must be larger than that of MoN in order to be mechanically stable. This stability range can be further influenced by considering the point defects, namely vacancies. It is shown that the stability of superlattices critically depends not only on the amount of vacancies, but also on their distribution as well as on the superlattice bi-layer period. Impact of the interface and its orientation on the tensile strength is also briefly presented.

To compare the calculated results with experiments, magnetron-sputter deposited superlattices with various bi-layer periods are studied using conventional XRD, conventional and high-resolution TEM, and mechanical testing. The structural analysis confirms single-phase cubic superlattices with a strong (100), (110) or (111) interface orientation, as dictated by the MgO substrate orientation. Quantitative EELS measurements are used to prove the non-stoichiometry of individual constituents, MoN and TaN, as a function of the bi-layer period.

BP-20 Effect of Mo Concentration on Structure and Properties of Zr-Mo-N Thin Films Deposited by Reactive Magnetron Sputtering, A Junior, Daniel Fernandez, L Félix, Universidade Federal de Sergipe, Brazil; R Hubler, Pontifícia Universidade Católica do Rio Grande do Sul, Brazil; F Mendes, Instituto Nacional de Tecnologia, Brazil; G Brito, Universidade Federal de Sergipe, Brazil; E Tentardini, Universidade Federal de Sergipe, Brazil, Brasil

Zirconium nitride (ZrN) thin films are mentioned in many studies because of their excellent characteristics that allow their application in cutting and molding tools. However, the columnar growth, micro cracks and porosity of that material compromise its mechanical properties and limit its oxidation resistance. One of the alternatives to solve that problem is the addition of a third element to its matrix. Some studies show that molybdenum addition result in expressive improvements in mechanical properties and wear resistance, as in TiMoN and CrMoN, however there are few works about the effect of Mo in ZrN coatings properties. The objective of this work is to study the influence of molybdenum on the structure, morphology, mechanical properties and oxidation resistance of zirconium and molybdenum thin films (ZrMoN). Thus, thin films of the system ZrMoN were deposited using reactive magnetron sputtering (RMS) technique, varying the molybdenum content in 23, 31 and 37 at.%. Thin films were

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characterized by GAXRD, SEM, XPS and high temperature oxidation tests at three different temperatures, 773K, 873K and 973K. GAXRD analysis showed a molybdenum accommodation in the lattice forming substitutional type solid crystalline solution and a small displacement of the ZrN peaks to the right as the Mo content rises. Sample with 23 at% of Mo into structure reach 33 GPa, the highest value for all coatings studied. All samples failed in oxidation tests, with reduction of hardness values; appearance of bubbles and loss of adhesion.

BP-21 Anti-staining Coatings on PET Fabrics by Using a Spraying/ Plasma-Polymerization Duplex Technique, Cheng-Wei Lin, Feng Chia University; Central Taiwan University of Science and Technology, Taiwan; J He, Feng Chia University, Taiwan

To fulfill better wearing quality, PET fabrics are considered for further treatment to resist environmental dust and oil stains. This study aims to prepare a hydrophobic surface on PET fabrics to minimize the risk of dust adhesions or oil stains by using a duplex technique combining spraying and low-surface-energy plasma polymerization. The anti-staining coated fabrics are tested their durability by using the AATCC 130 of washing test for barbecue sauce and ketchup.

Experimental results reveal that the duplex treated fabrics can achieve water contact angle (WCA) over 118°. Anti-staining tests performed at 1, 4, and 10 weeks after surface treatment show that the tested fabrics can tolerate 10 times of the washing test without altering surface appearance. Results of SEM and EDS analysis show that fluorocarbons still exhibit on the surfaces of PET fabrics after anti-staining tests. Above all, a spraying/plasma polymerization duplex coating on the surfaces of PET fabrics exhibits favorable hydrophobicity and anti-staining durability.

BP-22 Fracture Resistance of Nanocomposite/Metal Nitride Multilayers: Role of Interfaces, Naureen Ghafoor, P Persson, Linköping Univ., IFM, Thin Film Physics Div., Sweden; I Petrov, Linköping University, IFM, Thin Film Physics Division, Sweden, USA; J Barriero, F Mücklch, Saarland University and Materials Engineering Center Saarland, Germany; J Birch, Linköping Univ., IFM, Thin Film Physics Div., Sweden; W Clegg, Cambridge University, UK

The focus is deformation mechanisms of transition metal nitride nanocomposites coatings. The deformation in these materials is strongly dependent on interface structure and become more complex in nanocomposites involving high density of interfaces. We present mechanical response of TiN/ZrAlN multilayers and monolithic ZrAlN nano-composite coatings investigated through nano indentation and micropillar compression tests. The study highlights effect of interface structure on pre yield and post yield behavior of nano scale multilayer deformation in compression.

To understand stress-strain response in a uniaxial micropillar compression tests the pillars of height of 1 mm and diameter of 300 nm were compressed using in situ SEM nanoindenter equipped with a flat punch (diameter 5mm)[Ref 2]. The pillars were milled using focused ion beam. The interface structure of the multilayers is tuned by varying growth parameters during magnetron sputter deposition on MgO (001) substrates. The growth temperatures above 700 °C facilitated in situ segregation of ZrN- and AlN- rich domains within ZrAlN layer during growth [Ref 1]. The growth conditions and multilayer design are varied to tailor crystal structure of AlN rich domains from cubic to wurtzite and consequently to obtain coherent, semicoherent, and incoherent interfaces. Dependence of plastic deformation and work hardening on the multilayer period as well as on the coherency of involved interfaces is investigated. Micropillar compression tests revealed higher yield stresses and larger post yield displacements in 2 and 5 nm thin ZrAlN layers consisting of cubic phases of ZrN and AlN- rich domains forming coherent interfaces. For 15 and 30 nm thick ZrAlN layers, involving incoherent interfaces, the dominant crack propagation occur through layer interfaces. The dominant deformation mechanisms in connection with interface coherency and multilayer periodicity will be presented.

BP-23 Vacancies in Al-O-N Crystallites, Maria Fischer, D Scopece, C Pignedoli, D Passerone, H Hug, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Aluminum oxynitride (Al-O-N) in its transparent ceramic form provides attractive properties for hard coatings. Thin films of this material with different O and N contents were deposited by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS) and investigated with respect to the induced changes upon varying O/N ratios.

It was discovered that O addition leads to a gradual transformation of polycrystalline wurtzite AlN via Al-O-N nanocomposite towards amorphous Al₂O₃. The boundary between polycrystalline AlN and Al-O-N nanocomposite is set by the solubility limit of O in AlN and was found to be at 8 at% O. Below this critical value, O substitutes N in the wurtzite lattice. This leads to a continuous unit cell shrinkage in c direction measurable by XRD. Above 8 at%, O starts to surround crystallites in the form of an amorphous Al₂O₃ matrix.

The shrinkage of the c lattice parameter upon O incorporation can hypothetically be attributed to the generation of Al vacancies. Since O has one valence electron more than the N it replaces, the ideal wurtzite 1:1 stoichiometry of electron donor and acceptor as found in AlN can no more be matched. In order to maintain the wurtzite crystal structure, the proportional amount of Al has to reduce to fit the stoichiometry AlO_{1.5}N_{1-x}. The hypothesis that this is achieved through vacancies in the Al lattice positions was tested by ab initio DFT calculations. Lattice parameter changes upon O introduction and consequent Al vacancy defect generation were calculated and found to be in good agreement with the experimentally observed values. The obtained results were compared to data for the related ternary Al-Si-N system.

BP-26 Effects of Bias Voltage on Microstructure and Properties of Al-Doped Hydrogenated Amorphous Carbon Films Prepared by a Hybrid Deposition Technique, Songsheng Lin, W Xu, H Li, M Dai, Q Shi, C Wei, H Wang, K Zhou, Guangdong Research Institution of New Materials, China

Al-doped hydrogenated amorphous carbon films were deposited on Si wafers and stainless substrates by a hybrid deposition technique composed of middle-frequency magnetron sputtering and anode layer ion source. Effects of substrate bias voltage on the deposition rate, surface topography, microstructure, residual stresses and mechanical properties were characterized using scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and nano-indentation. It was shown that the aluminum atoms were embedded in carbon matrix without bonding with C atoms. The surface of the films evolved from a rough surface with quasi-columnar characteristic to a smoother surface with the applied bias voltage increased from 0 to -400V. The residual stresses of the films deposited at 0V and -50V were tensile stress, while it transformed to compressive stress with bias voltage increased to -100V or higher. The hardness of the film stayed in the highest level of nearly 17GPa, while the bias voltage ranging from -150 to -300V. The ball-on-disk tribo-meter was further used to study the tribological behavior, the results demonstrated that the film deposited at -150V exhibited excellent lubrication performance with a friction coefficient of about 0.047 and good wear resistance.

BP-27 Comparison of Chromium Carbide Thin Films Grown by Different Power Supply Systems, Z Li, C Wang, National Taiwan University of Science and Technology, Taiwan; B Lou, Chang Gung University, Taiwan; Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

The potential use of chromium carbide thin films has been a great interest to academia and industry due to their outstanding properties such as chemical stability, low coefficient of friction, adequate hardness and high wear resistance. In this study, the chromium carbide thin films were fabricated by a magnetron sputtering using different power supply systems, including direct-current (DC), high power impulse magnetron sputtering (HIPIMS), and superimposed middle-frequency (MF)-HIPIMS. The Cr target poisoning status was controlled by a plasma emission monitoring system by adjusting the gas flow ratio of Ar and acetylene (C₂H₂). The morphology and microstructure of thin films were evaluated by scanning electron microscope. The crystallinity of films was studied using X-ray diffractometer. The electron probe micro analyzer, X-ray photoelectron spectroscopy, and Raman spectroscopy were used to determine the chemical compositions and binding structures of thin films. The mechanical, adhesion and tribological properties were explored by using scratch tester, tribometer, and nanoindentation. The influence of different power supply systems on the microstructure, chemical composition, and mechanical properties of chromium carbide films were investigated in this work.

BP-28 Self-organized Formation of Different Nanostructure in Carbon-metal Films Prepared by Reactive Magnetron Sputtering, Hongxuan Li, W Wang, L Ji, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

Metal-containing carbon-based films (Me-C films) have been attracted much attention because metal-doping can effectively improve and regulate film's properties (such as reducing the internal stresses, enhancing

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the adhesion to the substrate and improving environmental sensitivity of tribology). It has been widely reported that various metals have been introduced into carbon-based films by different groups. However, it will bring wide differences in precisely controlling microstructure and interaction mechanism etc. aspects to metallic doping carbon-based films due to diverse metallic elemental, prepared methods and conditions.

This report highlights a peculiar phenomenon that spontaneous formation of various nanostructure in the carbon-based films during co-deposition of different metallic element process. Consideration of different interaction between metal and carbon, we choice copper, titanium, and nickel as three typically doping metals. The influence of various metallic elements on self-organizing special nanostructure in carbon-metal films is systematically studied. For copper, it is noncarbide and immiscible with carbon, self-organized nano-multilayered structure can be formed in the copper-carbon film when the copper concentration maintaining at 20%-40% at.%; Titanium are strong carbide former, the nanocomposite structure of titanium carbide nanocrystalline dissolved in the amorphous carbon matrix is observed in the titanium-carbon film; Nickel possess the ability to catalysis the growth of carbon nanowires, and self-organized carbon nanowires structure in nickel-carbon film has been successfully prepared, the field-emission tests of this self-assembled carbon nanowires structured film shows excellent behaviors.

BP-29 Anticorrosive Properties of (Zr-Si-Ti-N)Ni Thin Films Deposited by Co-Sputtering, EstrellaNatali Borja Goyeneche, J Olaya, Universidad Nacional De Colombia, Colombia

In the present work, the influence of nickel content on the structural and electrochemical properties of the TiZrSiN films was investigated. The nanostructured ZrSiTiN thin films with nickel additions were deposited onto stainless steel AISI 316L and TiAlV alloy substrates using the reactive magnetron co-sputtering technique. The structure was analyzed by X-ray diffraction and the chemical composition was identified by energy dispersive X-ray spectroscopy (EDS). The corrosion resistance was studied by potentiodynamic polarization test and electrochemical impedance spectroscopy using a 3.5 wt% NaCl corrosive solution. Nickel leads to improve the anticorrosive properties of thin composite films because to the incorporation of a physical barriers against the propagation of the corrosive electrolyte. The corrosive mechanism is discussed in this paper.

BP-30 Corrosion Resistance of Stainless Steel Coatings With and Without Silver Deposited by Sputtering, ClaudiaLiliana España, J Olaya, Universidad Nacional De Colombia, Colombia; A Candido Recco, Universidade do Estado de Santa Catarina, Brazil

The anticorrosive properties of stainless steel coatings deposited with different amounts of silver by unbalanced magnetron sputtering were studied. The structure of the coatings were characterized by means of X-ray diffraction, the morphology and chemical composition were evaluated by means of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) respectively. The corrosion resistance was determined through out of potentiodynamic polarization tests and electrochemical impedance spectroscopy using a Ringer's solution as a simulated biological fluid. It was determined that the coatings deposited in inert atmosphere presented BCC structure, while the coatings deposited in the reactive atmosphere shows the BCC and FCC phases. A compact morphology was observed in coatings with a higher silver content. The corrosion resistance was increased in the coated substrate compared to the uncoated substrate. Corrosion mechanism of coating deposited is discussed in this paper.

BP-31 Evolution of Structure and Mechanical Properties of Nanocrystalline Multi-layered Arc-evaporated AlCrN-AlTiN Coatings upon Thermal Loading Revealed by X-ray Nanodiffraction and Tribological Testing, Stefan Klima, N Jäger, M Meindlhuber, Montanuniversität Leoben, Austria; H Hruby, eifeler-Vacotec GmbH, Germany; J Keckes, R Daniel, Montanuniversität Leoben, Austria

Nanocrystalline coatings are typically characterized by inherent variations in the structure (texture and size of grains), residual stress and mechanical properties over the thickness, which is associated with the competitive nature of their growth. On the other hand, the microstructure and thus the coating properties may be intentionally controlled by a specific multilayer architecture, in which crystallographic structure, size of grains as well as the stress state may be influenced by layer thickness and templating effects. In order to understand the complex structure-stress-property variations in hierarchical nanostructured coatings, a multi-layered multi-phase arc-evaporated AlMeN-based coating system (where Me=Cr and Ti) was developed and studied by cross-sectional position-resolved

synchrotron X-ray nanodiffraction and tribological testing in the as-deposited state and after thermal treatment. Since both AlMeN systems are metastable transition metal nitrides having either cubic or hexagonal crystallographic structure depending on the Al-content, their phase composition was controlled either by the cathode composition or deposition conditions. Furthermore, potential (de)stabilization of the crystallographic structure of the metastable constituents was studied in detail for the multi-layered system, where AlCrN and AlTiN sublayers prepared at bias voltages ranging between -30 and -600 V alternated with layer thicknesses varying from 10 to 300 nm. The X-ray nanodiffraction analysis revealed that the cubic structure of the AlMeN layers may be stabilized even at high temperatures while combed with cubic sublayers in a multilayer structure, although they otherwise exhibit a dual phase structure as monolithic coatings. The role of the coating architecture on the structural stability and the stress state will be demonstrated for a number of multilayer design variations. Furthermore, coatings with a specific architecture were selected based on the results of the cross-sectional combinatorial approach and tested by pin-on-disk experiments at RT and 600 °C. The results document strong relationships between the architecture, phase composition, stress state, thermal stability and wear resistance of the coatings, which allow to establish specific design rules for thermally and mechanically stable multi-layered AlN-based coatings.

BP-32 Corrosive Resistance of Nanostructured ZrSiN-Ag Films Deposited by Reactive Sputtering, H Vanegas Parra, JhonJairo Olaya, J Alfonso, Universidad Nacional De Colombia, Colombia; S Calderon, International Iberian Nanotechnology Laboratory, Portugal; S Carvalho, University of Minho, Portugal

Due to their physical and chemical properties the multifunctional materials have been study extensively in the last years. In this work we present the growth of nanostructured ZrSiN-Ag films deposited on common silicon and stainless steel substrates via magnetron co-sputtering with aim of analyze the influence of silver amount on the crystalline structure and corrosive resistance. The coatings structure have been characterized through X-ray diffraction (XRD) and the morphology has been evaluated via scanning electronic microscopy (SEM); anticorrosive properties were carried out through potenciodinamic polarization test. The preliminary results, shows that the films are polycrystalline and the corrosion resistance improve as a function of the Si and Ag amount in the films deposited. The corrosion mechanism in the films will be discussed in this work.

BP-33 Mechanical Properties of ZrSiN-Ag Thin Films Deposited by Reactive Magnetron Sputtering, HenrySamir Vanegas Parra, J Alfonso, J Olaya, Universidad Nacional De Colombia, Colombia; S Calderon, International Iberian Nanotechnology Laboratory, Portugal; S Carvalho, University of Minho, Portugal

ZrSiN-Ag thin films were deposited by reactive magnetron sputtering in order to study the effect of addition of silver on the structure, chemical composition and mechanical properties in ZrSiN thin films. The structure of thin films was characterized by X-ray diffraction (XRD), the morphology by scanning electron microscopy (SEM) and the chemical composition by energy-dispersive x-ray spectroscopy (EDS). A nanoindenter was used to study the mechanical properties such as hardness and elastic module in function the silver content in the films deposited. The XRD results showed that nanostructured ZrSiN-Ag thin films were obtained. The ZrN film exhibited a face-centered cubic (f.c.c) phase with columnar structure while that the Zr-Si-N films showed a mixture of f.c.c and near-amorphous phases without columnar structure, similar to the ZrSiN-Ag films. The hardness obtained for ZrN film was of 58,80 GPa, which decreases as silver contents increase.

BP-34 Hardness and Adhesion of AlSiN Thin Films Deposited by the Simultaneous Laser Ablation of Two Targets, Enrique Camps, L Rivera, I Campos-Silva, Instituto Nacional de Investigaciones Nucleares, Mexico; S Muhl, Universidad Nacional Autonoma de Mexico, Mexico

Aluminum silicon nitride (AlSiN) thin films with different Si content were deposited using the simultaneous laser ablation of aluminum and silicon targets in a nitrogen atmosphere and a substrate temperature of 200 °C. Films were deposited at two values of working pressure, 0.6 and 1 Pa. The silicon content in the films ranged between 3 and 20 at. %, and was varied by changing the density of the plasma produced during the ablation of the silicon target, i.e. the highest the plasma density gave the highest the silicon concentration in the films. The plasma parameters (mean kinetic ion energy and plasma density) were measured using a planar Langmuir probe. Samples deposited with low silicon contents (up to about 6 at. %), contained nanocrystals embedded in an amorphous matrix. Those crystals

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were identified as hexagonal aluminum nitride (w-AlN). For higher concentrations of silicon the amorphous phase was predominant and the nanocrystals were no longer observed. The hardness of the films had a maximum value of 30 GPa, and an elastic recovery of about 50 % when the silicon content was close to 4 at. %. For higher silicon concentrations the hardness was lower at 19 GPa. Scratch tests were carried out on samples with different silicon contents. For the samples with low silicon contents (the highest hardness) delamination was observed at loads of 90 N, in the transition to the solid solution regime (Si content of 8 at. %) delamination was observed to begin at 10 N, and for the highest concentrations of silicon no delamination of the films was observed even for loads of 90 N.

BP-35 Plasma Enhanced Chemical Vapor Deposition of Carbon Film into a Small Hole 100 μm in Diameter with MVP and Source Gas Blowing, *R Ota*, Nagoya University, Japan; *Hiroyuki Kousaka*, Gifu University, Japan; *L Raja*, University of Texas at Austin, USA; *N Umehara*, *M Murashima*, *T Tokoroyama*, Nagoya University, Japan

Diamond-like carbon (DLC) is widely applied to mechanical parts because of its low friction performance, high wear and corrosion resistance. When it is applied to the internal surface of a hole, plasma enhanced chemical vapor deposition (PECVD) is typically used because of its excellent coating coverage to 3-dimensional internal surfaces. However, it is not feasible to generate plasma in a 100's- μm -diameter hole due to the formation of ion sheath whose width is comparable to the inner diameter. In this case, the precursor molecules of DLC such as CH_3 radical are transported by diffusion into the inside of a hole from plasma generated at the outside. However, the radical density decreases exponentially in axial direction by sticking loss to the internal surface of a hole. Consequently, the depth of the internal surface covered by DLC (referred to as coating depth) has no choice but to become almost the same as its diameter [1]. Since the aspect ratio of a hole in mechanical parts is typically more than 10 (e.g. fuel injector), it is strongly required to increase coating depth. Thus, in this research, we propose the novel coating method by PECVD coupled with source gas blowing to increase coating depth for an 100- μm -diameter hole. Particularly, We investigate the effect of blowing source gas and flow rate on the coating depth of DLC.

In order to deposit DLC to the inner surface of a small hole 0.1 mm in diameter and 5 mm in depth, PECVD employing MVP is conducted with blowing source gas from nozzle to the hole inlet. After DLC coating, film thickness is measured by 0.1 mm in axial direction of the hole and the maximum depth where a film thickness is detectable is defined as coating depth. We found that blowing source gases increases coating depth. Furthermore, the linear increase of coating depth from 0 to 1 mm was observed with the increase of the flow rate of blown gas from 0 to 780 sccm. We are going to further investigate the effect of source gas flux on coating depth by numerical simulation of plasma with the commercial software VizGlow at the conference.

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BP-37 Effect of Silicon Content on Structure and Properties of AlCrSiN Coatings Prepared by Arc Ion Plating for Milling Tools, *Wangryeol Kim*, *S Heo*, Korea Institute of Industrial Technology (KITECH), Republic of Korea; *Y Kim*, *J Kim*, KORLOY, Republic of Korea; *I Park*, Korea Institute of Industrial Technology (KITECH), Republic of Korea

Quaternary AlCrSiN coatings with silicon content ranging from 0 to 21 at.% were deposited on WC-Co alloy substrates by an arc ion plating technique using Cr-Al and Cr-Si composite targets in an $\text{N}_2/(\text{Ar}+\text{N}_2)$ gas mixture for hard material processing milling tools. The microstructure, mechanical, wear, tribological properties of the coatings were investigated by XRD, XPS, FESEM, HRTEM, surface 3D profiler, nano-indentation, scratch tester, and ball-on-disc tribo-meter. As the silicon content increased, the microstructure of the coatings changed from columnar grains to interconnected fine grains, and finally to nanocomposite structure, in which (Al,Cr)N nanocrystallites were surrounded by an amorphous silicon nitride matrix. The incorporation of silicon results in the (Al,Cr)N crystallite size refinement and the decrease of the average surface roughness. The nanohardness of the AlCrSiN coatings showed higher hardness values than that of AlCrN coating. The strengthening mechanisms include solid solution hardening and grain boundaries strengthening through the formation of a thin amorphous layer. Moreover, it was found that the improved nanohardness and the H/E ratio contributed to excellent wear resistance of

the coatings. The friction coefficient and wear rate of the AlCrSiN coatings first decreased and then increased with increasing silicon content. The friction coefficient and wear rate were also mainly related to the lubricant wear debris in this work.

BP-38 Coatings and Performance Evaluation of Ti-Al-Si-N-O Coated Cutting Tools, *Sungbo Heo*, *H Kim*, *U Jung*, Korea Institute of Industrial Technology (KITECH), Republic of Korea; *Y Kim*, *J Kim*, KORLOY, Republic of Korea; *I Park*, Korea Institute of Industrial Technology (KITECH), Republic of Korea

Functional graded Ti-Al-Si-N-O nanocomposite coatings were deposited onto WC-Co substrates by a filtered arc ion plating system using TiAl_3 and Ti_4Si composite targets under N_2 atmosphere. XRD and XPS analyses revealed that the synthesized Ti-Al-Si-N-O coatings were nanocomposite consisting of nanosized (Ti,Al,Si)N crystallites embedded in an amorphous $\text{Si}_3\text{N}_4/\text{SiO}_2$ matrix. The hardness of the Ti-Al-Si-N-O coatings exhibited the maximum hardness values of $\sim 43\text{GPa}$ at a Si content of $\sim 5.63\text{at.}\%$ due to the microstructural change to a nanocomposite as well as the solid-solution hardening. Ti-Al-Si-N-O coating with Si content of around 5.63 at.% also showed perfect adhesive strength value of 105.3N. These excellent mechanical properties of Ti-Al-Si-N-O coatings could help to improve the performance of machining tools and cutting tools with application of the coatings. Ti-Al-Si-N-O coatings were applied to insert tools. Their performances were evaluated about cutting-time and cutting-length to Inconel 718 super alloys. Performance of the coated tools were evaluated and compared with different Ti-Al-Si-N-O coatings onto cemented carbide substrates. Especially, the Ti-Al-Si(5.63at%)-N coated tool showed better performance and best tool life in this work.

BP-39 Transparent and Low Resistance Hard Amorphous Carbon Thin Films by HiPIMS for Electronic Applications, *Kerstin Thorwarth*, *R Ganesan*, *A Chacko*, EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *M Grein*, *R Bandorf*, Fraunhofer Institute for Surface Engineering and Thin Films, Germany; *D McKenzie*, *M Bilek*, The University of Sydney, Australia; *H Hug*, EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

High power impulse magnetron sputtering (HiPIMS) was used to deposit optically transparent amorphous carbon thin films with low electrical resistance. The films were deposited on Si substrate. The film of 75 nm thickness exhibit the sheet resistance of 2.5 $\text{k}\Omega/\square$ and high visible transmittance of 76 % at 450 nm. The room temperature mobility of the deposited amorphous carbon films lies in the range of 14 - 18 $\text{cm}^2\text{v}^{-1}\text{s}^{-1}$, which is higher than the previously reported values. The X-ray Photoluminescent studies and the optical bandgap by Tauc's method suggest that the bandgap of films lies between 1.75 to 2.35 eV, and depends on the values of negative bias voltage applied to the substrate. The films are totally hydrogen free (H content < 0.7 %) and exhibit densities varied from 2 to 2.6 eV. The measured hardness values are greater than 33 GPa for the films with thickness = $800 \pm 40\text{ nm}$, but deposited at similar deposition conditions. Such properties of the amorphous carbon films have a great potential in the application of transparent conducting electrodes.

BP-40 Reactive Magnetron Sputter Deposition of Bismuth Tungstate Coatings for Water Treatment Applications under Natural Sunlight, *M Ratova*, *Peter Kelly*, Manchester Metropolitan University, UK; *R Marcelino*, *C Amorim*, *P de Souza*, Federal University of Minas Gerais, Brazil

Photocatalysis is a promising method for decontamination of air, water and soil. In particular, photocatalytic purification of wastewater is becoming an increasingly popular process, with the wide range of titanium dioxide-based materials successfully applied as photocatalysts for water treatment application. However, the use of titanium dioxide for efficient water treatment application is restricted with two major limiting factors, namely a relatively high band gap value and low photonic efficiency. The high band gap value results in titania photocatalysts being activated only with ultraviolet (UV) irradiation (<5% of the solar spectrum), therefore, for practical use, additional irradiation sources are required. Consequently, it is rather difficult to achieve high reaction rates, as required when dealing with heavily-polluted industrial wastewater or high throughput systems. As photocatalytic wastewater treatment is aimed at being an economical and practical technique, it is desirable to avoid the extra costs of using artificial light sources in the photocatalytic treatment setup. Use of natural sunlight represents a cheap and sustainable irradiation source, however, as in the case of titania-based photocatalysts, its efficiency can be rather low. Therefore, there is an obvious need for the development of photocatalytic materials based on the use of low band gap semiconductors, combining visible light activity with high photonic efficiency and high surface area.

Thursday Afternoon Poster Sessions, April 26, 2018

In the present study narrow band gap semiconductor bismuth tungstate has been deposited onto 2 mm glass beads via reactive magnetron sputtering from a dual source system. The beads were used to increase the surface area, as opposed to flat substrates, and manipulated using an oscillating bowl placed under the magnetrons in order to provide uniform coverage. The atomic ratio of Bi/W was varied through the variation of the power applied to the magnetrons. The deposited coatings were analyzed by SEM, EDX, XRD, XPS and AFM. The photocatalytic properties of the coatings were assessed via their ability to degrade an methylene blue under artificial (fluorescent light) and natural (sunlight) irradiation. The photocatalytic performance of the bismuth tungstate-coated beads was compared to that of titanium dioxide coatings deposited onto identical beads. The results showed that the photocatalytic performance of bismuth tungstate-coated beads was superior to that exhibited by TiO₂-coated beads. Reactive magnetron co-sputtering has been shown to be a promising technique for deposition of narrow band gap bismuth tungstate onto irregularly-shaped substrates for potential use in water treatment applications.

Hard Coatings and Vapor Deposition Technologies

Room Golden West - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

8:00am **B4-3-1 Nano-Structural Ni Matrix Films Synthesized by Electrochemical/Chemical Composite Depositions, Zhixiang Zeng,** Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In this study, the chemical deposition was introduced into the electrochemical deposition system to tailor the micro-structures of Ni matrix films. The structures and micro-hardness of films were characterized by transmission electron microscopy and nano-indenter, respectively. Results show that not only nanocrystalline and amorphous films but also amorphous/nanocrystalline composite films could be one-step synthesized by electrochemical/chemical composite depositions. The crystalline size of Ni films could be refined to about 5 nm, which leading to the micro-hardness of about 12GPa.

8:20am **B4-3-2 NbC-Ni Coatings Deposited by DC Magnetron Sputtering: Effect of Ni Content on Mechanical Properties, Thermal Stability and Oxidation Resistance, Luis Varela,** University of São Paulo, Brazil; *F Fernandes, A Cavaleiro,* University of Coimbra, Portugal; *A Tschiptschin,* University of São Paulo, Brazil

Hard coatings have been widely used in the machine tool industry to increase the wear resistance and hence to improve their service life-time, as a result of their better mechanical properties. Most of the studies focused more in nitrides and less in carbides. In this study, we evaluated the effect of Ni additions on the properties of NbC films deposited by magnetron sputtering. In particular, we investigated the microstructure, structure, mechanical properties, oxidation resistance and thermal annealing of films. The properties of Ni rich coatings were compared to a NbC film deposited as reference. All the films displayed a columnar morphology with columns extending from the substrate up to the surface. Increasing the Ni content decreases the columns size of films and consequently, their level of compactness. Excluding the substrate contribution, all the diffraction peaks could be generally assigned to the f.c.c NaCl type structure. The introduction of Ni to the NbC film shifts the (111) and (200) diffraction peaks to higher and lower angles, respectively. A progressive decrease of grain size is observed with Ni additions, reaching a quasi-amorphous from Ni contents higher than 17 at.% Ni. TGA measurements showed that Ni additions increased the oxidation performance of the coatings. The onset point of oxidation of films is higher by 100 °C for Ni containing films independently of the Ni amount. The hardness of films increased to Ni content in the range of 0<at.% Ni<12 and then progressively decrease with further Ni additions. Annealing performed at 600 and 800 °C increased the hardness and Young's modulus of films. Elastic strain to failure (H/E) and plastic deformation resistance H^3/E^2 parameters showed a growing trend with Ni additions.

8:40am **B4-3-3 Stress-Dependent Elasticity of TiAlN Coatings, Marcus Hans,** RWTH Aachen University, Germany; *U Hangen,* Bruker Nano GmbH, Germany; *L Patterer, D Holzapfel, D Music, S Evertz,* RWTH Aachen University, Germany; *V Schnabel,* Laboratory for Nanometallurgy, ETH Zurich, Switzerland; *A Eriksson, J Ramm, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *H Rudigier,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Switzerland; *J Schneider,* RWTH Aachen University, Germany

In this work we compare the elastic properties of TiAlN coatings synthesized by cathodic arc on sapphire substrates with and without substrate rotation. Elastic properties as well as residual stress states are investigated as a function of temperature by *in situ* nanoindentation and X-ray diffraction up to temperatures of 500°C. Room temperature elastic modulus values of 459 ± 26 GPa and 501 ± 5 GPa were obtained by nanoindentation for coatings grown with and without substrate rotation (stationary), respectively. The elasticity enhancement by 9% due to stationary processing under otherwise identical deposition parameters can be understood by the formation of compressive residual stresses on the order of -5 GPa. The coatings grown utilizing substrate rotation are characterized by a tensile residual stress state of +1 GPa.

9:00am **B4-3-4 Evaluation of the Open Porosity of PVD-Coatings through Electrochemical Iron Detection, Juan Vega, H Scheerer, G Andersohn, M Oechsner,** Technische Universität Darmstadt, Germany

The open porosity of Plasma vapour deposition (PVD) coatings, namely the existence of open paths between the substrate and the environment through the coating is a critical factor that can lead to failure of the coatings in corrosive environments. Most of the coatings create a physical barrier by covering the surface of the substrate. Because of the open crystalline structure of some PVD-Coatings and the presence of imperfections, some parts of the substrate can be expose to corrosive environments. Corrosion takes place preferably on the substrate, due to the superior corrosion resistance of many PVD-Coatings. Corrosion processes underneath the coating could lead to delamination of the coating or even failure of the coated part. Electrochemical methods based on the measurement of the current density as response to the polarisation of the sample have been widely used to characterize the porosity and corrosion behaviour of PVD-Coatings, however the presence of metallic interlayers create a mixed electrochemical potential with the substrate, the results are in this case combined information about interlayers and substrate.

The present investigation uses the electrochemical ion detection to evaluate the open porosity of PVD-Coatings. In order to validate the method, samples with different open porosities and interlayers thicknesses were deposited on steel substrates. The method is based on the assumption that corrosion will occur on the substrate surface if open paths through the coating exist. A platinum mesh located on the sample's surface, held at oxidation potential of Fe^{2+} to Fe^{3+} is used to detect and quantify iron ions coming from the substrate. The current density on the platinum mesh will be increased if iron ions are available to be oxidized. By comparing the current densities of the coatings it is possible to classify them according to their open porosity. Because not polarisation of the sample is required, unlike other electrochemical methods used to evaluate the porosity, the method can be considered as non-destructive. The detection is not affected by metallic interlayers. The measurements can be done under free corrosion potential conditions, making long-term evaluations possible. In cases where the current densities without polarisation are similar, the sample can be polarised to increase the corrosion processes and the associated iron detection. The results show a good agreement with the microscopic inspection and microstructural characteristics of the samples.

9:20am **B4-3-5 Structural and Optical Properties of Si-Nb-N Composite Thin Films, Cristian Orozco,** University of Texas at El Paso, USA; *N Murphy, L Sun,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *R Chintalapalle,* University of Texas at El Paso, USA

Nitride nanocomposite thin films have generated significant attention as a result of their robust mechanical and good corrosion stability. Due to their excellent hardness (~40 GPa) and high wear resistance NbN coatings have found use in a wide variety of applications such as the coating of cutting tools and to strengthen the surface mechanical properties of superconducting cavities. The mechanical properties of NbN can be further improved through mixing with Si_3N_4 , leading to the formation of a nanocomposite structure. NbN- Si_3N_4 nanocomposite coatings have been actively studied due to their high hardness, high elastic modulus, and high resistance to oxidation. In this work, efforts were made to synthesize Nb-Si-N nanocomposite films with variable Nb-N and establish a correlation between structural and optical properties. The Nb-Si-Nfilms were deposited by pulsed DC and DC magnetron sputtering onto silicon substrates. Pulsed DC was used to ensure the stability for dielectric Si_3N_4 and remained at a constant power of 150W concurrent with variable power DC sputtering (0-150 W) for NbN. The N_2 flow rate was selected via hysteresis monitoring with the co-deposition at 150W Si and 150 Nb related to maximum nitrogen uptake and seeing the metallic, transition, and poisoned modes. X-ray diffraction (XRD) studies indicate that all the films were amorphous. Chemical analyses using X-ray photoelectron spectroscopy (XPS) indicate a progressive reduction in Si content with increasing Nb. Corroborating with structural and optical data, mechanical characteristics also indicate a change in elastic modulus and hardness of the Nb-Si-N films. A structure-composition-property relationship in Nb-Si-N films is established.

Friday Morning, April 27, 2018

9:40am **B4-3-6 HIPIMS Cr/CrN Multilayer Structure for Corrosion Resistant Decorative Coating**, *Yen-Chun Liu, S Hsiao, W Lo, Y Chen, J He, Feng Chia* University, Taiwan

Physical vapor deposition (PVD) processes have long been considered for decorative applications, as alternatives for electroplating processes. However, relatively little progress has been made due to corrosion issues brought by the existing defects in the coating structure resulting from the conventional PVD film morphology. By combining highly ionized PVD and multilayer structure, it is anticipated that corrosion protectiveness shall be improved further due to more effective barrier property to corrosive environment.

This study employs high power impulse magnetron sputtering (HIPIMS) to deposit Cr/CrN multilayer coatings on copper alloy substrates. The main advantages of HIPIMS are much denser, and smoother coatings compared to conventional PVD thin film deposition techniques. This paper briefly describes the corrosion resistance of the obtained HIPIMS Cr/CrN multilayer coatings characterized by electrochemical technique. Microstructures of these coatings are also examined to correlate their respective corrosion protective effectiveness.

10:00am **B4-3-7 Hardness-independent Extraordinary Wear Resistance in Magnetron Sputtered Cr-Si-N Coatings: The Importance of Fracture Toughness**, *Feng Huang, F Ge, C Jia*, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

A central problem of tribological hard coatings is to understand the relationship between wear resistance and mechanical properties (such as hardness, elastic modulus, fracture toughness, etc.). When high wear resistance is sought for brittle hard coatings, existing models all suggest a positive correlation with the coating hardness (H) or the hardness-to-modulus ratio (H/E). Here we report experimental observation showing a constantly high wear resistance, independent of the hardness, in brittle ceramic coatings. Nanocomposite Cr-Si-N coatings were prepared by magnetron sputtering under the assistance of energetic bombardment (by 10-60 eV ions) at a moderate ion-to-atom flux (about unity). We find that these coatings, with various amounts of nanopores but no uninterrupted column boundaries along the growth direction, achieved high wear resistance (i.e., wear rate approaching 10^{-17} m³/N m level) over a wide hardness range (12-36 GPa). Microscopic examination of the wear tracks reveals noticeable energy relief by limited inelastic deformation, such as crack propagation followed by crack bridging and crack deflection, in a localized to widespread manner with decreasing hardness. Contrary to previous models, the present results demonstrate that the wear resistance of brittle hard coatings is governed by fracture toughness (a measure of resistance to crack extension) rather than hardness (a measure of resistance against permanent deformation), and highlight the importance of energy absorption by limited inelastic deformation in achieving high wear resistance.

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