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

Hard and Multifunctional Nanostructured Coatings

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Nanocrystalline or quasi-amorphous ternary Me-Si-N (metal Silicon Nitride) systems have gained considerable interest because of their impressive physical, chemical and mechanical properties. In this article, the structural and mechanical properties of Ta–Si–N coatings prepared via reactive magnetron sputtering have been investigated as a function of varying N_2 percentage in the N_2/Ar gas mixture. It was demonstrated that decreasing the N_2 content in the gas mixture resulted in changing the film structure from face centered cubic (fcc) TaN (at 20% N_2) to a mixture of fcc $TaN_{1.13}$ and hexagonal (hex) Ta_2N (at 15% N_2), to hex Ta_2N (at 13% and 10% N_2) and finally to textured hex Ta_2N (at 7% N_2). X-Ray photoelectron spectroscopy revealed both Tantalum-Nitride and Silicon-Nitride binding states in the films. The hardness of the films varied from ~25 Gpa to ~35 Gpa with N_2 content varying from 7% to 15%. Especially the film deposited with 13% N_2 besides possessing highest hardness of ~ 35 Gpa, exhibited the highest hardness/modulus ratio (0.133), elastic recovery of ~60% and very low wear rate (7×10^{-6} mm^3/Nm). This film exhibited nanocolumnar structure, with columns being separated by an amorphous matrix 5-10 nm in width. Oxidation resistance of the Ta–Si–N coating was assessed by means of thermogravimetric analysis in a flowing air up to an annealing temperature of 1300 °C and the film depicted no increase in mass upto 800 °C. Consequently, the films maybe used as a new class of hard and oxidation resistant coatings.

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

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

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

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

Author Index

Bold page numbers indicate presenter