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

Properties and Characterization of Hard Coatings and Surfaces

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

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

In this work, an experimental and numerical study of the contact fatigue test on cobalt boride (CoB/Co_2B) coatings is presented. The boride layers were formed at the surface of Co-Cr-Mo alloy using the powder-pack boriding process at temperatures of 1123 K for 3 h and 1223 for 1 and 5 h of exposure times in order to obtain three different thicknesses. From the set of experimental conditions of the boriding process, contact fatigue tests were performed with a servo-hydraulic universal testing machine by repetitive impact of a sphere on the layer-substrate system. The methodology of the contact fatigue test consisted of two main stages. First a static critical load was determined, where radial cracks were considered as the failure criterion afterward fatigue conditions were conducted in low-cycle (n < 100,000) using sub-critical loads with a frequency of 6 Hz. The test results indicate that the thinner coating exhibited improved resistance to fatigue. In order to evaluate the stress field generated in the boride coating during the application of static and dynamic loads, a numerical simulations based in the finite element method was developed.

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

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

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

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

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

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

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

9:40am **B4-1-6 Synthesis and Characterization of Multilayered Coatings in the Ti-Al-N System by a Reactive Gas Pulsing Process***, **Ahmed El Mouatassim**, M Pac, P Henry,* LPMT, France*; C Rousselot,* FEMTO-ST, France*; C Tromas, F Pailloux, T Cabioc'h,* SP2MI, France

Nanostructured coatings of metallic nitrides are commonly used in the industry as protecting coatings for cutting tools due to an excellent combination of properties including a high hardness, improved wear properties and oxidation resistance. To improve their functionality towards various applications, it is necessary to test new deposition techniques beyond the conventional PVD techniques such as magnetron sputtering. The coatings here studied are synthesized by using a "Reactive Gas Pulsing Process" (RGPP) which is a promising new technique allowing one to obtain multilayer compositionally modulated coatings with potential excellent mechanical properties.

$Ti_xAl_{1-x}N/Ti_{x'}Al_{1-x'}N_y$ ($x \approx x' \approx 0.5$; $0 \leq y \leq 0.8$) 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^3$0.4) and those with ceramic/metal bilayers ($y \geq 0.4$) and those with ceramic/metal bilayers (y=0), the latter being softer with very poor tribological properties due to the presence of the TiAl phase. Very different internal stresses were also found for ceramic/ceramic and metal/ceramic multilayers. Observations in a TEM (HR, HAADF, SAED,…) combined with EELS experiments allowed to discuss the evolution of the microstructure and of the stoichiometry of the multilayer during the growth process. Complex phenomena like nitrogen interdiffusion and poisoning effect of the target during the deposition process have to be taken into account to discuss nitrogen amount and environment.

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

The transition metal nitride, TMN, films, including TaN, HfN, and MoN, were fabricated by RF magnetron sputtering with various microstructure features through input power and gas flow ratio control. With Ar/N_2 gas ratios and RF input powers from 8/12 to 18/2 and 75 to 300 W, respectively, the TMN nitride films evolved from crystalline, nanocrystalline to amorphous features. The multilayer films were further produced through tailoring of thin layers of above mentioned structural features to enhance the tribological behavior as protective coatings. Scratch and linear reciprocated pin-on-disc wear tests were practiced on singlelayer and multilayer TMN films to evaluate the adhesion strength and failure behavior . Severe cracking and chipping were found for the singlelayer TMN films with crystalline structure. Limited adhesive failure was observed for the multilayer coatings with alternate stacking of layers with different microstructures. Lower coefficient of friction for the crystalline/noncrystalline tailored multilayer TMN films during wear activities was also evident for their superior protective characteristics.

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

The incorporation of silicon into zirconium nitride (ZrN) thin films is a known alternative to effectively refine their grains and improve mechanical properties and oxidation resistance. However, it is not well clarified in literature information regarding the structure formation mechanism and the influence of Si content in the chemical and physical properties of Zr-Si-N thin films. Thus, the aim of this work is to investigate the influence of varying Si concentration in the microstructure, morphology, mechanical properties and oxidation resistance of ZrN films. Pure ZrN and Zr-Si-N thin films were deposited by reactive magnetron sputtering technique, with Si content set between 3 and 15%. Characterizations were carried out using GAXRD, TEM, XPS, and high temperature oxidation tests. It was identified amorphous and crystalline areas along the films microstructure, consisting in crystalline grains embedded in an amorphous phase, which were characterized by EDS as Zr and Si rich areas, respectively. GAXRD results indicate peak intensity reduction and broadening increase due silicon nitride segregation to grain boundaries, which is responsible for grain size reduction, reaching magnitudes lower than 10 nm, calculated by Scherrer. GAXRD peaks shift are observed for all samples and it can be explained due formation of a solid solution in which Si replaces Zr atoms in ZrN crystal lattice and due a strong interface between crystalline phase and amorphous one. XPS confirmed the presence of compounds like ZrN and Si_3N_4 and it is also possible to infer the formation of a solid solution of Si in ZrN lattice. Oxidation tests were performed at temperatures in the range of 773 K to 1373 K. ZrN film is almost fully oxidized at 773 K, while films with high silicon content maintain ZrN grains stable at 973 K. When oxidized, ZrN films form monoclinic ZrO_2 phase, but, in films with silicon addition, the stable phase is the tetragonal one. This happens due ZrN grain size reduction, because tetragonal phase has the lowest surface energy. Oxidation tests results confirm that there is a mechanism acting as diffusion barrier in films, preventing grains coalescence and oxygen diffusion into film structure. This mechanism is a direct consequence of silicon segregation process to grain boundaries, which ensures the formation of a nanostructure composed of ZrN grains embedded by an amorphous Si_3N_4 layer (nc-ZrN/a-Si_3N_4), allowing oxidation resistance improvement in at least 473 K.

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

In recent years, high power impulse magnetron sputtering (HiPIMS) has drawn a lot of attentions due to its high ionization of the working gas and the target atoms, and its ability to improve the quality of the resulting films, for example, better adhesion, higher density, and reduced surface roughness. Also, HiPIMS process allows the use of temperature-sensitive materials as the substrates. This feature opens a new window of applications. In this study, Ti-Cu, Cu-Ag, and TiN thin films were deposited using HiPIMS under various the target currents. The characteristics of these thin films, including microstructure, morphology, composition, adhesion to the substrate, and chemical bonding state are reported and discussed. Furthermore, the antibacterial activity, the corrosion resistance in simulated bodily fluid, the wear resistance against to the Al_2O_3 ball, and the biocompatibility test to MG63/3T3 were also presented.

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

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

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

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

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

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

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

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

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

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

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

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

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

References

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