Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B4-3

Properties and Characterization of Hard Coatings and Surfaces

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

A central problem of tribological hard coatings is to understand the relationship between wear resistance and mechanical properties (such as hardness, elastic modulus, fracture toughness, etc.). When high wear resistance is sought for brittle hard coatings, existing models all suggest a positive correlation with the coating hardness (H) or the hardness-to-modulus ratio (H/E). Here we report experimental observation showing a constantly high wear resistance, independent of the hardness, in brittle ceramic coatings. Nanocomposite Cr-Si-N coatings were prepared by magnetron sputtering under the assistance of energetic bombardment (by 10-60 eV ions) at a moderate ion-to-atom flux (about unity). We find that these coatings, with various amounts of nanopores but no uninterrrupted column boundaries along the growth direction, achieved high wear resistance (i.e., wear rate approaching 10^{-17} m^3/N m level) over a wide hardness range (12-36 GPa). Microscopic examination of the wear tracks reveals noticeable energy relief by limited inelastic deformation, such as crack propagation followed by crack bridging and crack deflection, in a localized to widespread manner with decreasing hardness. Contrary to previous models, the present results demonstrate that the wear resistance of brittle hard coatings is governed by fracture toughness (a measure of resistance to crack extension) rather than hardness (a measure of resistance against permanent deformation), and highlight the importance of energy absorption by limited inelastic deformation in achieving high wear resistance.

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