Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room On Demand - Session E2

Mechanical Properties and Adhesion

**E2-1 Structural, Nanomechanical and Tribological Properties of Manganese Phosphate Coatings*, Esteban Broitman (esteban.daniel.broitman@skf.com),* *I. Nedelcu,* SKF Research & Technology Development Center, Netherlands*; T. von Schleinitz,* SKF Research & Technology Development Center, Germany

Manganese Phosphate (MnPh) coatings are nowadays being used in rolling bearings applications due to their advantages such as wear resistance, corrosion resistance, improved fatigue life, and anti-fretting performance. There has been extensive research on their preparation methods, however, there is only one publication describing their nanoindentation hardness, and nothing is known about their elastic modulus.

In this work, MnPh coatings with a thickness of about 5 µm were deposited by a chemical conversion process. AISI 52100 steel substrates were placed in a phosphoric acid bath, where an acid-metal reaction took place locally depleting the hydronium (H_3O^+) ions, raising the pH, and causing a manganese phosphate dissolved salt to fall out of the solution and be precipitated onto the steel surface. Among the many possible grain size settings, a variant with 5-10 µm was chosen to do the measurements as the small grain sizes deliver more repeatable measurement results. Analysis of the surface microstructure and composition of the coatings by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Electron Dispersion Spectroscopy has revealed a polycrystalline coating with prismatic-shaped crystals, and about 20% content of Mn. The nanomechanical properties, studied by nanoindentation, exhibit a surface with hardness H_{IT} ~ 1 GPa and Young's modulus E_{IT} ~ 50 GPa. A method was develop to draw H_{IT} and E_{IT} maps correlated to their SEM morphology. A Mini-Traction Machine (MTM) was used in a ball-on-disc configuration to assess wear performance under severe boundary lubrication conditions. After tribological testing, XRD and SEM analysis has shown that the crystallinity of the original structure in the contact area strongly deteriorated due to the severe deformation of the original grains, while the hardness and elastic modulus inside the wear track increased to H_{IT} ~ 7.5 GPa and E_{IT} ~ 225 GPa, respectively.

E2-2 INVITED TALK: Controlled Spalling of Microscale, Single-Crystal Films of High-Quality, High-Value Semiconductors*, Corinne Packard (cpackard@mines.edu),* Colorado School of Mines, USA **INVITED**

Controlled spalling is a method to produce thin, continuous single-crystal films at semiconductor wafer scale. A stressed material with excellent adhesion to the wafer transmits forces sufficient to propagate a near-surface fracture in the crystal, resulting in the removal of a microscale-thickness, single-crystal film and leaving the remainder of the wafer intact. This talk illustrates the impact of nickel stressor film and laminate processing conditions on spall depth and fracture surface morphology, using germanium and gallium arsenide wafers as example high-value semiconductors. Fracture surfaces exhibit various features across nanometer- to centimeter-lengthscales; their morphology is characterized and cross-correlated to local optoelectrical performance in testbed photovoltaic cells.

E2-4 Industrial Applied Measurement Method of Localized Coating Property and Stress Profiles Within a Calotte Wear Crater via Nano-Indentation*, Troy vom Braucke (troy@gpplasma.com),* GP Plasma, Canada*; F. Papa,* GP Plasma, USA*; A. Harris, B. Beake,* Micro Materials Ltd, UK*; J. Gutiérrez, I. Martinez, A. Wennberg,* Nano4Energy, Spain*; C. Shin, J. Yun,* DONGWOO HST CO., Korea (Democratic People's Republic of)*; N. Bierwisch, N. Schwarzer,* Saxonian Institute of Surface Mechanics SIO, Germany

Current measurement techniques for the determination of coating stress, hardness, elastic modulus etc. rely on several assumptions when modeling or directly measuring lattice stress or stress relaxation. These measurement techniques can be time consuming, costly and lack the flexibility to be used in the rapid development cycles needed for industrial applications. We will discuss the shortcomings, potential error and uncertainty assumptions highlighting that we might be missing some fundamental properties of interest to better design functional coatings. Results are presented which show that it is possible to determine localized (relative to a reference) intrinsic stress profiles via a series of nano-indentations within a Calotte crater while mitigating the need to make several assumptions regarding material properties. These profiles can be determined from the indentation curve data through the application of the fundamental equation of elasticity combined with a holistic top-down approach, including uncertainty quantification. We demonstrate the method on a thick DLC coating and on thick sputtered AlTiN HiPIMS coatings, comparing stress depth profiles for samples deposited on single, two and three-fold rotation axes along with other important properties.

This method allows one to characterize stress profiles quickly and simply for industrial applications with nanoscale resolution. The benefit being that one can quickly relate the effects of process changes on stress states as a function of depth to better design coatings for functional use. Future work is proposed to further validate the method for absolute stress measurement.

E2-5 Nanostructured CVD W/WC Coating with Enhanced Resistance to Water Droplet Erosion and Cavitation*, Yury Zhuk (yzhuk@hardide.com),* Hardide Plc, UK

Water Droplet Erosion (WDE) damages the leading edges of steam and gas turbine blades, increasing turbine rotation drag and leading to costly maintenance. Cavitation Erosion (CE) damages pump and valve components, flow control and marine equipment. Both WDE and CE are complex phenomena which have significant similarity, so materials resistant to CE often show enhanced resistance to WDE. Protection of industrial equipment against WDE and CE is a pressing industry demand and advanced coatings are considered a promising approach to address it. This paper reports the testing of nano-structured CVD WC/W metal matrix composite coating resistance to WDE and CE and discusses the key factors affecting this advanced coating performance.

Two types of WC/W coatings were tested: "A" type is 100 microns thick and has a hardness range of 800-1200 Hv and "T" type is 50 microns thick with a higher hardness of 1100-1600 Hv. Both coating types are made of Tungsten Carbide nanoparticles dispersed in metal Tungsten matrix. This composition and structure enable a combination of enhanced fracture toughness with high hardness and the production of exceptionally thick hard CVD coatings to provide durable protection.

The coatings were tested for WDE resistance using 350 µm water droplets at 300 m/sec velocity. Uncoated 410 SS control samples suffered from major loss of material after just 7-hours of exposure to WDE, forming a 200 µm deep scar across whole tested area. After a much longer exposure of 90 hours, the coating samples showed negligible WDE damage, only measurable on the sample's edges. Thicker and less hard type A coating showed better performance when compared to thinner, harder type T.

The coating CE resistance was tested in accordance to ASTM G32-92 using ultrasonic induced cavitation in distilled water. The sample's weight was measured at regular intervals during the total 330 minutes exposure. All coating types showed a very low maximum CE erosion rate of 0.004….0.010 mg/min as compared to 15.6 mg/min for uncoated Ti6Al4V substrate. Less hard A type coating also shown better performance in this test.

Effects of the coatings' thickness, hardness, microstructure, and residual stresses on the WDE and CE resistance were evaluated.

The testing showed that the CVD WC/W coating can protect steam and gas turbine blades against WDE, and pump and valve parts against CE thus increasing equipment service life and maintaining its optimal performance for longer. The CVD technology produces a uniform coating on complex shaped parts like turbine blades, vanes, pump impellers, including non-line-of-sight areas.

E2-6 Toughening Magnetron Sputtered S-phase Stainless Steel Coatings by Cycling the N_2 Gas Flow Rate*, Carlos Mario Garzon (cmgarzono@unal.edu.co),* Universidad Nacional de Colombia - Bogotá, Colombia*; A. Recco,* Universidade do Estado de Santa Catarina, Brazil

Both superficial protective coatings and functional interlayers of stainless steel (SS) are being developed by diverse research groups in pursuit of superior electrochemical corrosion resistance, oxidation resistance, tribological performance, mechanical strength, and tailored optoelectronic properties. In particular, nitrogen-alloyed austenite phase in SS (so-called S-phase) displays superior corrosion resistance associated to anti-scratch capacity. However, S-phase coatings exhibit hampered ductility in comparison with its nitrogen-lean counterparts due to nitrogen-induced ductility dip. Thus, wear resistance of S-phase coatings could be impaired when tested under conditions of high contact loads, it due to early film cracking. In this contribution, we report on magnetron sputtered S-phase stainless steel coatings obtained from an 316L SS target by cycling the N_2 gas flow rate between 2.2 and 0.0 N_2 sccm. Direct-current magnetron sputtering experiments were carried out with a substrate temperature of 573 K, fixed Ar flow rate of 1.2 sccm and power density of 7.0 Wcm^{-2}, obtaining 1.7 µm thick coatings. SS coatings onto either SS or glass substrates were studied. Coatings with N-lean interlayers sandwiched between S-phase regions were thus obtained. Coatings with either one or three N-lean interlayers were studied. Two coating configurations were studied, varying the stacking ordering of N-lean and S-phase interlayers. Coating's cracking resistance was appraised by carrying out Vickers indentations on top of covered samples at increasing test loads, with maximum test load of either 30 kgf (SS substrates) or 15 kgf (glass substrates). On one hand, coatings onto SS substrates showed no crack formation. On the other hand, coatings onto glass substrates showed diverse patterns of crack formation. Radial crack length was recorded for those coatings onto glass, and it was observed an outstanding increase of resistance to indentation-induced cracking in the coatings obtained cycling the N_2 gas flow rate, regarding to the traditional homogeneous S-phase coatings. The observed coating toughening was attributed to a ductile barrier effect exerted onto propagating cracks by the N-lean interlayers and to an adequate distribution of coating residual stress. This contribution shows how the stacking configuration of N-lean and S-phase interlayers and the interlayer thickness affect the overall coating's toughness.

E2-7 Thin-film Adhesion: A Comparative Study Between Colored Picosecond Acoustics and the Stressed Overlayer technique, *Arnaud Devos (arnaud.devos@univ-lille.fr)*, Iemn, Umr Cnrs, France; *M. Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Thin-film adhesion is a main issue for a broad range of industrial applications due to the crucial role it plays for final device reliability. Adhesion of thin films can be easily checked with qualitative methods like tape test. In a very efficient manner one can compare the adhesion of different samples. But to identify which interface is the most critical from the adhesion point of view, more sophisticated methods are needed.

One way of measuring quantitavely the adhesion energy is to analyze the geometry of buckles that appear either spontaneously or by adding a stressed overlayer following the pionneer work of Hutchinson and Suo[1].

Alternatively, acoustic waves can be used to probe adhesion at a buried interface through an analysis of their reflection coefficient. To do acoustic measurement at the sub-micronic scale, one needs ultra-high frequency waves typically in the range of a few 10 to a few 100 GHz. Colored Picosecond Acoustics (APiC) is a technique that implements an acoustic pulse-echo technique at the nanoscale using a tunable ultrafast laser. The laser directly excites an acoustic pulse in the sample where it propagates at sound velocity. When such a pulse reaches an interface a part is reflected and a second laser is used to detect optically the returning echo. Such hypersonic waves can be used first to measure the acoustic time-of-flight in each layer of a stack. That gives informations about film thickness or elasticity. They can also be used to detect adhesion defect at an interface [2].

In this paper, the two techniques are compared by applying both of them to the same set of samples. Resolution and their respective capabilities to identify the critical interface and quantify the adhesion energy will be discussed.

References:

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E2-8 Comparing the Residual Stress Gradient Measurement of ZrN using FIB-DIC and Xray Diffraction, *W. Lin, Y. Chou,* National Chung Hsing University, Taiwan; *J. Huang,* National Tsing Hua University, Taiwan; ***Ming-Tzer Lin (mingtlin@nchu.edu.tw)***, National Chung Hsing University, Taiwan

Reliable measurement and modeling of residual stresses at the micrometer scale is a great challenging task for small scale structures and nanostructured thin films. Moreover, the specific location on micro scale evaluation of residual stress gradients is a very critical issue in the hard coating of thin films. The analysis of the residual strain depth profiles requires detailed knowledge of the in-depth lattice strain function, so the residual stress profile calculation can be carried out in a manner that takes into account the mechanical anisotropy and texture of the materials. The development of a microstructure independent procedure for depth resolved measurement of residual stress is an issue of strategic interest. Here, we perform a digital correlation (DIC) of the specimen images acquired by incremental focused ion beam (FIB) ring-core drilling with various depth steps. 2 um thick sputtered ZrN thin films deposited on the silicon substrate were used for this measurement. To observe the depth resolved residual stress profiles of each step on thin film samples, two FIB images of the specimen, one before and one after being drilled, were processed to extract the surface deformation from tiny changes in the FIB images using DIC. This combined with high-resolution in situ SEM imaging of the relaxing surface and a full field strain analysis by digital image correlation (DIC). A parallel residual stress measurement was also performed using both wafer curvature and a four-circle diffractometer with grazing incidence X-ray diffraction (XRD) cos^{2}asin^{2}j method at several azimuthal angles to obtain the average X-ray strain (AXS). The stress gradient of ZrN films along the X and Y-axis of the wafer were revealed and compared to evaluate the stress gradient of ZrN deposition.

E2-9 Investigation of Deformation Behavior Under Different Loading Directions in Transition Metal Thin Films, *Markus Schoof (schoof@imm.rwth-aachen.de)*, RWTH Aachen University, Germany

The aim of this project was to study the effect of transition metal species and the presence of oxygen on the mechanical properties of transition metal (oxy)nitride films, and in doing so to link quantum and continuum mechanics for material design. The growth of these films results in a strongly columnar microstructure, so it is necessary to understand the influence of this texture on mechanical properties. This will enable knowledge-driven materials design on the atomic and microstructural level for macroscopic applications such as protective coatings for polymer extrusion.

Uniaxial compression was thus performed using micro pillars at different angles to the growth direction. Two sets of (V, Al)N samples were used, one manufactured by HPPMS (high power pulsed magnetron sputtering) and one by dcMS (direct current magnetron sputtering). Micro pillars oriented between 0° and 90° to the growth direction were investigated to assess the effect of texture. Furthermore, load rate and pillar diameter were varied while keeping height diameter ratio constant.

For pillars with diameters greater than 0.75 µm, no influence on fracture stress or strain could be observed. Only with smaller diameters was an increase in fracture stress observed. Furthermore, it was shown that different load rates between 0.1 mN/s and 1.0 mN/s have no influence on fracture stress and strain. In pillars with varying grain orientation, different fracture mechanisms were observed depending on the grain alignment. Comparing the critical stresses for these mechanisms with the measured fracture stresses shown that the fracture behavior could be divided into three areas related on the active mechanism and the orientation to the growth direction. In all cases, the specimens produced with HPPMS showed a slightly higher fracture stress than those produced with dcMS. This behavior could be explained by the typical microstructures resulting from the growth process.

E2-10 Study of Corrosion-Resistance Behavior and Tribological Properties of Electrophoretically Deposited Graphene Coatings on Titanium Substrate for Marine Applications, *Madhusmita Mallick (madhusmita1509@gmail.com)*, *A. N,* IIT Madras, India

Titanium alloys are widely employed for marine applications due to its excellent properties of high specific strength and corrosion resistance behaviour. However, these alloys face serious biofouling problems and thereby may become susceptible to corrosion attack under extreme marine environment. The chemical inertness, thermodynamically stable and anti-permeability nature of graphene makes it a promising coating material for effective protection of metals against corrosion.

In the present work, the graphene coating was prepared on a titanium substrate through a cost-effective and easily scalable electrophoretic deposition technique (EPD). The surface morphology and microstructure analysis of bare titanium substrate and graphene-coated samples were done by field emission scanning electron microscopy (FESEM). Grazing incidence angle X-ray diffraction (GIXRD) was carried out to identify the crystal structure of graphene coatings. Moreover, phase purity and functional groups of graphene coatings were analyzed by Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) techniques. The tribological performance of bare titanium substrate and graphene-coated samples were investigated. Furthermore, electrochemical studies were carried out to evaluate the anti-corrosion behaviour of graphene-coated samples by Potentiodynamic polarization test. The results revealed that the corrosion current density in Tafel plot analysis was reduced significantly by 72% for a graphene-coated sample as compared to a bare titanium substrate. This improvement in corrosion resistance property of titanium alloys by graphene protective coatings through EPD technique can greatly serve as a suitable anti-corrosive coating material for marine applications. Results will be presented and discussed in detail.

E2-12 Effect of Residual Stress on the Mechanical Properties of Nitride-Based Protective Coatings Deposited by Pulsed-Plasma Sputtering Techniques*, **Etienne Bousser (etienne.bousser@polymtl.ca)**, E. Herrera-Jimenez, L. Martinu, J. Klemberg-Sapieha,* Polytechnique Montreal, Canada

Materials exposed to harsh environments face ever increasing economic, technological and, environmental challenges. The field of coatings and surface engineering technologies has thus been very active, addressing numerous challenges related to the stringent requirements of high-performance protective coating (PC) systems. Despite the progress in PC fabrication processes and coating architectures, the acceptance and further advances in this area are frequently limited by high residual stress (RS) in the coating systems, primarily related to the lack of fundamental and comprehensive knowledge of the stress generating mechanisms, their complex relation to the microstructure, and the availability of pathways to compensate it, and even to include it in the design.

Solid Particle Erosion (SPE) occurs in situations where hard solid particles present in the environment are entrained in a fluid stream, and impact component surfaces. Since the performance of surfaces against SPE is determined by mechanical properties such as hardness, toughness and coating adhesion, hard nitride-based PC are often used in such harsh environments. In this study, we will present our work on improving the understanding of the effects of RS amplitude and distribution on the mechanical properties of hard nitride-based PC deposited using pulsed-DC and High Power Impulse Magnetron Sputtering onto aerospace alloy substrates (Ti-6Al-4V and SS410).

First, we investigated the effect of three different interface treatments on the microstructure and mechanical properties of TiN coatings. We show that the interface treatments induce RS at depths of several microns within the substrate and microstructural changes to the substrate material significantly affecting the microstructure, mechanical properties and adhesion of the overlying coating. Moreover, we also show the effect of RS on the measurement of coating toughness using conventional indentation methods. The effect of coating composition and deposition process will be discussed with respect to RS and the measured toughness values. The microstructural characterization was done using Transmission Electron Microscopy, Transmission Kikuchi Diffraction and X-Ray Diffraction (XRD). The RS depth profiles were measured using the multireflection grazing incidence XRD method and Focused Ion Beam (FIB) micro-hole drilling. Finally, the coating mechanical properties were measured by depth-sensing indentation and micro-scratch testing while the toughness was also evaluated using Scanning Electron Microscopy with *in situ* mechanical characterization of micro-machined samples produced by FIB.

E2-13 Hyperelasticity and Viscoelasticity in Thin Organic Semiconductor Coatings*, **Steve Bull (steve.bull@ncl.ac.uk)**,* Newcastle University, UK*; A. Yadav, H. Gonabadi,* Newcastle University

A wide range of organic semiconductor coatings have been developed for optical and electronic applications and have been extensively characterised for their electronic and optical properties. What mechanical measurements have been made are focused on assessing the average properties of a film (e.g. using buckling to assess elastic moduli) but are not suitable to assess point-to-point variation in mechanical response which may be related to changes in coating microstructure due to crystallisation and/or phase separation or to understand the deformation mechanisms occurring. The assessment of non-linear elasticity and time-dependent mechanical response is also lacking. This presentation will address the strain and time-dependent mechanical properties of 100-300nm thin films of a range of organic semiconductors on a glass substrate using nanoindentation at very low loads (peak loads less than 50μN) with a relatively blunt indenter (500nm tip radius). Although a well-defined indentation is produced in many cases it is not clear that plastic deformation occurs (and by what mechanism) but viscoelastic deformation is significant in making the observed indent. The use of load and displacement control during a hold period to determine the relaxation modulus for very thin films will be discussed. Finite element modelling of the load-displacement curves reveals that including both viscoelasticity and hyperelasticity (rather than simple linear elasticity) is necessary to explain the measured load-displacement curves in for several different organic semiconductor materials.

E2-14 Abrasion Wear Resistance of Low Temperature Plasma Nitrided Inconel 625 Superalloy*, L. Varela, M. Ordoñez,* University of São Paulo, Brazil*; **Carlos Pinedo (pinedo@heattech.com.br)**,* Heat Tech & University of Mogi das Cruzes, Brazil*; A. Tschiptschin,* University of São Paulo, Brazil

In this work, Low Temperature Plasma Nitriding (LTPN) was carried out in an Inconel 625 superalloy at 420 °C for 20 h, in a 75% N_2 + 25% H_2 atmosphere. After plasma nitriding, the specimens were analyzed by various characterization techniques: X-ray diffraction, scanning electron microscopy, micro-hardness measurement, scratch and micro-abrasion wear tests. Microstructure, hardness and abrasion wear resistance of the untreated Inconel 625 is compared with the properties obtained after the LTPN treatment. Friction coefficient, mechanical failure mode and critical loads for damaging the nitrided case were determined using the linear scratch test, carried out at a linearly increased normal force. Microabrasion tests were conducted to evaluate the abrasion wear resistance. The microstructure of the as received material was composed entirely by polygonal (γ) FCC grains. The results showed that LTPN promotes the formation of a nitrided layer around 8.4 µm thick, 930 ± 20 HV hard, consisting of a nitrogen expanded FCC phase (γ_N), also known as S phase, ε-$Fe_{2–3}N$ and CrN nitrides. Colossal N supersaturation was detected in the expanded FCC layer, which promoted strong hardening and a state of compressive residual stresses. The scratch tests results showed that the nitrided layer strongly decreased the apparent friction coefficient, in comparison with the non-nitrided alloy. Tensile cracking was the prevalent mechanical failure mode of the nitrided layer. Microabrasion results showed that the LTPN treatment decreased the wear volume losses. For the nitrided samples wear coefficients were determined for the nitrided layer and for the substrate, indicating a change in the wear volume loss rate with the sliding distance.

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