## Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
## Room On Demand - Session E1
## Friction, Wear, Lubrication Effects, and Modeling

**E1-1 Multi-sensing Nano-wear with Electrical Contact Resistance and Friction Measurement***, **Ben Beake (ben@micromaterials.co.uk),*** Micro Materials Ltd, UK*; T. Liskiewicz,* Manchester Metropolitan University, UK*; A. Harris,* Micro Materials Ltd.*; S. McMaster, A. Neville,* University of Leeds, UK

Wear begins at the asperities but typically the contact pressures acting on these are unknown in a standard macro-scale tribological test. In contrast, testing at the nano-/micro-scale ("single asperity tribology") enables the onset of wear to be studied conveniently and correlations with friction forces investigated to aid the design of surfaces with improved wear resistance.

Reciprocating contacts occur in a wide variety of practical wear situations including hip joints and electrical contacts. In optimising materials for improved durability in these contacts it is important that the contact conditions (e.g. sliding speed) can be reproduced. Hence, a capability for rapid high-cycle linear reciprocating nano-scale wear tests has been developed (NanoTriboTest) with automatic recording of friction loops, cumulative energy dissipation and electrical contact resistance. The design has high level of lateral rigidity providing the necessary stability to perform nano- or micro-scale wear tests for extended duration (e.g. several hours, up to 300 m sliding).

In this study, high cycle, up to 40 mm long track length reciprocating nano-wear tests have been performed on multilayer DLC coatings, and the biomedical alloys Ti6Al4V and 316L stainless steel. Stainless steel showed ductile response throughout the load range but an abrupt transition to higher friction and fracture-dominated wear after ~20 cycles occurred on Ti6Al4V. Friction and wear evolution in the test was compared to that in nano-fretting (gross slip) and nano-scratch (unidirectional) tests [1-3].

Improved detection of the onset of wear and the subsequent failure mechanisms was achieved by a multi-sensing approach where changes to electrical contact resistance were shown to correlate directly with the measured friction. Nano-wear tests of noble metal-noble metal contacts (Au-Au and Ag-Ag) showed much longer endurance than gold vs. steel contacts although occasional isolated failures were observed in 35000 cycle tests.

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**E1-2 Interlayer Design to Increase Adhesion of a-C Coatings onto C17200 Copper-Beryllium Alloy Surface***, **Marcos Dantas dos Santos (mdantas@usp.br),** N. Fukumasu,* Polytechnic School of the University of Sao Paulo, Brazil*; A. Tschiptschin,* Metallurgical and Materials Engineering Department, University of Sao Paulo, Sao Paulo, Brazil*; R. de Souza, I. Machado,* Polytechnic School of the University of Sao Paulo, Brazil

Copper-beryllium (CuBe) alloys are widely used in the aeronautic and automotive industries due to its good thermal properties and corrosion resistance. However, reduced hardness and wear resistance can limit the use in manufacturing applications. To overcome these limitations, hard ceramic coatings can be applied to the tool surface, increasing the wear resistance, and reducing the friction coefficient. Among several coating options, amorphous carbon (a-C) coatings were selected in this work since this coating can present high hardness and a very low friction coefficient. Nevertheless, the main challenge in using a-C coatings onto CuBe alloys is the low adhesion between copper and carbon. This work focused on the development of a complex interlayer to increase adhesion under high contact, pure sliding, and dry tribological conditions. Two interlayer compositions (Ti/Si and Ti/TiN/Si) were analyzed based on the improved bonding between copper and titanium, while the amorphous silicon layer was applied to reduce the diffusion of carbon into the titanium-based layer. Pulsed Direct Current Magnetron Sputtering (pDCMS) system configuration was used to deposit the coatings using polycrystalline titanium, monocrystalline silicon, and polycrystalline graphite targets. The TiN interlayer was obtained by a reactive deposition process using argon and nitrogen gases. A polycrystalline graphite target was used to produce a hydrogen-free amorphous carbon coating over the tailored interlayers. The coatings were deposited onto C17200 CuBe discs, and silicon wafers substrates. Instrumented indentation tests were carried out in a Bruker Ti950 Triboindenter to evaluate coating hardness and elastic modulus. Increasing load scratch tests, using a diamond Rockwell C tip in a Bruker UMT-2 system, were conducted to evaluate coating adhesion to CuBe alloy substrate and measure friction coefficient and critical loads. Dry reciprocating ball-on-disk tribological tests were also conducted with this system, using two constant normal loads (10N and 20N) and a stroke of 4 mm. Scanning Electron Microscope (SEM), Raman spectroscopy and coherence correlation interferometry (CCI) were used to characterize the coatings and wear tracks after the tests. Results indicate that the Ti/TiN/Si compound interlayer improved the adhesion of the a-C coating, showing higher critical failure loads compared to other combinations. Also, ball on disc tests indicate the formation of a transfer layer at the ball surface, promoting reduced wear and failure of the coating when in contact with AISI5200 steel balls.

**E1-3 Tribologically Enhanced Self-healing of Niobium Oxide Surfaces***, **Samir Aouadi (samir.aouadi@unt.edu),** A. Shirani, J. Gu, B. Wei, D. Berman,* University of North Texas, USA

Activating a self-healing process is a viable approach for preventing the failure of ceramics experiencing mechanically-induced crack propagation. Previously, it was demonstrated that niobium oxide ($Nb_2O_5$) exhibits self-healing properties activated by the formation of Nb-Ag-O ternary oxide when heated above 945 °C in presence of silver. In this study, we explore the mechanism of lowering the high-temperature healing requirement by assisting the process of crack repair with a normal load and shear stresses. Specifically, we propose to use tribologically-induced local heating as a mechanism to enhance the self-healing ability of $Nb_2O_5$. During a pin-on-disk test, whereby a niobium oxide flat was sliding against a silver-coated ball, a sudden lowering of the coefficient of friction was observed at elevated temperatures (~600 °C). The better performance of the coating was associated with a surface reconstruction process initiated inside the wear track. Extensive characterization analysis of the wear track using energy-dispersive x-ray spectroscopy, Raman spectroscopy, and x-ray diffraction confirmed the presence of an Nb-Ag-O ternary oxide phase inside the wear track formed at elevated temperature. The formation of an Nb-Ag-O ternary oxide at a much lower than thermodynamically-required temperature suggests that the self-healing process can be initiated directly during mechanically induced stresses. Such a process is a new recipe for improving wear and crack resistance characteristics of ceramic components and maybe tuned to provide the desired frictional response.

**E1-4 Computer Simulations of FCC Alloys Subjected to Dry Sliding as Basis for a Near-Surface Deformation Mechanism Map***, **Stefan Eder (stefan.eder@ac2t.at),** M. Rodríguez Ripoll, U. Cihak-Bayr,* AC2T Research GmbH, Austria*; D. Dini,* Imperial College London, UK*; C. Gachot,* TU Wien, Austria

We study the microstructural response of five FCC CuNi alloys subjected to sliding with large-scale molecular dynamics simulations. The initial grains measure approximately 40 nm in diameter to ensure that plasticity is not dominated by grain boundary sliding, so our polycrystalline aggregate exhibits dislocation pile-up, twinning, and grain refinement analogous to polycrystals with much larger grains. We analyze the depth-resolved time development of the grain size, shear, twinning, and the stresses in the aggregate to produce a deformation mechanism map for CuNi alloys. This map captures the predominant microstructural phenomena occurring for a given composition and normal pressure, and will aid engineers in optimizing materials/surfaces to work within a required operating range. We compare tomographic visualizations of our atomistic model with focused ion beam images of the near-surface regions of real CuNi alloys that were subjected to similar loading conditions.

**E1-5 From Surface to Sub-surface Contributions to Friction at the Nanoscale***, C. Menezes,* UFSC, Brazil*; V. Pavinato, L. Leidens,* UCS - Caxias do Sul University, Brazil*; F. Echeverrigaray, F. Alvarez,* UNICAMP, Brazil*; A. Michels,* ***Carlos Figueroa (carlos.cafiguer@gmail.com),*** UCS - Caxias do Sul University, Brazil

The friction phenomenon is a complex manifestation of the nature originated in energy dissipation events owing to the lost work of non-conservative forces. In spite of different surface mechanisms describing the friction phenomenon at the nanoscale, the involved energy in such surface events is not enough to explain friction forces in wearless regime. Indeed, phononic, electronic and magnetic effects are not capable of providing a sufficient energy to explain friction forces. Thus, new contributions are mandatory to reach a satisfactory energy balance among friction mechanisms and lost work by non-conservative friction forces. The aim of the work is to establish sub-surface contributions to friction at the nanoscale. In this study, we report the friction forces at the nanoscale on iron nitride and oxide by nanoindentation followed of unidirectional sliding (NUS) and friction force microscopy (FFM). Two different experimental setups are reported. Moreover, the sub-surface elastic deformation due to indentation was modeled following the classical contact theory from Hertz by using the ABAQUS software. Firstly, the elastic deformation leads to reach elastic energies in the order of lost work of friction forces. Secondly, the sub-surface contributions seem to be more important than the surface contributions to friction at the nanoscale. We discuss these surface and sub-surface mechanisms by dissipation effects associated with surface phonon coupling and sub-surface energy-releasing due to elastic energy dissipation.

**E1-6 Ni-based Self-Lubricating Laser Claddings for Hot Forming and High Temperature Vacuum Applications***, H. Torres,* AC2T Research GmbH, Austria*; B. Prakash,* Lulea University of Technology, Sweden*; **Manel Rodriguez Ripoll (Manel.Rodriguez.Ripoll@ac2t.at),*** AC2T Research GmbH, Austria

This work proposes a novel self-lubricating Ni-based laser cladding able to control friction at high temperatures while maintaining a superb wear resistance. The cladding microstructure consists of nickel dendrites surrounded by borides and homogeneously scattered pure silver pockets encapsulated within molybdenum and chromium sulfides that arise from the thermal decomposition of $MoS_2$ during deposition. This resulting microstructure is able to control friction from room temperature to 600 °C in ambient air and at least until 300 °C in vacuum. In ambient air, the friction reduction mechanism is determined by the silver and chromium sulfide pockets. Atomic force microscope investigations show that chromium sulfides have a high hardness and a low intrinsic friction. They additionally support further friction reduction by silver smearing due to their high hardness. At higher temperatures, the contribution of silver diminishes due to oxidation so that the contribution of chromium sulfides to self-lubrication is dominant.

The self-lubricating cladding shows decreased friction against Al-Si-coated 22MnB5 steel under hot stamping conditions. The presence of silver leads to a noticeable decrease in friction down to 0.3 during Al-Si coating break-up on the counter body, due to smearing next to the affected region. In the case of hot stamping against AA6082 aluminium alloy, the self-lubricating claddings in synergy with solid lubricants decrease friction and counter body wear at high temperatures compared to grade 1.2367 hot work tool steel commonly used in hot forming. These findings illustrate that the implementation of Ni-based self-lubricating laser claddings can lead to decreased costs while at the same time ensuring the quality of the hot stamped components.

In the case of high temperature vacuum performance, the presented self-lubricating cladding is able to effectively control and reduce friction down to a value of 0.25 against 440C martensitic stainless steel at room temperature and 300 °C by the smearing of silver over the chromium sulfides. This friction reduction mechanism is enhanced by the thermal softening of the pure silver phase at elevated temperatures, contrary to air atmosphere, where smearing is hampered by oxidation. This overall tribological performance makes the presented cladding also as potential candidate for space applications.

**E1-7 INVITED TALK: The Thinnest of The Thin: Friction and Adhesion Behavior of Graphene and other Two-Dimensional Materials***, **Robert Carpick (carpick@seas.upenn.edu),*** University of Pennsylvania, USA **INVITED**

Two-dimensional materials provide a rich playground for exploring new and unexpected physical phenomena at the atomic limit of thickness, and provide opportunities for many applications including demanding tribological systems. This includes protective low friction coatings and additives, functional adhesive layers in flexible electronics, and nanoelectromechanical switches. I will focus on friction and adhesion behavior of nanoscale contacts with 2D materials measured with atomic force microscopy (AFM) and compared with molecular dynamics (MD) simulations. First, nanocontacts with 2-dimensional materials like graphene will be discussed. Friction is far lower than typical bare substrates, but depends on the number of 2D material layers present. An initial model attributing this to out-of-plane puckering [1] is now enhanced by MD showing a strong role of energy barriers due to interfacial pinning [2]. We also observe a large, order-of-magnitude increase in friction when graphene is fluorinated [3]. Using MD, we interpret this in the context of the Prandtl-Tomlinson (PT) model, where the potential energy surface (PES) corrugation controls friction. We also observe a non-monotonic dependence of friction on humidity for graphite. Using MD, this behavior is attributed to adsorbed water molecules that at low coverage act as pinning sites, but at high coverage form a quasi-ordered layer that provides a low friction incommensurate interface [4].

We also discuss 2D transition metal dichalcogenide (TMD) films including $MoS_2$. TMDs exhibit intrinsically low friction, although not as low as graphene. Like with fluorinated graphene, we attribute this to the (PES) corrugation [5]. To explore the temperature dependence, we use matched AFM and MD to study friction for tips sliding on monolayer and multilayer $MoS_2$ from cryogenic to elevated temperatures. Friction sometimes decreases dramatically with temperature (thermolubricity). However, the temperature dependence is at times weak, suggesting that atomic details of the contact can matter substantially, which we explore with MD simulations. Finally, new results from nanocontact experiments of 2D materials obtained *in situ* using transmission electron microscopy (TEM) will be presented. We observe nanoscale tip-on-tip contact and sliding behavior for few layer $MoS_2$, revealing intrinsic contact, adhesion, and friction properties of these ultrathin layers.

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**E1-9 Tribological Properties of Vanadium-doped Coatings via Reactive Molecular Dynamic Simulations***, **Ilia Ponomarev (ponomili@fel.cvut.cz)**, T. Polcar, P. Nicolini,* Czech Technical University in Prague, Czech Republic

Friction and wear cause a quarter of losses of the global energy production. A well-known practical approach to reduce friction is to introduce another substance, called lubricant, to the contact surfaces. A variety of lubricants, both liquid and solid, are available on the market; the global lubricants market size was estimated at $128.51 billion in 2018.

However, friction reduction in some specific conditions may still be a challenge. Providing lubrication in oxidative environments at high temperatures, which is essential for certain technological applications, such as cutting tools, may serve an example of such a problem. Traditional lubricants, both liquid and solid, are unsuitable for the task due to their lack of oxidation resistance.

A possible solution of the problem – a hard and oxidation-resistant coating (e.g. TiN, $Si_3N_4$), containing a dopant that would, upon operation, diffuse to the surface of the coating and provide lubrication. Vanadium is a popular choice as such a dopant; in the operation conditions (above 700ºC, humid air) it is known to form oxides on the surface, which in turn melt, providing liquid lubrication. However, the exact mechanisms of oxidation and the effects of conditions on the resulting $V_xO_y$ phases are not entirely clear.

We are studying the process of vanadium oxidation computationally. We use reactive molecular dynamics within Reactive Force Field (ReaxFF) approach. ReaxFF is an empirical potential, that is shown to be capable of performing at the Density Functional Theory (DFT) based methods level of accuracy, while consuming significantly less computational resources. ReaxFF enables nanosecond-long simulations for tens of thousands of atoms at the same computational cost, as hundreds of picoseconds for hundreds of atoms in DFT.

We develop a suitable ReaxFF parameterization and apply it to the oxidation simulations. We find vanadium pentoxide, $V_2O_5$, to be the predominant outcome of the oxidation. We study the effects of oxygen pressure, load, temperature and humidity on the oxidation rate and reaction outcome.

We further explore tribological properties of the $V_xO_y$ phases yielded by oxidation and find out the mechanism of the vanadium oxide action. Sliding simulations in a wide range of conditions provide the answer to the question, how much V do we need for providing lubrication.

**E1-11 Tribological Properties of Duplex PEO/Chameleon Coating on Aluminum Alloys***, Andrey Voevodin (andrey.voevodin@unt.edu), J. Shittu, A. Shirani,* University of North Texas, USA*; A. Yerokhin,* University of Manchester*; A. Korenyi-Both,* Colorado School of Mines, USA*; J. Mogonye,* Army Research Laboratories, USA*; D. Berman, S. Aouadi,* University of North Texas, USA

In this study, plasma electrolytic oxidation (PEO) was used to create a porous oxide structure on AA 6082 aluminum alloys. This surface treatment resulted in the formation of a graded hard ceramic coating with a porous outer region. The porous regions were burnished with solid lubricants to create a hard/solid lubricant duplex multifunctional structure with an adaptive tribological response. The tribological proprieties of the duplex system was investigated by carrying out pin-on-disk and reciprocating wear tests in humid air using a range of temperatures, loads, and sliding speeds. A low friction coefficient was maintained for all test conditions, suggesting the self-adaptive nature of the selected solid lubricant mixture. High temperature pin-on-disk tests were carried at 400 ° C with an apparatus equipped with an *in situ*Raman system to monitor real time chemistry changes in the wear track. *In situ*Raman spectroscopy provided new insights into the tribochemical processes that occur at elevated temperatures for different loads and sliding speeds.

**E1-13 Analysis of Coating Layers and Defects Using Atomic Force Microscopy***, Stefan Kaemmer (stefan@parksystems.com), G. Mendoza,* Park Systems Corporation, USA

Coatings provide important roles in industrial environments. They can protect the underlying material from harsh environments or improve the tribological properties of machine parts as an example [1]. Even small defects or imperfections can act as a failure center. The inspection of the coating quality becomes therefore an important step during the development and production of the coating process.

Atomic Force Microscopy (AFM) is a well-established technique for analysis of surface morphology with sub-nanometer resolution. It has become a routine tool in material research and semiconductor manufacturing for quality control of surfaces. For standard morphological analysis, the AFM is generally operated in Non-Contact mode, which allows for non-destructive, quantitative, three-dimensional analysis of the surface topography (figure 1). However, AFM does not only allow for the morphological analysis of surfaces. By combining AFM with other techniques information like the frictional properties, electrical conductivity, surface charges, magnetic properties etc. can be extracted and mapped with nanometer resolution as well. A recent development leverages the AFM resolution capabilities and enables the determination of the nanomechanical properties, like modulus and adhesion. This so called 'PinPoint" mode is based on fast force-distance curves that are executed at each pixel [3]. Figure 2 depicts a basic force curves and some of the information that can be extracted.

We will discuss applications and highlight how PinPoint AFM can help to determine the difference between a scratch before and after coating.

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## 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 quantitatively the adhesion energy is to analyze the geometry of buckles that appear either spontaneously or by adding a stressed overlayer following the pioneer 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.

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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) $cos^2asin^2j$ 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 ($\gamma_N$), 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.

## Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
## Room On Demand - Session E3

## Tribology of Coatings for Automotive and Aerospace Applications

**E3-1 Coating Properties and Wear Resistance of ta-C Deposited by Arc Ion Plating (AIP) Technique***, Yoshiyuki Isomura* ***(isomura.yoshiyuki@kobelco.com)****, T. Takahashi, J. Fujita,* Kobe Steel, Ltd., Japan*; S. Kujime,* Kobe Steel Ltd., Japan

Hydrogen free DLC, also referred to as ta-C (tetrahedral amorphous carbon), attracts a large practical interest particularly in the automotive industry because of its unique characteristics of high hardness, low friction, and wear resistance. While ta-C exhibits those excellent properties, further improvement and assurance of adhesion in sliding parts under high contact pressure in severe operating condition is a challenge. Practical requirement and evaluation of adhesion performance is sometimes even beyond the level of basic adhesion investigation such as Rockwell indentation test or scratch test.

In this study, ta-C was deposited using an industrial arc ion plating coating system equipped with a round-bar type arc evaporation source, which is specially designed and optimized for ta-C coating process. ta-C samples with controlled adhesion was intentionally deposited on the sliding test piece with controlled process parameters. Adhesion performance evaluated by the basic test was found to be not always consistent to the results of sliding test. In addition, different frictional wear characteristics were detected among samples with different adhesion performance. In order to understand the relation of sliding properties to adhesion performance more in detail, the intrinsic coating properties were also analyzed more thoroughly in terms of mechanical hardness by nanoindentation, surface roughness/macro-particle density, chemical bonding characteristics of sp2/sp3 fraction and hydrogen concentration. We aim to combine this knowledge of material science with a practical aspect of sliding and adhesion towards improvement of performance in application of ta-C coating.

**E3-2 Numerical Study of Cracking in Thin Hard Coating Layers Using a Cohesive Phase-Field Model and Experimental Validation***, Ali Rajaei Harandi* ***(ali.harandi@ifam.rwth-aachen.de)****,* RWTH Aachen, Germany*; S. Rezaei,* Technical University of Darmstadt, Germany*; S. Karimi Aghda, T. Brepols, J. Schneider, S. Reese,* RWTH Aachen University, Germany

Prediction of damage and cracking patterns in hard protective coatings play a vital role in the optimal design of these coating layers. Experimentally, in [1], it is shown that a micro-scale tensile test of a hard coating deposited on ductile substrates is a fast-tracking tool for determining the fracture parameters of such systems. This experimental approach is specifically valid when the first fracture mode is more dominant. On the numerical side, phase-field damage models are utilized, which have attracted much attention among several available methodologies. These models benefit from a robust response and the capability of modeling cracks without introducing any initial crack path. However, the damage field tends to widen based on the internal length-scale parameter. It could be problematic when it comes to simulations on a small-scale and create some boundary effects. To this end, a cohesive phase-field damage model is used. The relevant fracture parameters such as fracture toughness and maximum tensile strength are included in this model, for which the internal length-scale is considered as a purely numerical parameter. Furthermore, due to the specified morphology of the grains in the coating layers, as well as the evolution of damage based on multiple possible damage procedures, it is inevitable to use anisotropic damage models, [2,3]. To include them, a novel orientation-dependent fracture energy function is applied, based on the later reference. Finally, the numerical results considering the crack patterns and the crack density value is compared to the micro-scale tensile test of cubic metastable $V_{0.25}Al_{0.26}N_{0.49}$ coating deposited on the Cu substrate. It is shown in this study, how fracture characteristic parameters such as fracture toughness and maximum tensile strength, as well as the substrate elastic or elastoplastic behavior, will influence the overall damage behavior of the hard coating layer.


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**E3-3 Duplex TiN and TiAlN Coatings on Ti-6Al-4V Alloy Formed by a Combination of Plasma Nitriding and Cathodic Arc Evaporation***, V. Pankov,* ***Qi Yang (qi.yang@nrc-cnrc.gc.ca)****,* National Research Council of Canada

A duplex coating concept has been investigated as a mean for protecting Ti-6Al-4V aerospace components against high impacts and high localized loads. The duplex coating consisted of the first layer formed by low-pressure plasma nitriding using a high-density plasma source and the second layer deposited on the nitrided surface by cathodic arc evaporation. Substrate temperature, substrate bias, and process duration were selected as the nitriding process parameters. The substrate temperature during Ti-6Al-4V nitriding was maintained below 800°C to avoid α-to-β phase transformation. TiN and TiAlN coatings were used for the second layer. The microstructure, elemental composition, phase content, and hardness of the nitrided layer were analyzed by scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and nanoindentation, respectively. Adhesion between the duplex coating layers was measured by scratch adhesion testing. The fabricated duplex coatings were evaluated for their wear and impact resistance using pin-on-disk and drop weight impact testing. The obtained results were used to identify optimum process parameters for producing protective coatings with duplex design characterized by high impact resistance and high load-bearing capacity.

**E3-4 Determination of Method for Tribological Experiment on Ultra-Hard Coatings in Low-Viscosity Fuels*, Kelly Jacques (kellyjacques@my.unt.edu),*** University of North Texas, USA*; S. Berkebile, N. Murthy, J. Mogonye,* Army Research Laboratories, USA*; S. Dixit,* Plasma Technology Inc., USA*; D. Berman, T. Scharf,* University of North Texas, USA

In order to expand fuel operation capability of fuel systems to multiple fuels, fuel pump materials must resist scuffing and wear when lubricated with low viscosity, low lubricity hydrocarbons and alcohols under conditions of dynamic fluid pressure and flow. In this work, a high-frequency reciprocating tribometer was used to determine a set of tribological experimental parameters that emulate conditions within a fuel pump system, instigate material scuffing, and yield reliable and repeatable results. The ASTM D6079 standard for evaluating lubricity of diesel fuels by the high-frequency reciprocating rig was used as a basis for the development of new experimental parameters, of which the grinding lay orientation, temperature, counter body, substrate, contact load, and stroke length were altered. These experimental parameters were used to determine the onset of scuffing and wear of through-hardened 52100 steel substrates and various ultra-hard material coatings, including iron boride and tungsten carbides, possible candidates for steel protection. These materials were lubricated with F-24 (JP-8) and ethanol. Scanning electron microscopy, energy dispersive spectroscopy, white light interferometry, and optical microscopy were used to characterize the extent of wear and corrosion of the materials and counter bodies during the experiments. Overall, it was found that the ultra-hard coatings experience less wear and are more resistant to scuffing at low loads than the 52100 steel.

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

## Tribology and Mechanical Behavior of Coatings and Engineered Surfaces (Symposium E) Poster Session

**EP-1 About the Impossibility of a Mathematical Relationship between Hardness Values Measured by Vickers and Instrumented Nanoindentation Techniques*, Esteban Broitman (esteban.daniel.broitman@skf.com),*** SKF Research & Technology Development Center, Netherlands

The hardness of a solid material can be defined as a measure of its resistance to a permanent shape change when a constant compressive force is applied. At macro- and microscale, the Vickers hardness test is assessed from the size of an impression left under a load by a four-sided pyramid-shaped diamond indenter. The Vickers hardness number, HV, is then calculated as the indenter load L divided by the actual surface area of the impression $A_c$ measured after the indentation. On the other hand, the instrumented nanoindentation hardness $H_{IT}$, using a three-sided pyramid-shaped diamond indenter, is calculated as the maximum indenter applied load $L_{max}$ divided by the projected area of contact at maximum load $A_{pml}$, i.e., during the indentation [1].

There are many publications where authors try to compare their coating hardness values measured by nanoindentation with bulk hardness values that have been measured by Vickers tests. The comparison is usually made through a formula that is supposed to give an exact mathematical equivalence of hardness values between both methods: HV = 0.09 $H_{IT}$, with HV having units of kgf/mm$^2$ and $H_{IT}$ having units of MPa. In this work, I demonstrate that this exact equivalence can be established only for hardness values of materials with 0% indentation elastic recovery. In other cases, I will show that it is impossible to establish such mathematical relationship.

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**EP-2 Substrate Influence on the Adhesion of Metallic Films*, Megan J. Cordill (megan.cordill@oeaw.ac.at),*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; P. Kreiml,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria

Flexible and foldable electronics are becoming more visible for consumers. These devices are often manufactured with metallic films or islands deposited onto compliant polymer substrates. More research is needed to fully understand how to control the metal-polymer interface of the vital interconnecting metal lines found in flexible electronics to improve reliability. While the methods to quantify the interface adhesion are available, a direct comparison of the adhesion of a standard metallic films on different substrates has not been performed. Our results demonstrate that a sputtered Ti adhesion interlayer does not improve the adhesion of Ag films to polyimide (PI) or polyethylene naphthalene (PEN). In addition, the Ag-PI interface had a higher adhesion energy relative to the Ag-PEN interface due to the different polymer substrate chemistries which influence the interface structure and chemistry.

**EP-3 Effects of Sputtering Gas Systems on the Preparation of a-BN Films using RF Sputtering*, Yuki Yamada (s16A3132FM@s.chibakoudai.jp),*** *T. Markuko,* Chiba Institute of Technology Graduate School, Japan*; M. Imamiya,* Hana Saidan, Japan*; Y. Sakamoto,* Chiba Institute of Technology, Japan

Mechanical properties and the structure of boron nitride (BN) are similar to carbon materials. In particular, chemical inertness of BN such as excellent oxidation resistance and reaction with iron-based materials is better than carbon. In addition, structure of a-BN (amorphous BN) is similar to amorphous carbon such as Diamond-like carbon. a-BN is considered to have excellent tribological properties. However, little has been reported on tribological property of a-BN films. So, in this research, preparation of a-BN films by sputtering method and evaluation of the tribological property were investigated.

BN films were prepared by RF sputtering using Ar, Ar-$N_2$, and Ar-$N_2$-$H_2$ as sputtering gas systems. h-BN was used as a target. RF power and pressure were 500W and 0.5Pa, respectively. Deposits were evaluated using Raman spectroscopy. The tribology properties were investigated using a ball on disk friction test.

The peaks of sp$^2$-BN (near 1370 cm$^{-1}$) and a-BN (near 1600 cm$^{-1}$) were recognized in the Raman spectra prepared under all conditions. In addition, peak of sp3-BN (near 1310 cm$^{-1}$) was recognized in the Raman spectrum of Ar-$N_2$-$H_2$.

As a result of the friction test, it was confirmed that a low friction coefficient of 0.1 was exhibited at sputter gas Ar-$N_2$-$H_2$. In contrast, high friction coefficient was exhibited at sputter gas Ar and Ar-$N_2$. From the wear depth of the sample after the friction test, it was confirmed that the wear depth was the deepest in Ar and the shallowest in Ar-$N_2$. The difference in the wear depth is considered to be caused by the difference in the wear mechanism.

As a result of Raman spectroscopy of the adhesion to the ball after friction test, the peak of $H_3BO_3$ was recognized under conditions exhibiting high friction coefficient (sputtering gas; Ar, Ar-$N_2$). Conversely, no peak of $H_3BO_3$ was recognized under the condition exhibiting low friction coefficient (sputtering gas; Ar-$N_2$-$H_2$). Therefore, the high friction coefficient exhibited in Ar and Ar-$N_2$ are considered to be due to the formation of $H_3BO_3$ during the friction test. Furthermore, low friction coefficient exhibiting in Ar-$N_2$-$H_2$ is caused by no formation of $H_3BO_3$ during the friction test.

In conclusion, tribology properties of a-BN were varied on the structure by using of different sputtering gas systems, and low friction coefficient was exhibited at Ar-$N_2$-$H_2$ sputter gas.

**EP-4 Tribological Properties of Sputter-deposited Mo Films on Polyimide*, Edyta Kobierska (edyta.kobierska@unileoben.ac.at),*** *S. Hirn,* Montanuniversität Leoben, Austria*; M. Cordill,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria*; R. Franz, M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria

In the last decade, the shift from rigid to flexible electronics has gained momentum and is mainly driven by display and touch panel technologies that are developed for flexible substrates like polymers or textiles. Unlike rigid electronics, thin film materials used in flexible electronics must withstand various static and dynamical loading conditions in order to ensure that the flexible display remains operational for a sufficiently long period of time. Tribological loading conditions are among them, in particular in the case of wearable electronics, but have only been scarcely studied in literature. Therefore, the tribological propertied of Mo films which were deposited on polyimide substrates with a thickness of 125 µm were analyzed. The Mo films were synthesized by high power impulse magnetron sputtering to a thickness of about 1 µm. To induce different residual stress states in the Mo films, two deposition distances (8 and 14 cm) and two Ar pressures (0.5 and 1 Pa) were used. The tribological tests were performed in ball-on-disk configuration with 1000 laps applying a load of 0.244 N. As counterparts, different materials were chosen including $Al_2O_3$, 100Cr6, PEEK (polyether ether ketone), POM (Polyoxymethylene) and NBR50 (nitrile butadiene rubber) to test the Mo films in different tribological contact situations. The recorded coefficient of friction (COF) was highest in the tests against NBR50 with values up to 3 in the beginning of the test and a subsequent steady decrease. The COF in the tests against the other counterpart materials was generally between 0.5 and 1.5. In terms of wear, higher wear was observed for in the tribological tests against counterparts of high hardness, i.e. $Al_2O_3$ and 100Cr6. As expected, abrasive wear mechanisms are active in these cases as observed from images of the wear tracks recorded with a 3D laser confocal scanning microscope and a scanning electron microscope. Predominant adhesive wear was noticed in the tests against the polymers and the rubber counterpart. The obtained results generally serve as a basis to explore the tribological behavior of thin films on flexible substrates like polymers.

**EP-5 Tribocorrosion Behavior of Boride Coating on Cocrmo Alloy Produced by Thermochemical Process in 0.35% NaCl Solution***, A. Rentería,* 
Universidad de Guadalajara, México*; **Marco Antonio Doñu-Ruiz (marckdr_69@hotmail.com)**,* Universidad Politecnica del Valle de Mexico, México*; M. Flores-Martinez,* Universidad de Guadalajara, México*; S. Muhl,* Universidad Nacional Autónoma de México, México*; N. Lopez-Perrusquia,* Universidad Politecnica del Valle de México, México*; E. García,* CONACYT - Universidad de Guadalajara, México

This work presents the corrosion and tribocorrosion studies of the CoB and $Co_2B$ layer on CoCrMo alloy surfaces, produces by the thermochemical process. The boriding process was carried out at 850°C per 2 hrs, using dehydrated boron past such as boron source. The boride layers were characterized with XRD, SEM and optical profilometry in order to determine the structure, surfaces morphology and roughness, respectively. A solution of NaCl at 3.5% was used to study the corrosion and tribocorrosion performance of the coated and uncoated surfaces. The tribocorrosion tests were carried out in a sliding-contact system with reciprocal movement, using a ball of $Al_2O_3$ of 10 mm such as counterbody. The corrosion test showed that the boride surfaces presented a higher tendency to the corrosion with higher $E_{corr}$ and $I_{corr}$ than the uncoated surfaces, nevertheless, in the tribocorrosion characterization this surface had similar kinetic friction coefficient and lower wear volume than the uncoated surfaces.

**EP-6 Composite Coating on Cu Prepared by Plasma Electrolytic Aluminating***, C. Zhao, J. Sun, R. Cai,* 
***Xueyuan Nie (xnie@uwindsor.ca)**,* University of Windsor, Canada*; J. Tjong,* Ford Motor Company, Canada*; D. Matthews,* University of Twente, Netherlands

Metal-ceramic composite coatings were successfully prepared on pure copper by the plasma electrolytic aluminating (PEA) process. The mechanism of PEA processing and the microstructure of the prepared coatings were studied by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses. It has been revealed that the $Al(OH)_3$ passive film formed on the copper surface was indispensable for plasma discharges. XRD analysis indicated that the prepared coating consists of metallic Cu, $Cu_2O$, and $Al_2O_3$. Tribological tests reveal that the PEA treatment significantly increased the wear resistance in dry-sliding conditions, which could be attributed to the high hardness of the prepared coating. The wear mechanism changed from the adhesive wear of the pure copper to abrasive wear of the steel ball after the PEA treatment. Electrochemical tests show that the coated copper has much better performance against corrosion in 3.5 wt.% NaCl solution at room temperature.

Keywords:plasma electrolytic aluminating; copper; wear; electrochemical corrosion

**EP-7 A Numerical-Experimental Study of Borided AISI 316L Steel Under Cyclic Contact Loading***, **Daybelis FERNÁNDEZ (ingday1989@hotmail.com)**,* 
*O. DE LA ROSA, G. Rodríguez-Castro, A. Meneses-Amador,* National Polytechnic Institute, Mexico*; A. LÓPEZ-LIÉVANO, A. Ocampo-Ramírez,* Instituto Sanmiguelense, Mexico

Borided AISI 316L steels under cyclic contact loading were evaluated. Boriding was carried out by two powder-pack processes: continuous and interrupted process. surface hardened by the boriding process. Boriding processes were developed at 1173 K for 1 h (continuous process) and 4 h (interrupted process). A $Fe_2B$ monophase layer was obtained by the interrupted boriding, while a $FeB/Fe_2B$ bi-phase layer was formed by the continuous boriding. Cyclic contact tests were performed on a servo-hydraulic testing machine by cyclic loading of a sphere on the borided steel surface. Circumferential cracks because of the applied critical load (monotonic load) were observed at the borided steel surface. Subcritical loads with a frequency of 6 Hz were applied on the borided steel surface to evaluate the evolution of the damage caused. Stress field generated at the borided steel surface because of cyclic spherical contact was obtained by the finite element method. Interrupted boriding process showed a better resistance to cyclic contact loading than the continuous boriding process.

**EP-9 Novel Micromechanical Approaches to Understand the Influence of Hydrogen on Materials Behavior***, **Jazmin Duarte Correa** 
**(j.duarte@mpie.de)**, J. Rao,* Max-Planck-Institut für Eisenforschung GmbH, Germany*; X. Fang,* Technische Universität Darmstadt, Germany*; G. Dehm,* Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

The understanding of hydrogen interactions with different features (e.g. dislocations, grain boundaries, precipitates, etc.) in alloys and composites is essential either to control and benefit from the hydrogen technology, or to prevent the destructive outcome of hydrogen embrittlement. Failure mechanisms initiate at the atomic scale with hydrogen absorption and further interaction with trap binding sites or defects. Nanoindentation and related techniques are valuable tools to study independently such mechanisms due to the small volume probed. Even more, in situ testing while charging the sample with hydrogen can prevent the formation of concentration gradients due to hydrogen desorption.

Two custom electrochemical cells were built for in situ hydrogen charging during nanoindentation of the sample (Figure 1): “front-side” charging with the sample and indenter tip immersed into the electrolyte, and “back-side” charging where the analyzed region is never in contact with the solution and therefore the observed effects are only due to hydrogen. We discuss the advantages and disadvantages of both approaches during the study of the hydrogen effect on the mechanical behavior and incipient plasticity in bcc FeCr alloys. The newly developed back-side charging technique allows overcoming surface degradation that might occur during front-side charging. The presence of hydrogen on the top analyzed surface (Figure 1b) was assessed by Kelvin probe measurements, showing a fast hydrogen diffusion rate towards the upper surface as well as a pronounced release flow for the analyzed Fe-Cr alloys. This approach is being extended to the study of coatings, with especial interest at interfaces, often becoming hard trapping sites for hydrogen. These studies are therefore complemented with powerful characterization techniques (microscopy and analytics) to understand the role of hydrogen on the materials failure.

**EP-10 Enhancement in Dry Cutting Performance and Tribological Characteristics of Amorphous Carbon and Bimetal Nitride Coatings Deposited by HiPIMS Technology With Positive Pulses***, **David Matthews** 
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High power impulse magnetron sputtering (HiPIMS) technology with positive pulses was employed in the production of a-C, AlCrN and AlTiN coated tungsten carbide inserts for end milling applications. The results reveal positive effects for increasing productivity, improved surface finish and thickness uniformity, as well as enhanceddry cutting performance. Although HiPIMS is a proven PVD technology to deposit dense coatings it is well-known that drawbacks in coating production by HiPIMS include lower deposition rates, higher residual stress and lower adhesion when compared to techniques such as Cathodic-arc and pulsed-cathodic arc. In this work, the advantage of employing positive pulses to modulate ion fluence towards the coating substrate to modify the film properties is presented. Experimental results showed that a minimum threshold pulse duration of HiPIMS voltage and magnitude of HiPIMS current is required to exploit the full advantage of positive pulses. The optimized parameters for positive pulses yield increased coating deposition rates, reduced argon content and improved adhesion properties. The wear resistance of the films has also been substantially improved. Comparative studies on the positive pulse tailored coatings sliding in air and vacuum environments at different speeds elucidated the advantage of applying optimized positive pulse parameters on the wear behaviour of the coatings.

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