Advanced Surface Engineering Division
Room 202C - Session SE-TuA

Wear, Oxidation and Corrosion Protective Coatings

Moderators: Suneel Kodambaka, University of California Los Angeles, Andrey Voevodin, University of North Texas

2:20pm **SE-TuA-1 Dissociative Extraction of Carbon-based Tribofilms from Hydrocarbon Molecules on Catalytically Active Nanocomposite Coatings***,* ***Ali Erdemir****, G Ramirez, O Eryilmaz,* Argonne National Laboratory **INVITED**

Diamondlike carbon (DLC) coatings are now used in large volumes to mitigate friction and wear-related problems in a wide range of moving mechanical assemblies [1]. In our laboratory, we have developed a class of new catalytically active nanocomposite coatings that can extract DLC type boundary films directly from the hydrocarbon molecules of lubricating oils and gas molecules and thus provide superior friction and wear properties. Specifically, these composite coatings are composed of catalytically active hard and soft nanophases affording exceptional catalytic responsiveness to the hydrocarbon molecules trapped at the sliding contact interface. When tested under lubricated sliding conditions, these coatings can crack or fragment hydrocarbon molecules and then deposit them on sliding surfaces as lubricious and highly protective boundary films. Using TEM, UV Raman and TOF-SIMS, we elucidated the structural chemistry of these boundary films and confirmed that they were indeed similar to conventional DLC films that are currently deposited using plasma-based CVD and PVD processes. TEM also confirmed the presence of graphene and carbon-nano-onions scattered within the tribofilm. Under severe sliding, reciprocating, and scuffing test conditions, these carbon-based boundary films showed extreme resistance to wear and scuffing [2].

[1] S-C. Cha and A. Erdemir, eds., "Coating Technology for Vehicle Applications" Springer, New York, 2015.

[2] A. Erdemir et al., Nature, 536(2016)67-71

3:00pm **SE-TuA-3 Use of Carbon Nanotube-Silver Metal Matrix Composite Thin Films to Enhance Mechanical Properties of Grid Fingers and Busbars on Photovoltaic Cells***,* ***Cayla Nelson,*** University of New Mexico*; O Abudayyeh,* Osazda Energy, LLC*; Y Shen, S Han,* University of New Mexico

The hot spots created by cell cracks have recently been identified as the most common degradation mode in PV modules.[1] Even before they become hot spots, these cracks lead to high series resistance, reduced efficiency, and lost energy. To reduce this degradation, we have been investigating the use of multiwalled carbon nanotubes (MW-CNTs) as a reinforcement in metal matrix composites. We have demonstrated that these composites provide gap-bridging capability (> 40 mm), "self-healing," and fracture toughness against the cracks forming in the substrate and the metal contacts.[2-4] To accompany the experimental effort, finite element modeling (FEM) is used to relate the microstructure of the composite to its mechanical properties. The FEM models are compared to mechanical data taken by dynamic mechanical analysis (DMA). The composites are fabricated in a Ag/CNT/Ag layer-by-layer structure. The silver layer can be evaporated or electroplated, and the CNTs are spray-coated. The shape of the composite films is a dog bone structure that can be released from the substrate as a free-standing film. This release is necessary to extract the mechanical properties solely belonging to the composite. Fitting the FEM model to DMA measurements captures qualitative trends of how mechanical properties of the MMC change with CNT volume fraction. Combining mechanical modeling with experimental results provides predictive evaluation of CNT reinforced metal matrix composites.

[1] D. C. Jordan, T. J. Silverman, J. H. Wohlgemuth, S. R. Kurtz, and K. T. VanSant, "Photovoltaic failure and degradation modes," *Prog. Photovolt: Res. Appl.***25,** 318-326 (2017).

[2] O. Abudayyeh, N. D. Gapp, D. M. Wilt, and S. M. Han, "Methods to Mitigate Stress-Induced Metal Line Fractures for Thin-Film Solar Cells, Using Metal-Carbon-Nanotube Composites," Patent No. Application No. PCT/US2016/038197 (2016).

[3] O. K. Abudayyeh, G. K. Bradshaw, S. Whipple, D. M. Wilt, and S. M. Han, "Crack-Tolerant Metal Composites as Photovoltaic Gridlines," *Appl. Phys. Lett.***,** submitted (2018).

[4] O. K. Abudayyeh, N. D. Gapp, C. Nelson, D. M. Wilt, and S. M. Han, "Silver-Carbon-Nanotube Metal Matrix Composites for Metal Contacts on Space Photovoltaics," *IEEE J. Photovolt.***6,** 337-342 (2016).

3:20pm **SE-TuA-4 Study of Effects of Synergistic Environmental Exposures on Fiber-Reinforce Polymer Composites Protected by Metallic Coatings***,* ***Arash Afshar****, D Mihut, S Hill,* Mercer University School of Engineering

Polymer composites are good candidates for applications requiring high strength, low weight and corrosion resistance properties. Therefore, they are widely being used in marine, automotive, construction, aerospace industries to name a few. However, the main existing challenge is preventing the degradation of composite materials under prolonged exposure to harsh environmental conditions such as UV radiation and moisture. Composite samples with standardized sizes were exposed to combined UV radiation and moisture in the environmental chamber for different time intervals. Some samples were coated with optically thick metallic materials using high vacuum magnetron sputtering deposition and were later exposed to the same combined environmental conditions. It was observed that metallic coatings improved the surface resistance of the substrate composite materials and protected the mechanical properties throughout the course of exposure. The surface morphology of samples before and after exposure was observed using optical microscopy and the adhesion of metallic layers to the substrates was examined using scanning electron microscopy. The mechanical properties were also characterized using flexural and hardness tests over the exposure time.

4:20pm **SE-TuA-7 Atomistic View of Mg Metal Corrosion Using *in-situ* cryo-XPS and *ab initio* Computation***,* ***Vaithiyalingam Shutthanandan****, A Martinez, P Sushko, A Devaraj, E Stevens, O Marina, V Joshi, S Thevuthasan, V Murugesan,* Pacific Northwest National Laboratory

Magnesium metal is potential candidate for high strength to weight ratio alloys with wide application in aerospace and automotive industries. However, poor corrosion resistance under ambient environmental conditions is the bottleneck for industrial deployment. Designing passivation layers and/or corrosion resistance alloys require fundamental understanding of the corrosion process. The traditional *ex-situ* spectroscopic measurements of polycrystalline metal surface with ubiquitous surface impurities provided indistinct view of the corrosion process. To clearly distinguish the mechanism and sequence of corrosion process, we employed *in-situ* cryo-based x-ray photoelectron spectroscopy (XPS) measurements on well-defined Mg-single crystal surfaces in combination with *ab initio* atomistic modelling studies. Mg (0001) surfaces were exposed to ambient water conditions (i.e. D_2O and 5 wt% NaCl+95 wt% $D\text{-}_2O$ solution) and the subsequent interfacial reactions were studies through integrated experimental and theoretical approach. This study provides atomistic view of $Mg(OH)_2$ nucleation as main product of the corrosion process. Under salt conditions, the competitive nucleation process between $Mg(OH)_2$ and $MgCl_2$ were observed. High resolution helium ion microscopy images of the corroded surface show unique morphologies of nucleates including some well-defined faceted cubic crystals and micron size faceted ribbon like structures. By combining the energy requirements from computational modelling and the electronic states of corrosion products, the mechanism and sequence of corrosion process on Mg metal will be discussed.

4:40pm **SE-TuA-8 Scratch Behavior and Modelling of Cu/Si(100) Thin Films Deposited by Modulated Pulsed Power Magnetron Sputtering***, D Meng, Y Li,* ***M.K. Lei,*** Dalian University of Technology, China

A series of copper films on Si(100) substrate were deposited using modulated pulsed power magnetron sputtering under different sputtering pressure from 0.11 to 0.70 Pa. The scratch behavior of copper films on Si(100) was evaluated by scratch adhesion test with the aid of finite element modelling. With the increase of pressure, the surface morphology becomes rougher and the pattern transforms from compact fine granular structure to coarse and crack visible columnar structure, and the surface morphology of scratch tracks transforms from no obvious delamination to vast delamination. At pressure of 0.11 Pa, no obvious delamination can be observed, while copper films begin to delaminate with the growing pressure at 0.3 Pa and above at a certain load. Critical loads Lc_1 to Lc_4 were employed to assess the adhesion behavior of soft copper films on hard Si(100), the main exhibiting characteristics were the periodical plastic deformation on the side of scratch tip and semi-circular characteristic behind the scratch tip which were mainly caused by plastic deformation in the stick-slip process. Finite element modeling was employed to analyze the stress and strain responses of scratch on copper films by mainly using the maximum principal stress σ_1 as a function of normal loads in stress concentration zone A, B and C. The location of the peak σ_1 migrates from zone B to C which are tensile as the normal load increases, while peak σ_1 in zone A is compressive. The directionality of σ_1 for zone B tilts mostly at an out-of-plane angle mostly about 15º and 90º which may be responsible for the interface failure between the film and substrate. Critical loads Lc_1 and Lc_2 are evaluated through the migration of peak σ_1 from zone B to C, while critical load Lc_3 is associated with stress accumulation in zone C and stress accumulation in zone A is responsible for critical load Lc_4. The observed plastic deformation and failure modes are able to further illustrate the physical meaning of critical loads.

5:00pm **SE-TuA-9 Corrosion Resistance of Mechanically Reinforced Aluminium based Coatings obtained by PVD Techniques***, **Frederic Sanchette,*** UTT - Université de Technologie de Troyes, France*; J Creus,* Université de La Rochelle, France*; A Billard,* FEMTO-ST, France **INVITED**

Aluminium-based alloy films can be used for the protection of steels against corrosion However, the mechanical properties of such coatings must be reinforced, for example by addition of transition elements, which have low diffusivity and low solubility in aluminum. Various aluminium based alloys elaborated by Electron Beam Physical Vapour Deposition (EBPVD) or magnetron sputtering techniques are characterised in terms of mechanical properties and corrosion behaviour in saline solution. The incorporation of transition metals permits to modify the mechanical or physico-chemical characteristics of aluminium coatings, so several alloying elements are compared. Evolution of microstructure of the Al based coatings is discussed versus the alloying element content. Different compositions of alloys are examined.

This presentation summarizes the main results of studies conducted in this field since the early 1990s. This is a synthesis of the main tendencies reported during the evaluation of the mechanical and corrosion properties of these alloys.

The objective is to build a reactivity classification in saline solution of several Al based coatings synthe- sized by vacuum deposition techniques. Combined with the classification of mechanical properties, these standards would become relevant guides in the choice of PVD coatings and/or alloys for applications exposed to saline environments. In our study, this guide is helpful in the synthesis of nanometric multi- layer architectures, which proves to be a promising way to combine improved mechanical properties with sacrificial character for the future coating configurations.

5:40pm **SE-TuA-11 High Temperature Mechanical Properties of CrAlN and CrAlSiN Hard Coatings***, **Aljaž Drnovšek,** M Rebelo de Figueiredo, A Xia,* Montanuniversität Leoben, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H Vo, P Hosemann,* Univeristy of California Berkeley*; R Franz,* Montanuniversität Leoben, Austria

One of the most common methods used to characterize the mechanical properties of hard coating materials is nanoindentation. The further development of nanoindentation in recent years led to new ex-situ and in-situ systems that are capable of measuring mechanical properties such as hardness, elastic modulus and fracture toughness at elevated temperatures. In addition, new measuring procedures such as nano-dynamic mechanical analysis (n-DMA) enable measuring the hardness and elastic modulus at a continuous rate through the entire penetration depth at reduced thermal drift sensibility. This approach yields faster measurements at high temperatures which is beneficial in terms of tip degradation and generally renders the obtained results more reliable. With these new experimental possibilities, the mechanical properties of hard coatings synthesized by physical vapor deposition techniques can now be characterized close to the service temperatures that can reach up to 1000 °C.

In the current work, we tested two magnetron sputtered coatings that are widely used in industrial cutting applications, namely CrAlN and CrAlSiN. The latter is a further development of CrAlN coatings where the columnar growth is interrupted due to the addition of Si resulting in a nanocomposite composed of crystalline CrAl(Si)N grains and an amorphous SiN_x grain boundary phase. In particular in the case of CrAlSiN hard coatings, studies analyzing the mechanical properties at high temperature are scarce. High temperature nanoindentation measurements on both coatings were performed up to 700 °C in steps of 100 °C. The room temperature hardness values of 30 GPa (CrAlN) and 36 GPa (CrAlSiN) reduced by approximately 2 GPa per temperature step up to 500 °C. Above this temperature, the hardness of CrAlN continued to decrease while the hardness of CrAlSiN remained largely unchanged. In addition, high temperature tribological tests were conducted in air and inert atmosphere in the same temperature range in order to link the friction and wear behavior to the obtained mechanical properties. This data set is intended to serve as a first step towards a more comprehensive understanding of the high temperature mechanical and tribological properties of hard coatings which is vital for their further development and improvement.

6:00pm **SE-TuA-12 Thick CrN/AlN Superlattice Coatings for Solid Particle Erosion and High Temperature Wear Resistant Applications***, **Jianliang Lin,*** Southwest Research Institute

Energetic ion bombardment is critical to improve the structure and properties of coatings in plasma assisted depositions. Plasma enhanced magnetron sputtering (PEMS) is an advanced version of conventional magnetron sputtering by generating a global plasma, in addition to the magnetron plasma, in the entire deposition system using hot filament thermionic emission to enhance the ionization and bombardment. In this study, thick CrN/AlN superlattice coatings (15 to 20 µm) were deposited by reactive sputtering using a combination of PEMS and high power impulse magnetron sputtering (HiPIMS) techniques. These coatings were deposited at different PEMS plasma discharge currents (0 to 4 A) which represent different ion fluxes for the bombardment. The bilayer thickness of the nanolayers was controlled in the range of 4 to 7 nm. The microstructure of the coatings gradually changes from long columnar grains to extremely dense structure with an increase in the PEMS discharge current. These coatings exhibited high hardness, excellent adhesion, and excellent resistance to high temperature wear, oxidation and solid particle erosion. The high temperature wear resistance of selected coatings was measured using a high temperature pin-on-disc tribometer in the ambient air from 600 °C to 1000 °C. The solid particle erosion resistance of these thick CrN/AlN coating was evaluated and compared with other thick hard coatings, e.g. CrN, TiN, TiSiCN, etc., using an air jet sand erosion tester. In this presentation, PEMS/HiPIMS deposition process, the coating microstructures, erosion, and high temperature wear test results will be discussed.

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