## Tribology Focus Topic
## Room: 19 - Session TR+SE-WeM

### Tribology and Wear of Low-Friction Coatings and Materials
### Moderator: D.L. Burris, University of Delaware

8:00am **TR+SE-WeM1 Seeing Things as They Really are: *In Situ* Studies of Materials in Application Environments and the Development of Temperature-Adaptive Nanocomposites**, ***C. Muratore***, Air Force Research Laboratory, *J.J. Hu, J.E. Bultman*, UDRI/Air Force Research Laboratory, *A.A. Voevodin*, Air Force Research Laboratory **INVITED**

In the early 1940s, military pilots and those who serviced their planes were surprised by serious problems with ignition systems and diverse electrical troubles in their state of the art aircraft. Further study revealed that the graphite commutator brushes used in the electrical generator on the airplane (similar to the alternator in our automobiles) were the source of these technical difficulties, because they wore out 100 to 1000 times faster than expected. Over 70 years later, sensitivity of materials at contact interfaces to the extreme ambient environments aircraft are subjected to is still limiting aerospace capability. One of the reasons materials scientists haven't overcome these problems sooner is because it is difficult to do materials science, at least the part where you correlate performance to structure and composition, when there is such a big difference between the operating environment and the environment in which analysis is conducted. All the materials tribologist can really do is *post mortem* forensics work on materials designed to get hot after they have cooled down to a convenient handling temperature. During that cooling down time, phase changes and grain growth occur, perhaps misleading the researcher on the compounds or phases yielding high or low friction at interfaces in relative motion. In this talk we will review innovative characterization techniques designed to provide the insight necessary to produce environmentally adaptive tribological coatings, especially materials designed to operate over broad ranges of humidity (i.e, earth to space) and temperature (i.e., ignition to supersonic flight). Characterization of temperature adaptive nanocomposite lubricant materials, such as MoN/Ag and VN/Ag via Raman spectroscopy will be reviewed in depth.

8:40am **TR+SE-WeM3 Tribological Surface Chemistry of Model Lubricant Additives Measured in Ultrahigh Vacuum**, ***W.T. Tysoe***, University of Wisconsin Milwaukee

Additives are generally added to lubricants, which react with the surfaces to form a boundary lubricating film that can lower friction and/or prevent wear. At the high interfacial temperatures that occur under so-called extreme-pressure conditions, the surface reaction and film growth kinetics are dominated by thermal processes. In contrast, it is postulated that, under mild conditions, where the surface temperature rise is low, a surface film can be formed by a shear-induced, surface-to-bulk transport mechanism. This effect is investigated by studying the tribologically induced surface reactions of model sulfur- and boron-containing additives on copper surfaces in ultrahigh vacuum (UHV) where the background pressure is $\sim 1\times 10^{-10}$ Torr. The nature of the initial surface species that are formed by exposure of the copper surface to the model lubricant additive is investigated using a range of surface analytical techniques such as temperature-programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS) and X-ray photoelectron spectroscopy (XPS). This enables the nature of the initial surface species to be identified, and their thermal stability to be measured in some detail. The effect of rubbing these adsorbate-covered surfaces is investigated, also in UHV, by measuring the friction coefficient and contact resistance during rubbing. The chemical composition of the wear track is followed using high-spatial-resolution Auger spectroscopy to follow the fate of the surface species caused by rubbing and to test the above postulate.

In addition, the effect of low-coordination sites formed on the surface by rubbing on the reactivity of gas phase lubricants is explored and finally, this strategy is used to understand the tribochemistry of borate esters on copper under mild rubbing conditions.

9:00am **TR+SE-WeM4 Nanomechanical and Nanotribological Properties of ZnO Thin Films**, ***E. Broitman***, *L. Martínez de Olcoz Sainz*, Linköping University, Sweden, *C. Bojorge*, Cinso, Citedef-Conicet, Argentina, *J.B. Miller*, Carnegie Mellon University, *H. Canepa*, Cinso, Citedef-Conicet, Argentina, *L. Hultman*, Linköping University, Sweden

During the last years, with the advances in nanotechnology, zinc oxide (ZnO) thin films have attracted an increased attention for applications as sensor devices in microelectromechanical systems. In these applications, where high mechanical stress could be imparted on the film in contact situations, the knowledge of the coating nanomechanical and nanotribological properties is critical since they will affect the functions and durability of the films. Sol–gel method is a simple and low cost process for the fabrication of ZnO thin films; interestingly, there are only two publications partially dealing with their mechanical and tribological properties.

In this work, we studied ZnO thin films grown on glass substrates by sol–gel process. Single and multilayered films were deposited by spin-coating technique onto glass substrates, and subsequently transformed into nanocrystalline films using different thermal treatments Tt.

The microstructural properties and morphology of the films have been studied by X-ray diffraction (XRD), scanning electron microscopy, and surface probe microscopy. XRD patterns of films dried at room temperature show features characteristic of layered basic zinc acetate, a lamellar ZnO precursor, consisting of zinc hydroxide hydrate sheets separated by intercalated acetate groups. At higher Tt, ZnO diffraction patterns are dominated by features corresponding to the (100), (002) and (101) reflections of the crystalline zinc oxide "wurtzite" structure. The higher relative (002) intensity in some films is evidence of preferential growth of the structure along the c-axis, the axis of symmetry in the wurtzite structure.

The nanomechanical and nanotribological properties were measured by a Triboindenter TI-950 from Hysitron. The hardness H and reduced Young's modulus Er of the ZnO thin films were investigated by nanoindentation measurements with a Berkovich indenter at peak loads of 150 µN. The films with the lower Tt exhibit a wide dispersion in the values due to the inhomogenities on the degree of coating crystallinity. At the higher temperatures, the dispersion vanishes and we obtained H = 5.6 GPa and Er = 99 GPa. We also observed at low temperatures the presence of pop-in events that can be associated to the presence of the multilayers. The friction coefficient was measured at ambient conditions using a conical diamond tip in a reciprocal test, applying a normal force of 10 µN and a stroke distance of 10 µm. The friction coefficient decreases from 0.37 to 0.30 when Tt is increased. The different mechanical and tribological properties can be correlated to the changes in the microstructure upon different heat treatments.

9:20am **TR+SE-WeM5 Tribological and Compositional Properties of Electroless Nickel-Boron Coatings Annealed at Various Temperatures**, ***K. Gilley***, University of Florida, *Y. Riddle*, UCT Coatings Inc., *S.S. Perry*, University of Florida

In this study, the tribological and compositional properties of annealing temperatures on electrolessly deposited nickel boride coatings were investigated. All samples were coated in the same bath and had approximately the same starting composition: 31 atomic % Ni, 19 atomic % B, 42 atomic % O, and 8 atomic % C . Samples were annealed at temperatures of 250°C, 400°C, 550°C, and 700°C under a constant flow of oxygen. The tribological properties of the samples were tested using a novel pin-on-disc tribometer. The pin-on-disc tribometry was performed in air under ambient RH conditions, keeping conditions the same throughout all tests that were performed. The influence of the annealing temperature on surface composition was studied by X-ray photoelectron spectroscopy (XPS), used to identify and relatively quantify the elements present. Raman spectroscopy was used to differentiate between chemical species that were indistinguishable in XPS. Increasing annealing temperatures were seen to influence the tribological properties of the coatings to a large degree; with the samples with higher annealing temperatures having a significantly lower coefficient of friction, $\mu\approx 0.16$ for the sample annealed at 550°C and $\mu\approx 0.06$ for the sample annealed at 700°C, than the lower temperature annealed samples, $\mu\approx 0.5$ for samples annealed at 250°C and 400°C. Similarly, the chemical nature of the coatings were strongly affected by the differing annealing temperatures; with the higher annealing temperature samples showing heavy oxidation and migration of boron to the surface, while the lower annealed samples remained largely unchanged. The lowering of the friction coefficient in the samples annealed at 550°C and 700°C was attributed to the migration and subsequent oxidation of boron forming low friction $B_2O_3$ at the surface.

10:40am **TR+SE-WeM9 First Contact: SPR and SERS Studies of the Initial Transfer Behavior of PTFE**, ***K.L. Harris***, *B.A. Krick, D.W. Hahn, W.G. Sawyer*, University of Florida

Traditionally the tribological behavior of PTFE (polytetrafluoroethylene) has been studied in the steady state after many sliding cycles. Steady state studies neglect events that occur during the first contact and sliding cycles, as well as the early transient behavior of PTFE. In-situ surface plasmon resonance (SPR) tribology experiments allow for the observation of initial transfer after the first contact and first sliding cycle of PTFE. SPR showed transfer of PTFE after the first cycle of sliding, contrary to previous models of films formed by delamination wear debris. Surface enhanced raman spectroscopy (SERS) verified the chemical identity of the transfer film. Friction behavior of PTFE was shown to differ in the first cycle from the behavior seen after a transfer film was created and to depend on contact pressure and sliding speed.

11:00am **TR+SE-WeM10 Tribological Investigations of Octadecylphosphonic Acid (ODP) and Octadecyltrichlorosilane (OTS) Self-Assembled Monolayers: A Comparative Study of MEMS-type Interfaces**, *N. Ansari,* Auburn University*, S. Barkley, C. Bouxsein, M. Deram, N. Eigenfeld,* St. Olaf College*, O. Matthews,* Luther College*, A. Poda, W.R. Ashurst,* Auburn University*, B.P. Borovsky,* St. Olaf College*, E. Linn-Molin, **E.E. Flater***, Luther College

Since microelectromechanical systems (MEMS) are critically-limited by interfacial phenomena such as friction and adhesion, strategies have been developed to reduce friction in these systems. One common strategy is to coat MEMS surfaces with molecularly-thin self-assembled monolayer (SAM) coatings. Silicon MEMS are most commonly coated with silane-based SAMs, such as octadecyltrichlorosilane (OTS). Continued development of MEMS technology may require new material systems to be employed. Therefore, in this study, we investigate the frictional properties of octadecylphosphonic acid (ODP) monolayers deposited on aluminum oxide surfaces. Measurements using an atomic force microscope (AFM) and separately using a nanoindenter-quartz crystal microbalance system were performed each with a microsphere-terminated probe, allowing for a comparative study between different velocity regimes using contacts with similar sizes, surface roughnesses, and interfacial chemistries. AFM colloidal probe friction measurements indicate that while the frictional properties of aluminum oxide can be reduced with the use of an ODP monolayer, a more dramatic rubbing-induced modification is clearly evident for both bare and SAM-coated aluminum oxide substrates. These modification effects depend on scanning duration and environmental conditions such as humidity. We hypothesize that a tribochemical reaction occurs between aluminum oxide and ambient water, which has also been observed in macroscopic tribological studies of aluminum oxide published in the literature.

11:20am **TR+SE-WeM11 Diffusion of Gold Islands on Graphene**, ***B. Dawson****, M. Lodge, M. Ishigami*, University of Central Florida

Recent theoretical work has suggested that gold nanoclusters on graphite can exhibit both diffusional friction and a novel ballistic friction behavior [1]. This ability to tune friction at nanoscale interfaces can be useful for developing nanoscale motors and machines in general. Furthermore, understanding this nanotribological behavior can be utilized for various nanomechanical devices fabricated from graphene, which is chemically identical to graphite.

We have measured the frictional energy dissipation of gold nanoclusters on graphene as a function of temperature and cluster size using the quartz crystal microbalance (QCM) ring-down technique. By measuring this dissipation, it is possible to quantitatively measure the island diffusion coefficient and precisely monitor how the diffusion and slip time change with temperature, and directly compare these results with the recent theoretical studies. In addition, our measurements give insight into the nanotribological properties of a two dimensional material studied at higher sliding speeds than typically accessible using atomic force microscopy.

[1] R. Guerra *et al*. Nature Materials **9**, 634 (2010).

11:40am **TR+SE-WeM12 Synthesis and Tribology of $MoS_3$ Nanoparticles**, ***J.R. Lince***, The Aerospace Corporation, *A.M. Pluntze,* Colorado State University, *S.A. Jackson*, The Aerospace Corporation

There has been recent interest in the use of solid lubricant nanoparticles in coatings and as boundary additives in liquid lubricants. Examples include nanoparticles of $MoS_2$ and $WS_2$. The formation of these nanoparticles is nontrivial, requiring techniques such as gas phase syntheses and electric discharges. We are exploring simpler syntheses using wet chemical techniques. In particular, the synthesis of $MoS_3$ nanoparticles involves hydrothermal reaction between molybdate salts and sodium sulfide under controlled pH conditions.[1]

The use of $MoS_3$ as a tribological material has not been explored beyond its use as an oil additive.[2] We are investigating its potential for use in solid lubricant coatings. Bonded $MoS_2$ coatings experience widespread usage for lubricating mechanisms on virtually every spacecraft (i.e., using micron-sized $MoS_2$ particles). We formulated resin-bonded coatings using $MoS_3$ nanoparticles as the lubricating pigment, and compared their tribological performance to commercial bonded $MoS_2$ coatings. Surprisingly, the $MoS_3$-formulated coatings performed similarly to the $MoS_2$-based coatings. Specifically, they showed similar coefficients of friction (i.e., 0.04 to 0.06) and endurances in dry nitrogen (<0.1% RH). We will present results of surface analyses on worn coatings to reveal changes in composition and chemical state of the $MoS_3$ that might explain the measured low friction. In addition, results of tribological performance in humid air atmospheres will be presented.

We have also explored syntheses of $MoS_2$ nanoparticles using nanosize $MoS_3$ as a starting material. A recent study purported to create $MoS_2$ nanoparticles with the addition of an aqueous reducing agent during hydrothermal synthesis of $MoS_3$.[3] However, X-ray fluorescence analysis of the product of our synthesis showed that the S:Mo remained at 3.0 after using the reducing agent. Other conversion methods including vacuum reduction of the $MoS_3$ nanoparticles will be discussed.

References:

1. P. Afanasiev, "Synthetic approaches to the molybdenum sulfide materials," Comptes Rendus Chimie, 11(1–2) (2008) 159–182.

2. O.P. Parenago, V.N. Bakunin, G.N. Kuz'mina, A.Yu. Suslov, and L.M. Vedeneeva, "Molybdenum Sulfide Nanoparticles as New-Type Additives to Hydrocarbon Lubricants," Doklady Chemistry, 383(1-3) (2002) 86-88.

3. Y. Tian, X. Zhao, L. Shen, F. Meng, L. Tang, Y. Deng, Synthesis of amorphous $MoS_2$ nanospheres by hydrothermal reaction," Materials Letters 60 (2006) 527–529.

This work was funded in part by The Aerospace Corporation's Sustained Experimentation and Research for Program Applications program.

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