Thursday Afternoon, November 10, 2016

Tribology Focus Topic
Room 101A - Session TR+BI+SE+TF-ThA

Materials Tribology

Moderator: Michael Chandross, Sandia National Laboratories

2:20pm **TR+BI+SE+TF-ThA1 Reaction Pathways and Tribofilm Formation Kinetics at a Solid-Solid Interface***, H.L. Adams,* University of Wisconsin-Milwaukee*; A. Martini,* University of California Merced*; **Wilfred Tysoe**,* University of Wisconsin-Milwaukee **INVITED**

Perhaps the most difficult surface-science challenge is to monitor reaction pathways and kinetics at sliding solid-solid interfaces, in particular for opaque contacting materials [1]. Optical techniques can be used to interrogate the interface when one of the contacting surfaces is transparent, but they are often not sensitive to the first monolayer. Strategies for measuring reaction pathways and their kinetics for well-defined surfaces in ultrahigh vacuum (UHV) are described using the example of sliding-induced decomposition of adsorbed methyl thiolate species, formed by exposure to dimethyl disulfide, on copper. Surface science experiments show that methyl thiolates are stable up to ~425 K on copper, but decompose during rubbing; the effect of the external force is to lower the reaction activation barrier so that it proceeds at room temperature. The surface reaction products can be monitored immediately after sliding in UHV using surface spectroscopies (for example, Auger spectroscopy). However, the reaction kinetics can also be monitored in situ first, by measuring the gas-phase species evolved as a function of the number of times the surface is rubbed, where methane and ethane are detected and second, by measuring the change in friction force due to the evolution of the nature of the species present on the surface. This allows the elementary steps in the tribofilm formation pathway to be identified and their rates measured.

[1] Heather L. Adams, Michael T. Garvey, Uma Shantini Ramasamy, Zhijiang Ye, Ashlie Martini, and Wilfred T. Tysoe, Journal of Physical Chemistry C, **119**, 7115–7123 (2015)

3:00pm **TR+BI+SE+TF-ThA3 Nanotribology of Graphene Revisited: The Influence of Contact Size and Substrate Topography***, A. Balkanci,* Bilkent University, Turkey*; Z. Ye, A. Martini,* University of California Merced*; **Mehmet Z. Baykara**,* Bilkent University, Turkey

Two-dimensional (2D) materials have been the focus of intense research in recent years thanks to their outstanding electronic and mechanical attributes. In particular, graphene exhibits exceptional potential as a solid lubricant appropriate for use in nano-/micro-scale mechanical systems. As such, a comprehensive evaluation of its frictional properties on such small length scales is of crucial concern. While pioneering studies toward this purpose have revealed strongly layer-dependent frictional behavior [1], the precise roles that contact size and substrate topography (important design parameters for mobile components in nano-/micro-scale devices) play in the lubricative nature of graphene have not been explored yet in detail.

In this contribution, we present a combined experimental and numerical study aimed at evaluating the influence of contact size and substrate topography on the nanotribological characteristics of graphene. In particular, atomic force microscopy (AFM) is employed under ambient conditions to measure friction forces on mechanically-exfoliated graphene as a function of applied load, number of graphene layers, and contact size. To study the influence of contact size on measured frictional properties, AFM probes with different tip apex sizes are obtained by thermal evaporation of gold and platinum onto the probes. In conjunction with the experiments, molecular dynamics (MD) simulations are performed that involve the calculation of friction forces experienced by model tip apexes of varying size on single- and few-layer graphene. Moreover, substrates with various RMS roughness and correlation length values are employed in the MD simulations to investigate the effect of substrate topography on frictional behavior. Results reveal that a subtle interplay between contact size and substrate topography determines the layer-dependent frictional behavior of graphene, providing a new perspective to the nanotribology of this remarkable material.

[1]: C. Lee *et al.*, Science **328**, 76 (2010)

3:20pm **TR+BI+SE+TF-ThA4 Iron-Doped Diamond-Like Carbon Coatings (Fe-DLCs): Synthesis, Characterization, and Tribology--Seminal Results***, **Parag Gupta**,* Northwestern University/Argonne National Lab.*; M.E. Graham,* Northwestern University

Iron-doped diamond-like carbon coatings (Fe-DLCs) of ≈ 0.1 to 35 at.% Fe content have been synthesized, characterized, and tribologically tested. Coatings were deposited on Si(111), 52100 steel ball, and H-13 steel flat substrates using a closed-field unbalanced magnetron sputter deposition process with unmodified and modified graphite target states, the latter with press-fit cast gray iron slugs. Process parameters of target modification, target power, acetylene flowrate, and substrate bias were varied and used in establishing a process-conditioning window to create predictable coatings.

Mechanical characterization was done to determine deposition rate, thickness, internal stress, and hardness. Cross-sectional characterization was done to determine coating uniformity, to understand coating adhesion and morphology, and to confirm interlayer presence and morphology (if deposited). Surface characterization was done to determine surface roughness and mechanical anisotropy. Chemical characterization was done to determine elemental concentration and chemical anisotropy. Finally, structural characterization was done to determine carbon bond order.

Using a ball-on-flat reciprocating tribometer, highly-doped Fe-DLCs were studied at either room temperature or ≈ 100 °C and with either coating / coating or steel / coating contact. Electrical contact resistance between interfaces was measured *in situ*. A contact pressure of ≈ 1 GPa was employed alongside an average sliding speed of 1.0 cm / s, except when non-monotonic sequential speed stepping was prescribed. The boundary-lubricated sliding tests were conducted in the presence of poly-alpha-olefin SAE grade 30 synthetic base stock oil (PAO10) with and without molybdenum dithiocarbamate (MoDTC) and zinc dialkyldithiophosphate (ZDDP) additives, both at 0.5 wt.%. Coatings were also tested in unlubricated conditions.

Friction responses were determined, and wear assessments were conducted. Tribofilm and debris analyses were done. The results were compared to those from DLC, CrN + DLC, Si-DLC, and W-DLC coatings obtained from Oerlikon Balzers. Results indicate that Fe-DLC samples containing between 12 and 35 at.% Fe exhibit negligible wear in the presence of PAO10 with MoDTC and ZDDP, affirming the influence of iron in catalyzing protective tribofilms. Additionally, wear on such samples in both lubricated and unlubricated conditions is far lower than that observed for other coatings, indicating that these Fe-DLCs are robust in any conditions.

4:00pm **TR+BI+SE+TF-ThA6 Tribo-Rheometry of Soft Matter***, J. Kim, **Alison Dunn**,* University of Illinois at Urbana-Champaign **INVITED**

Hydrogel surfaces are biomimics for sensing and mobility systems in the body such as the eyes and large joints due to their compliance, controllable chemistry, permeability, and integrated aqueous component. Recent studies have shown that polymer concentration gradients in the top microns of crosslinked hydrogel surfaces result in a less dense surface region. In addition, the lubrication of hydrogel interfaces is driven by the effective mesh size, a parameter which follows from the local density. Given the similarity of a dilute crosslinked hydrogel surface with a dilute polymer solution, we probe the surface of a polyacrylamide hydrogel using stepped-velocity tribo-rheometry over 5 decades of sliding speed, with an annular aluminum countersurface. Three distinct lubricating regimes emerge based on a) hysteretic torque response depending upon increasing or decreasing sliding speeds, and b) characteristic torque overshoot following velocity step changes. This evidence supports the analogy of a rheology-like lubrication response. We postulate that the mechanisms of hydrogel-against-hard material lubrication are due to distinct complex fluid behavior characterized by weakly or strongly time-dependent response. Tribo-rheometry is particularly suited to uncover the lubrication mechanisms of complex interfaces such as are formed with hydrated hydrogel surfaces and biological surfaces.

4:40pm **TR+BI+SE+TF-ThA8 Friction Coefficient Lowering in High-hardness Boron Nitride Films Under Ultra-high Vacuum***, **Masao Noma**,* Shinko Seiki Co., Ltd, Japan*; K. Eriguchi,* Kyoto University, Japan*; M. Yamashita,* Hyogo Prefectural Institute of Technology, Japan*; S. Hasegawa,* Osaka University, Japan

Solid lubricant material with low friction coefficient is of technological interest for its usage under harsh environments such as ultra-high vacuum. At present, MoSi -containing films [1] are the most widely employed for space applications because of their low friction coefficients (0.02–0.05) in vacuum [2]. However, the mechanical hardness and the oxidation resistance temperature are 10–20 GPa [3] and 360 °C [4], respectively, inapplicable to a long term operation in space. Boron nitride (BN) films have been considered an alternative material because of their superior high hardness and oxidation resistance temperature, 45 GPa and 1200 °C, respectively [5]. We have proposed a novel reactive plasma-assisted coating technique (RePAC) for forming 1-µm-thick high-hardness BN films (~50 GPa) [6][7]. In this study, we present "friction coefficient lowering" phenomena in the high-hardness BN films under ultra-high vacuum (~10^{-6} Pa), which is in sharp contrast to "friction coefficient increase" usually observed for other hard coating materials. The time-dependent high-vacuum friction measurement revealed that the friction coefficient decrease from 0.1 to 0.03 was found for the substrate bias voltage from −90 to −180 V in the RePAC. In this (incident ion energy) region, the cubic BN phase was formed in the turbostratic BN background, leading to the high-hardness of ~50 GPa at atmosphere [7]. Moreover, the obtained low friction coefficient was confirmed to be stable (<0.05) for long time exposures to the vacuum (~96 hrs). The friction coefficients of the present BN films are comparable to widely reported values of MoS_2 films. The BN film prepared by the RePAC is one of promising hard coating materials for harsh environment (e.g., space) applications.

[1] M. Chhowalla, and G. A. J. Amaratunga, *Nature* **407** (2000) 164.

[2] G. Colas et al., *Wear* **305** (2013) 192.

[3] N. M. Renevier et al., *Surf. Coat. Technol.* **142-144** (2001) 67.

[4] K. C. Wong et al., X. Lu, *Wear* **264** (2008) 526.

[5] C. B. Samantaray and R. N. Singh, *Int. Mater. Rev.* **50** (2005) 313.

[6] M. Noma et al., *Jpn. J. Appl. Phys.* **53** (2014) 03DB02.

[7] K. Eriguchi et al., AVS 61st Int. Symp. & Exhibition, SE+NS+TR-TuM3 (2014).

5:00pm **TR+BI+SE+TF-ThA9 Nanoscale Friction Properties of Water Intercalated Graphene on Mica and its Isotope Effects*, Hyunsoo Lee,*** Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST)*; J.-H. Ko,* KAIST, Republic of Korea*; J.S. Choi,* Electronics and Telecommunications Research Institute, Republic of Korea*; J.H. Hwang,* IBS & KAIST, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea*; M.B. Salmeron,* Lawrence Berkeley National Laboratory (LBNL)*; J.Y. Park,* IBS & KAIST, Republic of Korea

We demonstrate that the frictional behavior of hydrophobic graphene on hydrophilic mica is affected by water intercalation after exposure to humid air using atomic force microscopy. The single- and multi-layer graphene were formed by mechanical exfoliation on freshly cleaved muscovite mica. The adsorption of the ice-like water layer between graphene and mica led to friction enhancement, as compared with a pristine graphene/mica sample, which is presumably due to additional frictional energy dissipation at the solid–liquid interface. Moreover, friction on the graphene increased as the number of stacking water layers increased. The magnitude of friction increase was, on the other hand, reduced as following increase of the number of covering graphene layer above intercalated water layer, and then the friction is eventually not distinguished from the multi-layer graphene stack excluded water adsorption. Using the first-principle density functional theory calculations we explain this unexpected behavior by the increased spectral range of vibration modes of graphene caused by water, particularly the low frequency flexural modes, and by the better overlap of the graphene vibration modes with the mica phonons, which favors a more efficient dissipation of the frictional energy. Additionally, we found that the intercalation of deuterium oxide (D_2O) leads to the lower friction, compared to H_2O intercalated graphene on mica. We attribute this isotope effect with to the low vibrational frequency of D_2O adsorbate, which results in the low rate of frictional energy dissipation at the interface.

5:20pm **TR+BI+SE+TF-ThA10 The Remarkable Friction Behavior of Copper at Cryogenic Temperatures*, Andrew Kustas,*** Sandia National Laboratories*; J. Curry,* Lehigh University*; T. Babuska, M. Chandross, P. Lu, T.A. Furnish, N. Argibay,* Sandia National Laboratories

It is commonly accepted that unlubricated, self-mated pure metal contacts over the course of sliding invariably cold-weld and gall, leading to undesirably high friction and wear. Recent work with nanostructured pure metals has shown that in fact it is possible to obtain low friction ($\mu < 0.5$) with pure bare metals such as pure Cu and Au at room temperature. Here we discuss those findings, and more recent work that shows the impact of temperature, stress and microstructure evolution on friction of self-mated pure metals. Variable temperature friction experiments were used to show the existence of a temperature-dependent transition for Cu from high ($\mu > 1$) to low ($\mu = 0.25$) friction, achieved by sufficiently reducing temperature and promoting the development of nanocrystalline surface films that are unachievable at room temperature at the relatively high applied stresses imposed. In-situ electrical contact resistance (ECR) measurements were used to indirectly measure the evolution of the microstructure (grain size) at the interface throughout the experiment. Microscopy was then used to verify claims of nanocrystalline surface film formation at low temperatures. Lastly, an analytical model based exclusively on materials properties is presented that incorporates stress and temperature over time to predict grain size, connecting grain size to friction behavior, for pure FCC metals. While more work is needed to develop the proposed framework, a model that intrinsically connects grain size to friction behavior of metals based exclusively on materials properties is transformational to alloy design, and raises a number of compelling and highly fundamental questions for further research.

5:40pm **TR+BI+SE+TF-ThA11 Understanding Friction in MoS2, Part 1: Stress, Time and Temperature*, Tomas Babuska,*** Sandia National Laboratories*; J. Curry,* Lehigh University*; M. Chandross, M.T. Dugger,* Sandia National Laboratories*; B. Krick,* Lehigh University*; N. Argibay,* Sandia National Laboratories

In the 90 years since the first patent was issued for molybdenum disulfide (MoS_2) as a friction and wear reducing additive, great strides have been made in understanding its remarkable lubricity. However, much remains to be understood about the mechanisms of friction at the molecular scale. Firstly, we present results of investigations into the origins of the well-known non-Amontonian behavior of MoS_2. We show that the apparent return to Amontonian behavior previously reported with steel is in fact associated with an elasto-plastic transition of the contact, and that the stress-dependent friction predictable varies as a function of substrate composition and microstructure (hardness). Time-dependent friction evolution (i.e. run-in behavior) was also found be strongly a function of substrate material composition and stress; these results imply a potentially useful connection between stress and microstructure evolution in both film and substrate that is discussed. We also report on investigations into the temperature-dependent friction and wear behavior of pure MoS_2. In the range -150 to 250°C, we report dramatic deviations from previous literature, as well as the existence of transitions between thermal and athermal behavior as a function of temperature. Evidence of deviations from classical Arrhenius behavior is presented, and the implications of these findings discussed in the context of thermally-activated friction models at the molecular scale. Finally, we end with a discussion of how these findings collectively advance our ability to develop a practical predictive friction model for MoS_2 that includes temperature, stress, substrate effects, defect density and commensurability as their foundation.

6:00pm **TR+BI+SE+TF-ThA12 Understanding Friction in MoS2, Part 2: Water, Oxidation and Run- in*, John Curry,*** Lehigh University*; M. Chandross, T. Babuska,* Sandia National Laboratories*; N.C. Strandwitz, H. Luftman,* Lehigh University*; M.T. Dugger, N. Argibay,* Sandia National Laboratories*; B. Krick,* Lehigh University

Effects of water vapor and oxidation resistance for amorphous (sputtered) and highly ordered (N_2 sprayed) MoS_2 were investigated with a high-sensitivity, low energy ion scattering (HS-LEIS) spectrometer, molecular dynamics simulations and accompanying tribological testing in each environment of interest. Recent studies have shown that N_2 sprayed MoS_2 coatings possess a preferential surface parallel basal plane texture as deposited due to the kinetic energy imparted during spraying, effectively shearing MoS_2 particles onto the surface. As such, the highly ordered structure of the sprayed coatings both at the surface and throughout the bulk of the film are hypothesized to act as a diffusion barrier to environmental contaminants. Coatings were exposed to molecular oxygen at 250°C and atomic oxygen at 20°C for 30 minutes each and subsequently depth profiled in the HS-LEIS. Results show that N_2 sprayed coatings were successful in limiting the depth of oxidation for both types of exposure. The main contributor, however, to increased initial friction post exposure was the type of coating (amorphous vs highly oriented). Tribological experiments in dry and humid nitrogen showed the initial friction response to be unaffected for sprayed samples while greatly affected for sputtered. Spiral orbit tribological testing was utilized in dry and humid nitrogen environments to further assess the effect of prolonged sliding on purely amorphous MoS_2 with and without formation of a transfer film. It is hypothesized that water does not poison friction behavior of established films of highly oriented MoS_2, but it does poison the ability to form long range order and sintering of crystallites.

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