

Monday Morning, October 19, 2015

Advanced Surface Engineering

Room: 212A - Session SE+AS+NS+TR-MoM

Nanostructured Thin Films and Coatings

Moderator: Robert Franz, Montanuniversität Leoben, Austria, Andrey Voevodin, Air Force Research Laboratory

8:20am **SE+AS+NS+TR-MoM1 Reactively Sputter Deposited Ternary AlN-based Coatings**, *Joerg Patscheider*, Empa, Switzerland, *E. Lewin*, Uppsala University, Sweden

The protection of surfaces against preventing premature failure by abrasion-resistant nitride coatings has been investigated and put into daily operation ever since. Despite these efforts, the wide range of available protective coatings cannot be used, when glass and other optically transparent materials have to be protected due to the opacity of transition metal nitrides for visible light. For such applications thin films based on Al-A-N with additions of elements from group 14 with A = Si, Ge or Sn are attractive candidate materials, as their transparency in the visible range opens new opportunities of applications. Furthermore, the addition of these elements causes the formation of solid solutions and of nanocomposites, leading to enhanced hardness in the case of A = Si and Ge. Once nanocomposites are formed, enhanced hardness of more than 30 GPa is observed in the case of Al-Si-N and more than 20 GPa for Al-Ge-N and Al-Sn-N. The choice of the additional A element allows for the preparation of highly transparent coatings for the case of Si and the control of color in the range from yellow to red by tuning of the UV absorption edge in the case of Ge and Sn. The role of deposition conditions and their implications on the structure these ternary nitride coatings will be discussed.

8:40am **SE+AS+NS+TR-MoM2 Mo₂BC Coatings for Metal Forming: Interactions Between Tool Surface and Aluminium by Theory and Experiment**, *Jochen Schneider*, RWTH Aachen University, Germany, *H. Bolvardi*, Oerlikon Balzers, Liechtenstein, *D. Music*, RWTH Aachen University, Germany

Low temperature growth strategies for Mo₂BC coatings are reviewed and initial theoretical and experimental data pertaining to the applicability of these coatings during forming of Al based alloys are discussed. A Mo₂BC(040) surface was exposed to O₂. The gas interaction was investigated using *ab initio* molecular dynamics and x-ray photoelectron spectroscopy (XPS) of air exposed surfaces. The calculations suggest that the most dominating physical mechanism is dissociative O₂ adsorption whereby Mo - O, O - Mo - O and Mo₂ - C - O bond formation is observed. To validate these results, Mo₂BC thin films were synthesised utilizing high power pulsed magnetron sputtering and air exposed surfaces were probed by XPS. MoO₂ and MoO₃ bond formation is observed and is consistent with here obtained *ab initio* data. Additionally, the interfacial interactions of O₂ exposed Mo₂BC(040) surface with an Al nonamer is studied with *ab initio* molecular dynamics to describe on the atomic scale the interaction between this surface and Al to mimic the interface present during cold forming processes of Al based alloys. The Al nonamer was disrupted and Al forms chemical bonds with oxygen contained in the O₂ exposed Mo₂BC(040) surface. Based on the comparison of here calculated adsorption energy with literature data, Al - Al bonds are shown to be significantly weaker than the Al - O bonds formed across the interface. Hence, Al-Al bond rupture is expected for a mechanically loaded interface. Therefore the adhesion of a residual Al on the native oxide layer is predicted. This is consistent with experimental observations. The data presented here may also be relevant for other oxygen containing surfaces in a contact with Al or Al based alloys for example during forming operations.

9:00am **SE+AS+NS+TR-MoM3 Molecular Dynamics Simulations of TiN/TiN(001) Growth**, *Daniel Edström*, *D.G. Sangiovanni*, *V. Chirita*, *L. Hultman*, Linköping University, Sweden, *J.E. Greene*, *I. Petrov*, University of Illinois at Urbana Champaign

The Modified Embedded Atom Method (MEAM) interatomic potential within the classical Molecular Dynamics (MD) framework enables realistic, large-scale simulations of important model materials such as TiN. As a step toward understanding atomistic processes controlling the growth of TiN on a fundamental level, we perform large-scale simulations of TiN/TiN(001) deposition using a TiN MEAM parameterization which reproduces experimentally-observed surface diffusion trends, correctly accounts for Ehrlich barriers at island step edges [1], [2], and has been shown to give results in excellent qualitative and good quantitative agreement with *Ab Initio* MD based on Density Functional Theory (DFT) [3], [4]. 85% of a monolayer of TiN is deposited on 100x100 atom

TiN(001) substrates at a rate of 1 Ti atom per 50 ps, resulting in simulation times of 212.5 ns. The TiN substrate is maintained at a typical epitaxial growth temperature, 1200 K during deposition using N:Ti flux ratios of 1:1, 2:1, and 4:1 and incident energies of 2 and 10 eV to probe the effects of N₂ partial pressure and substrate bias on TiN(001) growth modes. We observe nucleation of Ti_xN_y molecules; N₂ desorption; the formation, growth and coalescence of mixed <100>, <110>, and <111> faceted islands; as well as intra- and interlayer mass transport mechanisms. For equal flux ratios at 2 eV incidence energy, islands begin to form atop existing islands at coverages ≥ 0.25 ML, leading to 3D multilayer growth. Increasing the N:Ti flux ratio shifts the growth mode to layer-by-layer growth and changes the stoichiometry from under- to over-stoichiometric. We discuss the implications of these results on thin film growth and process tailoring. Our classical MD predictions are supported and complemented by DFT-MD simulations.

[1] D. G. Sangiovanni, D. Edström, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Dynamics of Ti, N, and TiN_x (x=1-3) ad molecule transport on TiN(001) surfaces," *Phys. Rev. B*, vol. 86, no. 15, p. 155443, 2012.

[2] D. Edström, D. G. Sangiovanni, L. Hultman, V. Chirita, I. Petrov, and J. E. Greene, "Ti and N adatom descent pathways to the terrace from atop two-dimensional TiN/TiN(001) islands," *Thin Solid Films*, vol. 558, pp. 37-46, 2014.

[3] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ab initio and classical molecular dynamics simulations of N₂ desorption from TiN(001) surfaces," *Surf. Sci.*, vol. 624, pp. 25-31, 2014.

[4] D. G. Sangiovanni, D. Edström, L. Hultman, I. Petrov, J. E. Greene, and V. Chirita, "Ti adatom diffusion on TiN(001): Ab initio and classical molecular dynamics simulations," *Surf. Sci.*, vol. 627, pp. 34-41, 2014.

9:20am **SE+AS+NS+TR-MoM4 Stress Design of Multi-layered Coatings**, *Wolfgang Seidl*, Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, Vienna University of Technology, 1040 Vienna, Austria, *M. Arndt*, Oerlikon Balzers, Oerlikon Surface Solutions AG, 4946 Balzers, Liechtenstein, *P. Polcik*, Plansee Composite Materials GmbH, 86983 Lechbruck am See, Germany, *P.H. Mayrhofer*, Vienna University of Technology, Austria

Residual stresses within physical vapour deposited coatings are a major concern, as they are often the origin of failure and delamination. Furthermore, stresses, which typically scale with the thickness, limit the thickness of the coating. With increasing stresses, the interface region is increasingly stressed and weakened, promoting delamination and buckling effects. CrN coatings are known to allow for moderate compressive or even tensile stresses, enabling the preparation of coating thicknesses above 20 μ m. Although CrN coatings exhibit excellent tribological and wear resistance properties, their thermal stability with respect to Cr-N dissociation is limited to 900 °C, which limits their application field. However, several applications require higher thermal stability in combination with relatively thick ceramic coatings. Therefore, we study in detail the requirements to develop nitride-based coatings with thicknesses exceeding 20 μ m.

The residual stresses of arc evaporated TiN, CrN, TiAlN, CrAlN, and TiAlTaN coatings, prepared with an industrial sized coating plant (Balzers Oerlikon INNOVA), are investigated as a function of their thicknesses by measuring the curvature of one-side coated Si(100) cantilevers. Based on these studies we developed multilayer arrangements of TiN/CrN, TiAlN/CrN, TiAlN/CrAlN, and TiAlTaN/CrAlN thick coatings. Their stresses are designed through variations in bilayer period and arrangements of the cathodes at the sidewalls of the industrial chamber.

The individual coatings and multilayers are additionally investigated with respect to growth morphology (by cross sectional scanning electron microscopy), hardness and indentation moduli (by nanoindentation), structure and crystallographic phases (by X-ray diffraction).

9:40am **SE+AS+NS+TR-MoM5 Atomistic Guided Development of Hard Coatings and Thin Films for Severe Applications**, *Paul Mayrhofer*, Vienna University of Technology, Austria **INVITED**

This work summarizes recent developments on applying thin film structure and architecture concepts to hard coatings for optimized performance in various application fields.

The hardness of materials rapidly decreases at elevated temperatures as generally the density of structural defects, such as point defects, dislocations, and grain boundaries, decreases. Additional strengthening can be provided by age-hardening mechanisms, which originate from decomposition-processes of supersaturated phases to form new obstacles

retarding plastic deformation. Furthermore important is the resistance against oxidation and corrosive attack.

By using ab initio calculations and sophisticated experimental methods we will have a detailed insight into various mechanisms responsible for excellent mechanical strength, thermal stability and oxidation resistance properties of Ti–Al–N based hard coatings. For these materials we will also compare the effect of various architecture and alloying concepts with e.g., Y, Zr, Hf, Nb, and Ta.

Another important class of hard coatings is based on the material systems CrN and Cr–Al–N. After a short overview on ab initio and experimental studies in comparison to their sister system Ti–Al–N, we will have a small excursion on the influence of architecture – using the model system CrN/AlN multilayers or their superlattices – on the mechanical properties and especially fracture toughness. Furthermore, based on recent ab initio investigations suggesting that the inherent fracture toughness of CrN can be increased by alloying with Mo or W, we will explore in detail the challenges in studying Cr–Mo–N or Cr–W–N materials by ab initio and experiments.

The various thin film structure and architecture concepts allow the utilization of multifunctional properties facilitating the development of next generation's hard coatings.

10:40am SE+AS+NS+TR-MoM8 Crystallographic Stabilization of δ -WC Thin Films by Alloying with B, using Reactive Magnetron Sputtering of W in Trimethylboron (CH_3)₃B. *Hans Högborg, L. Tengdelius, M. Samuelsson, G. Greczynski, F. Eriksson, L. Hultman, Linköping University, Sweden*

The hardness, oxidation resistance, and high temperature stability of hexagonal δ -WC (B_h) in cemented carbide is a key component in metal cutting. Such a property envelop suggest many potential thin film applications. However, the literature shows that thin film growth of δ -WC by for instance magnetron sputtering is complicated typically resulting in the deposition of films containing the phase γ -WC (B1) with a carbon content lower than nominal, i.e. WC_{1-x} . As the properties of this phase is less favorable compare to those of δ -WC, growth of WC_{1-x} must be avoided in an optimized thin film material. In this study, we attempt to promote the formation of δ -WC films by alloying with B. Our hypothesis is that the preferred growth of WC_{1-x} films depends on the preference of C to occupy octahedral sites found in the B1 structure and where the larger B atom may act to stabilize the B_h structure by better filling out the larger trigonal prism interstitials in this structure. We use reactive magnetron sputtering of W, using trimethylboron (CH_3)₃B (TMB) as C and B precursor. The 5 min depositions were carried on Si(100) substrates in a Kr plasma held at a constant pressure of 0.53 Pa. The gaseous TMB was introduced close to the substrates. The influence of TMB flow, ranging from 1-10 mln, was studied for a growth temperature of 500 °C. Also, the influence of growth temperature, from room temperature to 900 °C, was investigated for a constant TMB flow of 10 mln. X-ray photoelectron spectroscopy shows that the content of B and C scales with the flow into the plasma with no B and ~3 at.% C at 1 mln and 6.5 at.% B and 17.8 at.% C at 10mln. In contrast, temperatures up to 600 °C show no impact on the B and C content in the films, while higher temperatures give a solid state reaction with the substrate. X-ray diffraction shows broad peaks indicative of small grain sizes and with peaks at 2θ angles matching those of the phases WC_{1-x} or W. In the in the temperature range 300 to 600 °C, 100-textured WC_{1-x} films are deposited and with a shift to a weak 111 orientation at lower temperatures. At 500 °C, TMB flows of 5 to 10 mln results in the growth of 100-textured WC_{1-x} films, while lower flows yield W films. Films are deposited with thicknesses up to ~1000 nm, corresponding to a deposition rate of 3.3 nm/s. The microstructure is generally fine-grained, but with broken columns at 500 and 600 °C and a TMB flow of 1 mln. The mechanical properties of the films will be reported.

11:00am SE+AS+NS+TR-MoM9 Epitaxial and Polycrystalline WN_x and MoN_x Films Deposited by Reactive DC Magnetron Sputtering. *Brian Ozsdolay, K. Balasubramanian, Rensselaer Polytechnic Institute, C.P. Mulligan, U.S. Army Armament Research Development & Engineering Center, Benét Laboratories, M.J. Guerette, L. Huang, D. Gall, Rensselaer Polytechnic Institute*

WN_x layers, 1.45- μm -thick, were deposited by reactive magnetron sputtering on MgO(001), MgO(111), and Al_2O_3 (0001) in 20 mTorr N_2 at $T_s = 500$ -800 °C. X-ray diffraction ω - 2θ scans, ω -rocking curves, ϕ scans, and reciprocal space maps show that all layers deposited from 500-700 °C exhibit the cubic rock-salt structure, with a relaxed lattice constant that decreases from 4.299 to 4.171 Å as the N-to-W ratio decreases from $x = 1.20$ for $T_s = 500$ °C to $x = 0.83$ for $T_s = 700$ °C, as measured by energy dispersive and photoelectron spectroscopies. $T_s = 500$ -600 °C yields a polycrystalline 111-textured microstructure on all substrates. In contrast, deposition at 700 °C results in epitaxial growth of WN(111) and WN(001)

on MgO(111) and MgO(001), respectively, while deposition on Al_2O_3 (0001) yields a 111-preferred orientation, misoriented cubic WN grains as well as N-deficient BCC W. $T_s = 800$ °C causes nitrogen loss and WN_x layers with primarily BCC W grains and $x = 0.04$ -0.06. The measured elastic modulus ranges from 110-260 GPa for $T_s = 500$ -700 °C and decreases with increasing N-content, and increases to 350 GPa for $T_s = 800$ °C. For samples deposited at $T_s = 700$ °C, nanoindentation on WN on MgO(001), MgO(111), and Al_2O_3 (0001) provides hardness values of 9.8 ± 2.0 , 12.5 ± 1.0 , and 10.3 ± 0.4 GPa, and elastic moduli of 240 ± 40 , 257 ± 13 , and 242 ± 10 GPa, respectively. The corresponding shear moduli measured by Brillouin light scattering are 127 ± 2 GPa, 121 ± 2 GPa and 115 ± 2 GPa. MoN_x layers, 1- μm -thick, deposited on MgO(001) also exhibit a cubic rock salt structure with x decreasing from 1.18 for $T_s = 500$ and 600 °C to $x = 0.76$ for $T_s = 800$ °C but remaining approximately constant for $T_s = 800$ -1000 °C. Layers with $T_s > 700$ °C contain both epitaxial MoN_x (001) and 111-oriented grains. The out-of-plane lattice constant decreases from 4.22 to 4.18 Å for 111 oriented grains and from 4.17 to 4.06 Å for epitaxial 001-oriented grains, as T_s is increased from 700 °C to 1000 °C.

11:20am SE+AS+NS+TR-MoM10 Phase Stability and In Situ Growth Stresses in Thin Cu/Nb Multilayered Films. *Qianying Guo, L. Wan, R.L. Martens, G.B. Thompson, University of Alabama*

As the length scale of individual layers are reduced in a Cu/Nb multilayer, fcc to bcc and bcc to fcc transformations were noted for Cu and Nb respectively. These transitions have been modeled using a thermodynamic phase diagram where interfacial and volumetric energy considerations determine stability and the bilayer thickness of the multilayer is a state variable for predicting those transformations. Using HRTEM, the evolution of the interface from incoherent-to-semicoherent-to-coherent is determined and related to the structural component of the interfacial energy reduction that drives the crystalline transformations. When equal thicknesses of each layer were < 1 nm, the layers underwent an additional transformation from a crystalline to amorphous structure. This has been rationalized by the positive enthalpy of mixing between these two species as they intermixed during the sputter deposition process. The chemical intermixing and local clustering at and near the interface has been quantified by atom probe tomography. These phase transformations have been related to real-time, intrinsic growth stress measurements. All of the multilayers were in a compressive stress state, but a notable reduction in the compressive stress value occurred with each transformation. The collective characterization of the film, via TEM, atom probe, and stress evolution, have provided insights into the structural stability of crystalline phases at the nanoscale.

11:40am SE+AS+NS+TR-MoM11 Droplets in Cathodic Arc Evaporated $(\text{Al,Cr})_2\text{O}_3$ -based Coatings and the Nucleation of Dedicated Crystalline Structures. *Christian M. Koller, CDL AOS, TU Wien, Austria, R. Hahn, TU Wien, Austria, J. Ramm, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, S. Koložvári, Plansee Composite Materials GmbH, Germany, P.H. Mayrhofer, CDL AOS, TU Wien, Austria*

Corundum-type Al_2O_3 coatings demonstrate excellent thermo-mechanical properties, giving rise to widespread applications as protective films on, e.g., cutting inserts or components. These coatings are typically synthesised by chemical vapour deposition (CVD) at temperatures of 900 °C or higher, which excludes temperature sensitive substrates. Physical vapour deposition (PVD) proved to be a suitable method for low temperature synthesis of nitrides with excellent properties. However, the growth of single-phased corundum-type α - Al_2O_3 by PVD is still a difficult task under standard production conditions. In general, a mixed phase composition of metastable cubic phases is observed, which influence the thermo-mechanical performance of the coating. The utilisation of targets produced by powder metallurgical methods allows for the combination of aluminium with other elements, suitable to promote dedicated crystal structures as demonstrated by AlCr and more recently AlCrFe, where dense crystalline coatings with an increased amount of hexagonal phase fractions were realised. Although the alloying with Cr and Fe is a promising concept with good prospects, the mechanism to form the hexagonal structure in these materials is yet not understood. Therefore, the aspect of layer-nucleation is investigated in more detail. A significant part of hexagonal crystallites in $(\text{Al,Cr,Fe})_2\text{O}_3$ coatings is triggered by nucleation onto small particles incorporated in the coating. They originate from the cathode surface and are generated during the cathodic arc process. Cathode surface modifications, macroparticle incorporation and the associated coating microstructures are elucidated by detailed X-ray diffraction and electron microscopy studies. Implications on the coatings' properties and possible technological concepts are discussed.

Thursday Morning, October 22, 2015

Tribology Focus Topic

Room: 230B - Session TR+TF-ThM

Nanolubricants and Coatings

Moderator: Tevis Jacobs, University of Pittsburgh

8:00am **TR+TF-ThM1 Mechanical Mixing and Wear Formation in Metallic Tribocouples**, *Martin Dienwiebel*, P. Stoyanov, T. Feser, Karlsruhe Institut für Technology (KIT), Germany, R. Merz, Insitut für Oberflächen und Schichtanalytik GmbH, Germany, P. Romero, Fraunhofer Institute for Mechanics of Materials IWM, Germany, F.C. Wählich, INM - Leibniz-Institute for New Materials, Germany, P. Stiemmer, University of Duisburg-Essen, Germany, M. Moseler, Fraunhofer Institute for Mechanics of Materials IWM, Germany, R. Bennewitz, INM - Leibniz-Institute for New Materials, Germany, A. Fischer, University of Duisburg-Essen, Germany **INVITED**

During sliding of metallic surfaces in dry or lubricated conditions the near surfaces undergo significant changes in terms of topography, composition and microstructure [1] and a so-called "third body" or "tribomaterial" [2] develops. The third-body formation strongly influences the frictional and wear behavior of the system.

In this talk we present several experiments on pure metals and alloys that were performed using a novel experimental platform for the on-line correlation of friction, wear and topography under lubricated sliding [3]. Fast topography data is measured in real time by digital holography microscopy (DHM), wear is measured by the Radionuclide wear technique (RNT) and the nanoscale topography is obtained *in-situ* by liquid atomic force microscopy (AFM). The tribological systems that we recently studied include a-brass (CuZn) sliding against steel [4], tungsten and tungsten carbide [5], [6]. The experimental findings were compared to MD simulations. In order to characterize the mechanical behavior, nanoindentation and micropillar compression tests were performed that show that the third body material is softening during the initial running-in [7].

References

- [1] M. Scherge, D. Shakhvorostov, K. Pöhlmann, *Wear*, 255 (2003) 395-400.
- [2] M. Godet, *Wear*, 100 (1984) 437-452.
- [3] S. Korres, M. Dienwiebel, *Rev. Sci. Instr.*, 81 (2010) 063904.
- [4] T. Feser, P. Stoyanov., M. Dienwiebel, *Wear*, 303 (2012) 465-472
- [5] P. Stoyanov et al. , *Tribol. Lett.*, 50 (2013) 67-80.
- [6] P. Stoyanov et al., *ACS Appl. Mat. & Int.s*, 5 (2013) 6123-6135.
- [7] P. Stoyanov et al., *ACS Nano* 9 (2015) 1478

8:40am **TR+TF-ThM3 Influence of MoDTC Degradation on Tribological Performances of Steel-Steel Contacts under Boundary Lubrication Conditions**, *Clotilde Minfray*, M. De Feo, M.I. De Barros Bouchet, Ecole Centrale de Lyon - LTDS, France, B. Thiebaut, Solaize Research Center, France, T. Le Mogne, B. Vacher, J.M. Martin, Ecole Centrale de Lyon - LTDS, France

Nowadays, MoDTC is one of the best-known friction modifier additives used in engine oils for its friction reduction properties. A vast number of papers tackle the subject and converge on the fact that the generation of MoS₂ flake in the contact (in tribofilm) is at the origin of the friction reduction. But it is also known that this positive friction reduction effect is not so durable in time. Therefore, the investigation of MoDTC chemical degradation mechanism and its impact on the tribological properties in steel/steel contacts is of great interest.

It is proposed here to age a lubricant made of mineral base oil blended with 1%w of MoDTC with a thermo-oxidative procedure (open air - 160°C) for different durations. The aged lubricants are then tested under boundary lubrication conditions, with ball-on-flat reciprocating tests running at 100°C. Balls and flats are both in AISI52100 steel.

Concerning the results, clear differences are found in terms of friction behavior as a function of ageing time. A relation between ageing and induction time needed to reach the "low" friction regime is also established. Tribofilms generated on flats were then analyzed by means of XPS surface analysis and FIB-TEM observations for a precise chemical and morphological characterization of each flat sample. The possible presence of two types of molybdenum oxi-sulfide compounds, more or less oxidized, is suggested by XPS results and discussed regarding the friction behavior. Moreover, the TEM observations carried out suggest tribofilms differences

in terms of morphology, size and organization. Finally, the effect of MoDTC ageing on friction behavior is discussed considering the composition of tribofilms but also taking into account MoDTC depletion in the bulk of the lubricant, thanks to High Performance Liquid Chromatography (HPLC) experiments.

9:20am **TR+TF-ThM5 General Model for Tribology of Metallic Contacts**, *Michael Chandross*, Sandia National Laboratories, S. Cheng, Virginia Tech, N. Argivay, Sandia National Laboratories **INVITED**

The tribology community presently relies on phenomenological models to describe the various seemingly disjointed steady-state regimes of metal wear. Pure metals such as gold -- frequently used in electrical contacts -- exhibit high friction and wear. In contrast, nanocrystalline metals, such as hard gold, often show much lower friction and correspondingly low wear. The engineering community has generally used a phenomenological connection between hardness and friction/wear to explain this macroscale response, and thus to guide designs. We present a suite of recent simulations and experiments that demonstrate a general framework for connecting materials properties (i.e. microstructural evolution) to tribological response. We present evidence that the competition between grain refinement (from cold working), grain coarsening (from stress-induced grain growth), and wear (delamination and plowing) can be used to describe transient and steady state tribological behavior of metals, alloys and composites. We will present the results of large-scale molecular dynamics simulations and targeted experiments that explore the seemingly disjointed steady-state wear regimes of metals and alloys, with a goal of elucidating the structure-property relationships, allowing for the engineering of tribological materials and contacts based on the kinetics of grain boundary motion.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000

11:20am **TR+TF-ThM11 Superlubric Sliding of Gold Nanoparticles on Graphite under Ambient Conditions**, *E. Cihan*, *Mehmet Z. Baykara*, Bilkent University, Turkey

Forming a complete understanding of the physical mechanisms that govern friction on the nanometer and atomic scales is an ongoing endeavor for scientists from various disciplines. While atomic force microscopy (AFM) has proven to be invaluable for the detailed study of nano-scale frictional properties associated with various surfaces, issues related to the precise characterization of the contact formed by the probe tip and the sample surface remain largely unsolved.

In recent years, an alternative approach to nanotribology experiments has involved the lateral manipulation of well-characterized nanoparticles on sample surfaces via AFM and the measurement of associated frictional forces [1]. In line with this idea, we present ambient-condition nano-manipulation experiments involving gold nanoparticles (AuNP) thermally deposited on highly oriented pyrolytic graphite (HOPG), a sample system which has been recently characterized in detail [2]. It is observed that AuNPs experience remarkably low frictional forces during sliding. A detailed study of friction with respect to contact area firmly confirms the occurrence of *superlubric* sliding under ambient conditions for this sample system. The potential reasons behind the observed phenomenon are discussed with support from theoretical considerations.

- [1]: D. Dietzel, U.D. Schwarz, A. Schirmeisen, *Friction* 2, 114-139 (2014)
- [2]: E. Cihan, A. Özoğul, M.Z. Baykara, *Applied Surface Science*, (2015), DOI: 10.1016/j.apsusc.2015.04.099

11:40am **TR+TF-ThM12 Monitoring the Gas-Phase Products of a Shear-Induced Reactions in Ultra-high Vacuum**, *Heather Adams*, University of Wisconsin-Milwaukee, M.T. Garvey, Illinois Applied Research Institute, O. Furlong, Universidad Nacional de San Luis, Argentina, W.T. Tysoc, University of Wisconsin-Milwaukee

Although tribochemical reactions are common in manufacturing, analysis of the mechanism and products is severely limited by the difficulty of probing a solid-solid interface that changes on small time scales. A method to analyze the gas-phase products of a tribochemical reaction in ultra-high vacuum has been developed to allow insight to be obtained into the decomposition pathways of short-chain alkylthiols on copper foils. A UHV-tribometer is used to probe the alkylthiol-covered copper foil by using a mass spectrometer to measure the products evolved from the surface.

Alkylthiols have been chosen due to their thermal stability on a copper surface¹, and their ability to form a tribofilm. Previous studies have found

that sulfur moves into the sub-surface layer with rubbing, and the carbon is removed from the surface.²

The shear-induced decomposition of methyl thiolate produces gas-phase methane and measuring the amount of methane produced during each sliding cycle allows the shear-induced reaction rate to be measured. The results are analyzed to give insight into how sheer stress lowers the energy barrier for the decomposition reaction.³

1. Furlong, O. J. *et al.* The surface chemistry of dimethyl disulfide on copper. *Langmuir***26**, 16375–16380 (2010).

2. Furlong, O., Miller, B., Kotvis, P., Adams, H. & Tysoe, W. T. Shear and thermal effects in boundary film formation during sliding. *RSC Adv.***4**, 24059 (2014).

3. Adams, H. L. *et al.* Shear-Induced Mechanochemistry: Pushing Molecules Around. *J. Phys. Chem. C***119**, 7115–7123 (2015).

Thursday Afternoon, October 22, 2015

Tribology Focus Topic

Room: 230B - Session TR+AS+NS+SS-ThA

Molecular Origins of Friction

Moderator: Nicolas Argibay, Sandia National Laboratories

2:20pm TR+AS+NS+SS-ThA1 **Atomic-Scale Mechanisms of Single Asperity Sliding**, *Ashlie Martini, X. Hu*, University of California Merced, *M.V.P. Altoe*, Lawrence Berkeley National Laboratory

INVITED

Isolating a single asperity to characterize its response to sliding is a heuristic approach to understanding the fundamental mechanisms that underlie friction and wear. A single asperity can be realized experimentally as the tip of an atomic force microscope cantilever. When the tip slides across a surface, friction is measured with atomic lattice-scale resolution and wear can be quantified in terms of nano- or even atom-scale volumes of material removed. However, challenges remain in interpreting these measurements because the observed friction and wear are due to processes that take place in the interface buried between the tip and the substrate on which it slides. Further, the nanometer scale of the contact implies that discrete atomic events in the interface may determine sliding behavior. Together, these observations suggest that the experiments could be complemented by atomistic models of the apex of the tip, near-contact substrate material and, of course, the interface itself. Although the simulations are limited to relatively small size and time scales, they have the potential to provide detailed information about mechanisms underlying phenomena that occur over short periods of time and small sliding distances. Specifically, in this research, we focus on the initial stages of friction and wear, and the processes that occur during the first tens of nanometers of sliding. The simulations are carefully designed such that they faithfully capture the corresponding experiments, including matching the materials, crystallography and geometry of the contacting bodies as observed through transmission electron microscope images of the tip and atomic force microscope images of the substrate taken at 10 nm intervals during the sliding process. The experiments offer an unprecedented view of wear occurring single atomic layers at a time, and the simulations provide detailed complementary information about the atomic-scale mechanisms underlying this process.

3:00pm TR+AS+NS+SS-ThA3 **Investigation of Epitaxy and Friction in Model Boundary Films**, *Hongyu Gao*, University of California Merced, *W.T. Tysae*, University of Wisconsin-Milwaukee, *A. Martini*, University of California Merced

Sliding friction of boundary films is investigated using ultrahigh vacuum (UHV) tribometer measurements of model alkali halide films on metals with complementary molecular dynamics (MD) simulations. We focus on a model system consisting of thin potassium chloride (KCl) films on an iron (Fe) substrate. The interaction potential between KCl and Fe is tuned using activation energy obtained from temperature programmed desorption (TPD) data and structures inferred from low-energy electron diffraction (LEED) measurements. The simulation is then used to explore the effect of film thickness and pressure on the formation of an epitaxial KCl film. The nature of this film and its near surface structure is then correlated with sliding friction behavior.

3:20pm TR+AS+NS+SS-ThA4 **Temperature Dependence of Atomic-scale Friction on Two-dimensional Materials**, *Zhijiang Ye*, University of California Merced, *X.Z. Liu, K. Hasz, R.W. Carpick*, University of Pennsylvania, *A. Martini*, University of California Merced

Temperature plays an essential, yet complex role in determining atomic-scale friction. Recent studies of the temperature dependence of atomic-scale friction have reported different trends that suggest distinct and possibly contradictory underlying mechanisms. Specifically, friction is usually found to decrease with increasing temperature (due to thermolubricity), but this behavior is not always observed (attributed to adsorbates or meniscus effects). To understand the origins of these trends, we use molecular dynamics (MD) simulations and parallel replica dynamics (PRD) to study the temperature dependence of atomic friction on two-dimensional (2-D) materials, such as molybdenum disulfide. The MD simulations are designed to be closely-matched with corresponding atomic force microscope (AFM) measurements [1, 2]. Using the simulations and experiments, we explore how friction varies with temperature and how that variation is affected by other parameters, including sliding velocity, material, and environment. These studies provide new insights into how temperature affects friction on 2-D materials, and into the origins of atomic-scale friction generally.

References:

1. Xin-Z. Liu, Zhijiang Ye, Yalin Dong, Philip Egberts, Robert W. Carpick, and Ashlie Martini. Dynamics of Atomic Stick-Slip Friction Examined with Atomic Force Microscopy and Atomistic Simulations at Overlapping Speeds, *Phys. Rev. Lett.* **114**, 146102 (2015).

2. Qunyang Li, Yalin Dong, Danny Perez, Ashlie Martini, and Robert W. Carpick. Speed dependence of atomic stick-slip friction in optimally matched experiments and molecular dynamics simulations. *Physical Rev. Lett.* **106**, 126101 (2011).

4:20pm TR+AS+NS+SS-ThA7 **Single Molecule Experiments to Explore Friction and Adhesion**, *Rémy Pawlak, S. Kawai, A. Baratoff, T. Meier*, University of Basel, Switzerland, *W. Ouyang*, Tsinghua University, China, *T. Glatzel*, University of Basel, Switzerland, *E. Gnecco*, IMDEA-Nanociencia - Universidad Autónoma de Madrid, Spain, *A. Filippov*, Donetsk Institute of Physics and Engineering, Ukraine, *M. Urbakh*, Tel Aviv University, Israel, *E. Meyer*, University of Basel, Switzerland

INVITED

Controlled manipulation processes of single-molecules with an atomic force microscope (AFM) provide valuable information about their interactions with surfaces, leading to fundamental insights into adhesion and friction properties. To understand such phenomena at such scale, tuning-fork based AFM operated at low temperature is an appropriate tool since complex manipulations of single-molecules can be readily performed and detected via advanced force spectroscopic techniques [1]. With such approach however, the measured frequency shifts are related to normal force gradients, and thus the interpretation of friction phenomena is not fully straightforward. To overcome this issue, we developed analytical models to simulate the experimental AFM data which allow us to determine adhesive energy and nanoscale friction. In this presentation, a first example will be given by the vertical pulling of long polymeric chains on Au(111), where their detachment leads to oscillations of the normal and lateral forces [2]. As in Frenkel-Kontorova (FK) models of friction, the polymer is represented by a chain of units connected by springs of stiffness k , each one interacting with a 2D periodic substrate potential. Force and gradient variations are dominated by the sequential detachment of each molecular units if k is large enough to cause superlubric sliding. A second example will show vertical and lateral manipulations over a Cu(111) surface of a single porphyrin molecule attached to the AFM tip apex. In the frequency shift traces, atomic sawtooth modulations are systematically observed while sliding over the surface and are related to the internal degree of freedom of the molecular structure [3].

References:

[1] R. Pawlak, S. Kawai, T. Glatzel, E. Meyer. *Single Molecule Force Spectroscopy* (ncAFM, vol.3, Springer, Japan 2015).

[2] S. Kawai et al., Quantifying the atomic-level mechanics of single long physisorbed molecular chains, *Proc. Nat. Acad. Sci.*, **111**, 3968–3972 (2014)

[3] R. Pawlak et al. *Intramolecular response of a single porphyrin molecule during AFM manipulations*. Submitted.

5:00pm TR+AS+NS+SS-ThA9 **Effects of Humidity on the Adhesion and Friction of Carbon-Based Materials**, *Judith Harrison, M. Fallet, K.E. Ryan*, United States Naval Academy, *T. Knippenberg*, High Point University, *S.H. Kim, A. Al-Azizi*, Pennsylvania State University

Atomic-scale wear in nanoscale contacts is of particular importance for tip-based nanomanufacturing applications. As a result, wear resistant materials, such as diamond-like carbon (DLC), have been used to coat AFM tips to improve the lifespan and reliability of AFM probes and surfaces. Unfortunately, the tribological performance of these materials is known to depend on environmental conditions, such as humidity levels. We have performed macroscopic and atomic force microscopy friction experiments and molecular dynamics (MD) simulations aimed at examining adhesion and wear of DLC in humid environments.

Macro-scale friction tests showed friction and transfer film dependence on humid conditions. Low humidity suppresses transfer film formation while keeping the friction low. Intermediate humidity, however, does not reduce transfer film formation and increases the friction. The effect of humidity on friction was found to agree with the adhesion dependence on relative humidity as measured with atomic force microscopy.

Because it is difficult to elucidate atomic-scale mechanisms via experimental methods, molecular dynamics simulations have been employed to examine this behavior. Adhesion and sliding simulations of non-hydrogenated, ultrananocrystalline diamond (UNCD) and DLC surfaces with various levels of hydrogen in the presence of water using the qAIREBO and the ReaxFF potentials have been performed. Because both of

these potentials are able to model chemical reactions, the atomic-scale mechanisms responsible for adhesion and wear can be identified. Results obtained with both potentials will be compared to the experimental results.

5:20pm **TR+AS+NS+SS-ThA10 Single Asperity Tribochemical Wear of Silicon AFM Tips Sliding on Aluminum Oxide**, *Erin Flater, S. Sorenson, Luther College, N. Ansari, A. Poda, W.R. Ashurst, Auburn University, B.P. Borovsky, St. Olaf College*

Understanding of tribological mechanisms at the submillimeter scale continues to be relevant since friction and wear limit the commercial viability of small-scale mechanical devices such as microelectromechanical systems (MEMS). For example, tribochemical processes play a significant role in many materials systems, including silicon oxide and aluminum oxide, which are relevant materials for MEMS devices. Our work focuses on understanding tribological processes at the interface of silicon AFM tips and amorphous aluminum oxide surfaces. We observe wear of silicon tips after repetitive sliding on the aluminum oxide surface, which occurs even at low contact pressures, implying that the wear process is chemical in nature. We quantify tip wear by intermittently interrupting the wear experiment to perform indirect *in-situ* tip imaging on a sharp-spiked sample. We use these tip images to quantify volume of material lost during scanning. Wear as a function of sliding distance is modeled using reaction rate theory and is compared to the Archard wear model. While some of our results appear to agree with an Archard model, these results may be more appropriately interpreted in light of the more fundamental reaction rate theory.

5:40pm **TR+AS+NS+SS-ThA11 Molecular Simulation of Indentation as a Probe of Scanning Probe Tip Mechanical Properties**, *J. David Schall, K. Vummaneni, Oakland University, J.A. Harrison, United States Naval Academy*

Scanning probe tips should be robust, have low adhesion, and low wear to ensure repeatability and long tip life. As new tip materials are developed these properties must be quantified and compared to existing tip materials. In this study, molecular simulation is used to measure the elastic modulus and work of adhesion of a variety of tips against a common substrate material, in this case H-terminated diamond (111). The tip materials investigated include Si, SiC, amorphous SiC, diamond, diamond like carbon and ultra-nanocrystalline diamond (UNCD). SiC was recently proposed as a new high hardness, low wear tip material. In simulation the tip geometry can be controlled to enable direct comparisons between each tip material. Both dynamic simulations at 300K and quasi-static indentions using stepwise energy minimization with and with out adhesion between tip and substrate were used. Simulations of sliding friction and wear have also been conducted to investigate the correlation between tip materials properties and friction and wear.

Tribology Focus Topic

Room: Hall 3 - Session TR-ThP

Tribology Poster Session

TR-ThP1 Adhesion of Hard Coating on Neutral Nitrided Tool Steel Surfaces, *P. Abraha*, Meijo University, Japan, *Takuma Matsuda*, Meijo University, Japan

Hard thin films such as titanium nitride and titanium aluminum nitride films are widely used to improve the durability of cutting tools, punches, and dies that are extensively used in the manufacturing industries. In general, the hardness of hard coating films is about three to five times that of tool steel surfaces causing a remarkably high stress that would eventually lead to the detachment of the hard coating. One way of improving the adhesion of hard coatings is to increase the surface hardness of the tool steel, narrowing the gap, to maintain a reasonably stronger bondage.

In this research, neutral nitriding operation was performed on the SKH 51 tool steel surface before TiAlN coating. Neutral nitriding is a plasma process that allows only the neutral species to diffuse into the interstitial layer of the tool steel surface. The process delimits the formation of the undesirable brittle compound layer to a much higher treatment time while keeping the as-finished surface conditions. The scratch test was performed to provide a measure of coating/tool steel adhesion.

The results of our experiments show that in nitriding SKH 51 tool steel for 6 hours, the hardness of the tool steel surface was increased by about two times, 1400 Hv compared to the untreated sample (750 Hv). The scratch tests show that a well-defined failure of the coating occur at a higher critical load in tool steel samples that are neutral nitrided compared to samples without the pre-treatment. Our results demonstrate that neutral species based nitriding is effective for high adhesion of hard coating materials on tool steel surfaces.

TR-ThP2 Neutral Nitriding of Austenite Stainless Steel at Low Temperature, *Jun Tamura*, *P. Abraha*, Meijo University, Japan

Stainless steels have very good corrosion resistance but the lower surface hardness poses marked limitation on the range of tribological applications that can be envisaged. Here plasma nitriding treatment was performed to improve the hardness without altering the corrosion resistance of austenitic AISI 304 stainless steels.

In nitriding the AISI 304 stainless steel, the passive Cr₂O₃ layer that protects the surface from corrosion is removed first as it hinders the diffusion of nitrogen species into the bulk of the stainless steel material. The removal of the passive layer was done by argon sputtering and the subsequent nitriding was performed in electron beam excited plasma apparatus under nitrogen and hydrogen atmosphere. The sample temperature was controlled at 400, 450, and 500 degree centigrade. Treated and untreated samples were characterized by means of morphological analysis, Vickers hardness measurements, optical microscope, and x-ray diffractometry.

The results of our experiments show that in neutral nitriding of stainless steel under low temperature, 400 degrees centigrade, the surface hardness increased to 780 Hv, more than two times, that of the untreated surface. Moreover, the cross sectional images show clear nitrogen expanded austenite layer without the formation of compound layer. Measurements of surface roughness and conditions of the surfaces were reasonably maintained. The above results indicate that stainless steels can be used as sliding or meshing mechanical parts in environments such as vacuum chambers and underwater machinery.

TR-ThP3 Non-Oxidized Metallic Transfer Film Formation Originated from Metallic Nanoparticles Embedded in Diamond-like Carbon under Sliding in Air, *Takanori Takeno*, *H. Miki*, *T. Takagi*, *K. Adachi*, Tohoku University, Japan

This study clarifies the formation mechanisms of thin layer on the counter material when nanocomposite coatings consisted of nanoparticles and diamond-like carbon were sliding against steel ball in air. When low friction was obtained in such combination, thin metallic film was formed on the counter material. What we could find is that such metallic film does not contain oxygen less than the one coming from native oxidized surface.

Hybrid deposition system composed of CVD and PVD sources allows us to make nanocomposite structure based on diamond-like carbon (DLC) coatings. Thanks to magnetron sputtering system, target material in sputtering source is extracted as a form of nanoparticle, and its size varies depending on deposition condition and type of material. During sputtering process, hydrocarbon plasma is generated, and hydrogenated amorphous

carbon phase is formed. Typical structure of the composite coatings is that nanometer-sized metallic particles are well dispersed in amorphous carbon host matrix. Friction tests are conducted under vacuum or dry conditions. Various analytical techniques including transmission electron microscope (TEM), secondary ion mass spectrometer (SIMS), Raman spectroscopy, Scanning Electron Microscope equipped with energy dispersive X-ray spectrometer (SEM-EDS), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

Once iridium was selected as an inclusions in diamond-like carbon host matrix, Ir-containing DLC showed friction coefficient of less than 0.1 despite friction coefficients of Ir and DLC showed ~ 0.3. In-situ electrical contact resistance measurements revealed that such coating provides not only low friction coefficient but also low electrical contact resistance, several tens ohms. When low friction and electrical contact resistance was achieved, metallic thin film was formed on the counter material. EDS analyses revealed that chief material forming the metallic film is Ir. It could be understood that nanoparticles formed metallic thin film on the counter materials during friction. It is worth noting that such transfer film does not contain oxygen even friction tests were conducted under air. Same phenomena could be observed with Cu- and Ag-containing DLCs. Even for both cases, metallic transfer films were formed during friction tests, and we could not detect oxygen from the transfer by EDS. Possibly, tribochemical reaction occurred and oxygen from air reacts to carbon in DLC, then gas phase or wear particles of carbon-oxides were formed. Details on a possible chemical reaction between the coatings and air will be discussed at the conference.

TR-ThP4 Achieving Very Low Friction with Molybdenum Disulfide Nanoparticles Embedded into Hydrogenated Amorphous Carbon Coatings, *Kazuki Ikoma*, *K. Adachi*, *T. Takeno*, Tohoku University, Japan

Solid lubricants are usually used at severe environment (ex. vacuum). Among these lubricants, MoS₂ is widely used for many mechanical systems and shows low friction by forming transferred layer with MoS₂ lamellar structure. However, one of the drawbacks of MoS₂ is that it must be kept in dry nitrogen condition to avoid oxidation of molybdenum-disulfide.

We have proposed amorphous carbon coatings containing Molybdenum disulfide (MoS₂-DLC) as a new solid lubricant. It is well known that amorphous carbon coating is used for a gas barrier coating decreasing gas permeability. So, we have made the coatings with nanocomposite structure that MoS₂ clusters with several nm in diameter are embedded in hydrogenated amorphous carbon (a-C:H) host matrix. It was reported that friction coefficient obtained by MoS₂ sliding against SiC ball decreased with increasing MoS₂ concentration. It is worth noting that MoS₂-DLC with proper MoS₂ concentration showed lower friction than MoS₂ coatings. Further reduction of friction could be obtained by changing a deposition parameter leading to a modification of host matrix of amorphous carbon. Therefore, not only concentration of MoS₂ but also properties of amorphous carbon host matrix are very important for achieving low friction.

This study focuses on hydrogenated amorphous carbon host matrix to achieve low friction. Especially, deposition parameter that controls properties of carbon host matrix was changed to produce various amorphous hydrogenated carbon host matrix containing MoS₂ nano-clusters. After the friction tests, a thin transferred layer proving low friction is well analyzed by various analytical techniques including transmission electron microscope (TEM), secondary ion mass spectrometer (SIMS) and Auger electron spectroscopy (AES). It was clarified that thin transferred layer was composed of two phases. Dominant one contains mainly MoS₂ with lamellar structure. It is worth noting that there is very thin carbon-rich layer with ~ 5 nm between MoS₂-rich layer and the counter material of SiC, and carbon at thin carbon layer comes from carbon host matrix. Taking into account the selective transfer of carbon from the coating and the possibility that such carbon-rich layer becomes a kind of support for forming lubricious MoS₂ layer, friction properties could be controlled by the properties of carbon. In this study, formation mechanisms of such two-phase thin layer are clarified, first. Then, we try to achieve very low friction with low MoS₂ concentration with optimized phase of carbon phase in the coating. Finally, design guideline for achieving low friction utilizing MoS₂-DLC coatings is proposed.

TR-ThP5 Study of Wear-corrosion Mechanisms of CoCrMo Alloys Alone and Coated with TiAlN Coatings, *Martin Flores*, *O. Jimenez*, Universidad de Guadalajara, Mexico, *E. Andrade*, Universidad Nacional Autonoma de México

The wear-corrosion phenomenon is present in biomedical alloys that are used in artificial implants to replace natural joints. This damage limit the service life of such implants, the hard coatings can improve the resistance to

wear and corrosion. The coatings of TiAlN were deposited on CoCrMo alloys by magnetron sputtering. In this work we study the wear mechanism of the samples coated and alone in a simulated body fluid with an ion concentration similar to that in the human blood. The structure of coatings was studied by means of XRD and the composition by RBS and EDS techniques. The tribocorrosion behavior of CoCrMo alloys alone and coated with TiAlN coatings was studied in simulated body fluid. The tribocorrosion was performed using a ball on plate reciprocating tribometer, the tests were conducted at 37 °C of temperature. The loads used were between 0.5 N to 2N, the oscillating frequencies was 1Hz. The corrosion and tribocorrosion were studied using open circuit potential (OCP) and potentiodynamic polarizations. In order to study the wear mechanisms, the debris, the topography and composition of worn surfaces were analyzed by means of SEM and Raman spectroscopy. The coatings improve the corrosion and tribocorrosion resistance of CoCrMo alloys and change the wear mechanisms of the substrate.

TR-ThP6 Frictional Property Optimization of Metal Oxide Thin Films by a Combinatorial Optimization of Crystal Orientation for Tribology (COCOT) Technique, Michiko Sasaki, M. Goto, A. Kasahara, M. Tosa, National Institute for Materials Science, Japan

Combinatorial technology has much attention as the effective method for the development of novel functional materials. Also, the combinatorial technique have been used as one of the analysis methods in tribology research.

In this study, we were performed crystal structure analysis by combinatorial optimization of crystal orientation for tribology (COCOT) technique at the sliding surface of after the friction measurement (while changing the load continuously) of metal oxide thin film such as ZnO and Cr₂O₃.

As a result, it is a correlation in the crystal optimization of the sliding surface and the counter ball materials had an effect on the friction coefficient of the thin films.

Friday Morning, October 23, 2015

Tribology Focus Topic

Room: 230B - Session TR+AS+BI+NS-FrM

Nanoscale Wear and Biotribology

Moderator: J. David Schall, Oakland University

8:20am TR+AS+BI+NS-FrM1 2D or not 2D? The Impact of Nanoscale Roughness and Substrate Interactions on the Tribological Properties of Graphene, James Batteas, Texas A&M University **INVITED**

Control of friction and wear is a ubiquitous challenge in numerous machined interfaced ranging from biomedical implants, to engines, to nano- and micro-scaled electromechanical systems (MEMS) devices. While lubricant additives are one approach to the development of surface coatings that can impede wear and reduce friction, in some cases, such approaches are simply not amenable and the development of ultrathin films are required. Recently, the robust mechanical properties of graphene has made it a material of interest as a means of modifying surface frictional properties. While graphene can readily adapt to surface structure on the atomic scale, when deposited on substrates with nanoscopic roughness (~10 – 20 nm rms as is common in many machined interfaces) a conformal coating cannot be fully formed due to competition between adhesion to substrate nanoscopic asperities and the bending strain of the graphene. This often leaves a mixture of supported and unsupported regions which respond differently to applied load and shear strain. Here we describe a combination of AFM nanomechanical and confocal Raman microspectroscopy studies of graphene on silica surfaces with controlled nanoscopic roughness to examine the how this impacts the frictional properties of graphene. Composite interfaces where graphene is supported on self-assembled alkylsilane monolayers will also be described along with the synergistic influence of such mixed interfaces on the frictional properties of the surface.

9:00am TR+AS+BI+NS-FrM3 Atomic-Scale Wear and Wear Reduction Mechanisms Elucidated by *In Situ* Approaches, R.W. Carpick, University of Pennsylvania, Tevis Jacobs, University of Pittsburgh **INVITED**

As technologies shrink to nanometer length scales, tribological interactions play an increasingly dominant role. A lack of fundamental insight into the origin of friction and wear at the nanoscale hinders the advancement of such technologies. Furthermore, macroscopic tribological applications often involve contact between nanostructured materials or at nanoscale asperities, due to surface roughness. Observing and understanding the nanoscale mechanisms at play is inhibited by the hidden nature of the buried interface and the challenge of performing observations at the nanometer scale. Recent advances in *in situ* methods are enabling tribological mechanisms at previously inaccessible interfaces to be studied with unprecedented resolution and sensitivity. We will discuss the application of two *in situ* experimental methods to develop new physical insights into tribological processes. The first approach addresses contact and wear phenomena at the atomic scale by *in situ* sliding in a transmission electron microscope [1], and the second addresses the generation of tribofilms from anti-wear additives using atomic force microscopy while immersed in additive-infused oil [2].

References:

- [1] Jacobs, T.D.B. and Carpick, R.W. "Nanoscale Wear as a Stress-Assisted Chemical Reaction," *Nature Nanotech.*, 8, 2013, 108-112.
- [2] Gosvami, N.N., Bares, J. A., Mangolini, F., Konicek, A.R., Yablon D.G., and R. W. Carpick. "Mechanisms of Antiwear Tribofilm Growth Revealed *In Situ* by Single Asperity Sliding Contacts," *Science*, 348, 2015, 102-106.

9:40am TR+AS+BI+NS-FrM5 Influence of Polysaccharide Conformation on Friction and Adhesion, Rowena Crockett, Empa, Switzerland **INVITED**

The friction behavior of the polysaccharide dextran has been investigated on surfaces coated with PLL-dextran brushes as well as randomly orientated covalently attached chains in aqueous solution. It was found that while there was a strong dependence of friction on load for the dextran brushes, the randomly orientated chains showed a more constant friction coefficient. Polysaccharides play an important role in bioadhesion, but are also used in the mining industry to assist in the separation of minerals. Despite the high adhesion associated with polysaccharides, investigations showing that they can be used to achieve low friction have also been reported. It was proposed that this transition from low friction to high adhesion is achieved as a result of hydrogen bonding. That is, as the load increases, water is forced out of

the contact and the number of hydrogen bonds between the polysaccharide and surface increase, inducing a transition to high adhesion.

10:20am TR+AS+BI+NS-FrM7 Tribological Rehydration of Cartilage: A New Insight into an Old Problem, David Burris, A.C. Moore, University of Delaware **INVITED**

The bulk of cartilage lubricity is due to its multi-phasic structure and the pressurization of interstitial fluid during loading. Unfortunately, the same pressure gradients that support load and lubricate the contact also drive fluid from the tissue over time. This observation led McCutchen, the researcher responsible for the discovery of this unusual lubrication mechanism, to ponder how the joint prevented the loss of interstitial fluid over time. He proposed that articulation intermittently exposes the loaded zone to the bath, thus allowing the tissue to imbibe fluid. It wasn't until 2008 that Caligaris and Ateshian showed that interstitial pressure can be maintained if the contact migrates across cartilage more quickly than the diffusive speed of fluid in the tissue; because the joint involves a migrating contact, they proposed that this discovery resolved any uncertainty about how the joint maintains lubrication. However, joints spend only a fraction of the day articulating and the majority of the day exuding fluid in static compression. If the migrating contact simply prevents the loss of fluid by moving quicker than the fluid can respond, we contend that it cannot explain long-term maintenance of interstitial fluid in the joint; there must be an active uptake mechanism in which articulation drives fluid back into the cartilage surface at a rate that outpaces exudation. This paper explores the origins of this mechanism and in doing so uncovers several phenomena that cannot be explained by existing theory. Contrary to existing theory, we show that stationary contacts are able to sustain fluid pressures in a manner similar to the migrating contact. Furthermore, we demonstrate active recovery of interstitial fluid in a stationary contact without exposing the loaded zone to the bath. The results demonstrate that sliding alone, even at sub-physiological speeds, forces fluid back into the cartilage at rates that outpace exudation rates. The results suggest that interstitial or weeping lubrication is the primary lubrication mechanism in the joint and that hydrodynamic effects prevent the loss of this mechanism in the long-term.

11:00am TR+AS+BI+NS-FrM9 Biomimetic Aspects of Lubrication with Polymer Brushes and Gels, C. Mathis, L. Isa, Nicholas Spencer, ETH Zürich, Switzerland

The role of the solvent is crucial in lubrication with polymer brushes and gels. Firstly it is important in maintaining the structure of the brush or gel layer in an unloaded state. Under loading, however, a new phenomenon becomes crucial, namely the Darcy flow of the solvent through the porous system. This aspect brings in a new set of properties to consider: the viscosity of the solvent determines the rate at which the solvent is forced through the porous network, and the sliding speed determines the extent to which the solvent is expelled from beneath the contact. The very act of expulsion of solvent is actually a process that bears a portion of the load. This phenomenon is well known in cartilage, and has been dubbed "fluid load support". This presentation will illustrate the ways in which this biomimetic approach can be utilized to protect polymer brushes and gels from wear, thus increasing their attractiveness as applicable lubricating systems, and will describe the approaches that can be used to quantify the process.

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Meyer, E.: TR+AS+NS+SS-ThA7, 5
Miki, H.: TR-ThP3, 7
Minfray, C.: TR+TF-ThM3, **3**
Moore, A.C.: TR+AS+BI+NS-FrM7, 9
Moseler, M.: TR+TF-ThM1, 3
Mulligan, C.P.: SE+AS+NS+TR-MoM9, 2

Music, D.: SE+AS+NS+TR-MoM2, 1

— O —

Ouyang, W.: TR+AS+NS+SS-ThA7, 5
Ozsdolay, B.D.: SE+AS+NS+TR-MoM9, 2

— P —

Patscheider, J.: SE+AS+NS+TR-MoM1, **1**
Pawlak, R.: TR+AS+NS+SS-ThA7, **5**
Petrov, I.: SE+AS+NS+TR-MoM3, 1
Poda, A.: TR+AS+NS+SS-ThA10, 6
Polcic, P.: SE+AS+NS+TR-MoM4, 1

— R —

Ramm, J.: SE+AS+NS+TR-MoM11, 2
Romero, P.: TR+TF-ThM1, 3
Ryan, K.E.: TR+AS+NS+SS-ThA9, 5

— S —

Samuelsson, M.: SE+AS+NS+TR-MoM8, 2
Sangiovanni, D.G.: SE+AS+NS+TR-MoM3,
1
Sasaki, M.: TR-ThP6, **8**
Schall, J.D.: TR+AS+NS+SS-ThA11, **6**
Schneider, J.M.: SE+AS+NS+TR-MoM2, **1**
Seidl, W.M.: SE+AS+NS+TR-MoM4, **1**
Sorenson, S.: TR+AS+NS+SS-ThA10, 6
Spencer, N.D.: TR+AS+BI+NS-FrM9, **9**
Stemmer, P.: TR+TF-ThM1, 3
Stoyanov, P.: TR+TF-ThM1, 3

— T —

Takagi, T.: TR-ThP3, 7
Takeno, T.: TR-ThP3, 7; TR-ThP4, 7
Tamura, J.: TR-ThP2, 7
Tengdelius, L.: SE+AS+NS+TR-MoM8, 2
Thiebaut, B.: TR+TF-ThM3, 3
Thompson, G.B.: SE+AS+NS+TR-MoM10,
2
Tosa, M.: TR-ThP6, 8
Tysoe, W.T.: TR+AS+NS+SS-ThA3, 5;
TR+TF-ThM12, 3

— U —

Urbakh, M.: TR+AS+NS+SS-ThA7, 5

— V —

Vacher, B.: TR+TF-ThM3, 3
Vummaneni, K.: TR+AS+NS+SS-ThA11, 6

— W —

Wählisch, F.C.: TR+TF-ThM1, 3
Wan, L.: SE+AS+NS+TR-MoM10, 2

— Y —

Ye, Z.: TR+AS+NS+SS-ThA4, **5**