

Tuesday Morning, October 29, 2013

Tribology Focus Topic

Room: 203 C - Session TR+SE-TuM

Low Friction Materials

Moderator: R. Bennewitz, INM - Leibniz-Institute for New Materials, D. Irving, North Carolina State University

8:20am **TR+SE-TuM2 Ultra Low Friction Surface Designed by Biomimetic Approach**, A. Takahara, Y. Higaki, M. Minn, M. Kobayashi, JST ERATO Takahara Soft Interfaces Project, Japan

The environmentally friendly biomimetic lubrication system was designed by tethering polyelectrolytes on the substrates with sufficiently high grafting density, so-called 'polymer brushes'. The hydrated brushes in aqueous media formed water lubrication layer to reduce friction coefficient, which is useful not only for artificial joints and bio-devices but also for various mechanical devices. Macroscopic tribological properties of polyelectrolyte brushes bearing ammonium salt, sulfonic acid, or phosphorylcholine unit were characterized by ball-on-plate type tribotester in the air, water, and salt solution through sliding a glass ball on the surface under a normal pressure of ca. 130MPa. The low friction coefficient below 0.02 was observed in polyelectrolyte brushes in water.

8:40am **TR+SE-TuM3 Thin Organic Monolayers on Inorganic Substrate: Ultra-Low Adhesion Friction and Wear Resistance Properties**, S.P. Pujari, H. Zuilhof, Wageningen University, Netherlands

Micro and Nano Electro Mechanical Systems (MEMS/NEMS) are considered to be an important technology for the development of several products in daily life such as electronics, medical devices, and packaging. Despite the tremendous progress in micro-fabrication, the development of highly robust surfaces, having ultra-low adhesion as well as friction and resistance against wear, is still a challenging subject of accomplishment. To this aim, new fluorine-containing terminal alkynes and alkenes were synthesized and self-assembled onto inorganic substrates (Si(111), SiC, and CrN) to obtain fluorine containing organic monolayers. The resultant covalently bound organic monolayers have similar surface properties as polytetrafluoroethylene (PTFE), but they are more stable than traditionally coated PTFE.

A combination of spectroscopic (XPS, IR), nanoscopic (AFM), and contact angle measurements shows that these monolayers were ordered and highly hydrophobic. Increasing the amount of fluorine on the alkyne precursor resulted in monolayers with a greatly reduced adhesion to silica probes, as well as an almost 5-fold decrease in the coefficient of friction on the surface. Overall, this yields a friction coefficient that is – to the best of our knowledge – lower than reported for any other thin organic monolayer. In addition, these monolayer-coated Si(111), SiC, and CrN surfaces perform superiorly over uncoated.^{1,2,3} For instance, at a normal force of ~7 μ N, the monolayer-coated samples are still nearly undamaged, while an uncoated Si surface displays already wear marks of 8 nm deep. The remarkable tribological properties make these fluorinated monolayers promising candidates for the development of robust, high-performance MEMS/NEMS systems.

1. Ultralow Adhesion and Friction of Fluoro-Hydro Alkyne-Derived Self-Assembled Monolayers on H-Terminated Si(111) Sidharam P. Pujari, Evan Spruijt, Martien A. Cohen Stuart, Cees J. M. van Rijn, Jos M. J. Paulusse, and Han Zuilhof Langmuir 2012 28 (51), 17690-17700.

2. Covalently Attached Organic Monolayers onto Silicon Carbide from 1-Alkynes: Molecular Structure and Tribological Properties Sidharam P. Pujari, Luc Scheres, Tobias Weidner, Joe E. Baio, Martien A. Cohen Stuart, Cees J. M. van Rijn, and Han Zuilhof Langmuir 2013 29 (12), 4019-4031.

3. Tribology and Stability of Organic Monolayers on CrN: A Comparison between Silane, Phosphonate, Alkene, and Alkyne Chemistries Sidharam P. Pujari, Li Yan, Regeling Remco, and Han Zuilhof Langmuir 2013 Submitted.

9:00am **TR+SE-TuM4 Mechanical and Tribological Behavior of Carbon-Based Coatings Sliding against PEEK Polymer Counterfaces**, E. Broitman, Linköping University, Sweden, S. Laino, University of Mar del Plata, Argentina, S. Schmidt, Linköping University, Sweden, P.M. Frontini, University of Mar del Plata, Argentina, L. Hultman, Linköping University, Sweden

Carbon-based coatings are known for their good mechanical and tribological properties. By tuning the C sp³-to-sp² bonding ratio and by alloying the carbon with other elements, it is possible to tailor hardness, elasticity, friction and wear resistance. Also, polyether-ether-ketone (PEEK)

polymers are increasingly used by the industry because of their corrosion resistance, mechanical stability, and self-lubricating ability. Huge amount of data regarding their individual interaction with steel counterfaces is available; however, very little information is found regarding the interaction of both materials.

In this work, we studied mechanical and tribological properties of carbon nitride (CN_x) and carbon fluoride (CF_x) coatings sliding against PEEK. The coatings were deposited on SKF3-steel balls by high power impulse magnetron sputtering (HiPIMS) using an industrial deposition system CemeCon CC800/9ML. CN_x was prepared at room temperature (RT) and 180 °C (HT) by reactive sputtering from C target in a N₂/Ar discharge at 400 mPa. CF_x was prepared at RT by reactive sputtering from a C target in a CF₄/Ar mixture at 400 mPa. PEEK 6 mm-thick unfilled plates were produced via injection molding (GATONE™ 5600). The friction and wear properties were measured by a pin-on-disk device using 6.35 mm-dia coated and uncoated balls against PEEK in dry slide at pressure contacts from 860 to 1240 GPa. Optical and scanning electron microscopy, and EDX spectroscopy were used to observe the wear tracks and analyze the presence and composition of transfer films. A triboindenter TI-950 (Hysitron) was used to measure hardness, elastic modulus, and roughness of the materials.

For uncoated steel counterfaces, the running-in friction (μ) takes place during the first 300 s, and shows peak values in the range 0.40-0.47. In the steady state, μ decreases to 0.30-0.35. The contact area shows big and deep scratches, oxidation, and no film transfer.

RT-CF_x and HT-CN_x coatings have similar behavior. Both have running-in periods of 1000 s, μ in the range 0.25-0.45, which increases in the steady state to 0.45-0.50. The microscopy reveals that the coatings have failed; big wear scars and the presence of film transfer are easily observed.

RT-CN_x coatings show the best performance. At the end of 1000 s running-in period μ is in the range 0.25-0.33, and increases slightly to 0.35-0.38 after 6000 s. The coatings show a very small wear scar and the presence of film transfer.

Our results demonstrate that a RT-CN_x coating on a steel counterface sliding against a PEEK polymer improves the tribological behavior of the sliding couple, and also is advantageous due to the coating chemical inertness.

9:20am **TR+SE-TuM5 Microstructure, Mechanical and Friction Behavior of Magnetron-sputtered V-C Coatings**, M. Stüber, P. Stoyanov, Karlsruhe Institute of Technology, Germany, E. Nold, Fraunhofer-Institute for Mechanics of Materials IWM, Germany, J. Schneider, H.J. Seifert, S. Ulrich, Karlsruhe Institute of Technology, Germany

Transition metal carbides exhibit superior mechanical and tribological properties at a wide range of environmental conditions and contact pressures. More recently, vanadium carbide coatings have been considered for a number of industrial applications (e.g. automotive components, cutting tools, ball bearings) due to their high corrosion resistance and mechanical stability at elevated temperatures. While some studies have provided significant new insights on deposition methods of vanadium carbides, the friction and wear mechanisms of these coatings have received little attention. The goal of this study is to link micro- to macroscale tribology in order to provide an excessive understanding of the sliding mechanisms of various vanadium carbide-based (VC_{1-x}) coatings. More generally, we are studying the influence of V:C ratio over a wide range of normal loads and contact areas. The coatings are prepared using non-reactive d.c. magnetron sputtering with a segmented VC/graphite target (i.e. target diameter of 75 mm, 500 W target power, substrate temperature < 150°C, and Ar gas pressure of 0.6 Pa). The resulting V:C ratios vary between 1:1 and 1:3. The microstructures of the as deposited coatings are characterized using X-ray diffraction and cross-sectional focused ion beam imaging, while elemental analysis is performed by means of X-ray photoelectron spectroscopy, electron probe microanalysis, and micro-Raman spectroscopy. Mechanical properties measurements show that the hardness (H) and the reduced modulus (E_r) of the coatings decrease with increasing the carbon concentration (i.e. H ranges between 15 and 33 GPa and E_r ranges between 239 and 391 GPa for the low and high vanadium concentration respectively), which correlates well with the adhesion results obtained from scratch tests. However, reciprocating micro- and macroscale tribological tests reveal higher friction values and increased wear with the high vanadium content coatings. This sliding behavior is attributed to differences in the third body formation and velocity accommodation modes, which are analyzed *ex situ* by means of XPS, micro-Raman spectroscopy and atomic force microscopy. The results obtained on the V:C coatings are compared to friction and sliding mechanisms in W:C systems.

9:40am **TR+SE-TuM6 Interaction of Stearic Acid with Iron-based Surfaces Coupling Experimental and Numerical Approaches for a Better Understanding of its Friction Behavior**, C. Minfray, C. Matta, S. Loehle, T. Le Mogne, J.M. Martin, Ecole Centrale de Lyon - LTDS, France, R. Iovine, Total, Solaize Research Center, France, Y. Obara, R. Miura, A. Miyamoto, Tohoku University, Japan

Organic friction modifiers (OFMs) have been used for many years in metallic contacts to reduce friction under mild conditions. The interest for such friction modifiers is still very strong because environmental regulations ask for slightly hazardous lubricant additives. It is proposed here to revisit adsorption and friction behavior of fatty acids by coupling experimental and computational chemistry approaches.

The OFM studied is stearic acid, used as pure additive or blended at 1%w in PAO4 synthetic base oil. The surfaces of interest are iron-based materials (including pure iron and iron oxides) as they can be encountered in a steel/steel contact under mild or severe friction conditions. Adsorption and friction properties of such systems were studied experimentally (friction, XPS and PM-IRRAS surface analyses) and adsorption kinetics was also studied by computational chemistry (UA-QCMD).

Adsorption experiments of stearic acid (gas form) on the different surfaces (gold, pure iron, iron oxides) were carried out in an environmentally controlled chamber for different adsorption time (10 min to 2 hours). This was followed by *in-situ* XPS analyses of the surfaces. XPS analyses results, especially the position of the C1s peak contribution from the carboxylic group, show differences depending on the nature of surfaces.

Computational chemistry study was also performed to investigate the *in vacuo* interaction of stearic acid molecules with the different model surfaces (pure iron, Fe₂O₃, and FeOOH). An ultra-accelerated quantum chemical MD (UA-QCMD) simulator has been used in order to deal with chemical reaction dynamics for large complex systems. Different models have been built starting with one single molecule up to self-assembled monolayer (SAM) on iron based surfaces at 50 °C. We found differences in adsorption energy (physisorption or chemisorption) depending on the kind of surface and regarding the presence of one single molecule or a SAM.

Eventually, friction experiments were carried out on a cylinder-on-flat reciprocating tribometer using samples in AISI52100 steel. The lubricant was stearic acid blended at 1%w in PAO4 and temperature was set to 50°C, 100°C and 150°C with an applied load of 50 N (corresponding to a maximum contact pressure of 320 MPa). After the tribological tests, PM-IRRAS analyses were conducted on the tribofilms. Results show the presence of stearic acid in the wear track as well as carboxylate forms.

All experimental and simulation results of both adsorption and friction experiments are discussed for a better understanding of complex interactions between stearic acid and iron-based surfaces.

10:40am **TR+SE-TuM9 Low Friction on Metals – Glide Planes and Molecular Lubricants**, R. Bennewitz, INM - Leibniz-Institute for New Materials, Germany **INVITED**

Nanotribological investigations of flat crystalline metal surfaces by means of friction force microscopy often result in extremely low friction coefficients. Experimental results indicate that the actual glide occurs between the low-indexed crystalline surface and a metallic neck, which forms by transfer of metal to the tip of the force microscope [1]. In the case of Au(111) surfaces, the apparently simple gliding process requires surfaces diffusion to operate, as evident from a failure of atomic friction mechanisms at lower temperatures [2]. Friction coefficients measured by friction force microscopy approach values known from macroscopic experiments when the tip plastically deforms the surface by scratching [3].

Electrochemical methods allow for an *in-situ* modification of surfaces by electrochemical oxidation, reduction, ion adsorption, or change in surface reconstruction. All of these influence nanometer-scale friction. For example, variation of the surface reconstruction reveals that friction increases with atomic-scale roughness [4]. Friction experiments in ionic liquids demonstrate that the preferential adsorption of anions or cations opens an opportunity for reversible switching of lubrication [5].

[1] N.N. Gosvami et al., Microscopic Friction Studies on Metal Surfaces, Tribol Lett 39 (2010) 19

[2] N.N. Gosvami et al., Ageing of a Microscopic Sliding Gold Contact at Low Temperatures, Phys. Rev. Lett. 107 (2011) 144303

[3] M. Mishra et al., Friction model for single-asperity elastic-plastic contacts, Phys. Rev. B 86 (2012) 045452

[4] F. Hausen et al., Surface structures and frictional properties of Au(100) in an electrochemical environment, Surf. Sci., 607 (2013) 20

[5] J. Sweeney et al., Control of Nanoscale Friction on Gold in an Ionic Liquid by a Potential-Dependent Ionic Lubricant Layer, Phys. Rev. Lett., 109 (2012) 155502

11:20am **TR+SE-TuM11 Few Layer Graphene as a Potential Solid Lubricant**, D. Berman, A. Erdemir, A.V. Sumant, Argonne National Laboratory

In recent years, reducing friction and wear-related mechanical failures in moving mechanical systems has gained increased attention due to their adverse impacts on efficiency, durability and environmental compatibility of such systems. Accordingly, search continues for novel materials, coatings, and lubricants (both liquid and solid) that can potentially reduce friction and wear. The majority of the existing solid lubricants (MoS₂ graphite, hexagonal boron nitride, etc.) requires full coverage, strong bonding, and relatively thick layers to provide lubricity to sliding interfaces. Moreover, their lifetimes and lubricating properties vary a great deal when operated under different environmental and tribological conditions. In this study, we demonstrate that a few layers of graphene are able to drastically reduce friction and wear of sliding steel surfaces under both inert and humid environments. The reduction in wear is as much as 4 orders of magnitude while friction is cut down by factors of 4 to 5. We believe that the anti-corrosion property of graphene coupled with its self-lubricating nature is mainly responsible for such remarkable friction and wear properties and the surface microscopic and spectroscopic studies confirm our hypothesis by confirming the presence of very thin and continuous graphene layers on both the ball and disk surfaces which were slid against one another under 1 N load in both humid air and dry nitrogen environments. In addition, we show that graphene application as well as re-application does not require any additional processing steps other than just applying a small amount of ethanol solution containing graphene on the surface of interest making this process simple, cost effective, and environmental friendly. Most of all, we found that unlike conventional solid lubricants which are all sensitive to environmental conditions, graphene provides low friction and wear regardless of the operating environment.

[1] D. Berman, A. Erdemir, A.V. Sumant: "Few layer graphene to reduce wear and friction on sliding steel surfaces". Carbon, 54, 454-459 (2013)

[2] D. Berman, A. Erdemir, A.V. Sumant: "Reduced Wear and Friction Enabled by Graphene Layers on Sliding Steel Surfaces in Dry Nitrogen", Carbon, in press. <http://dx.doi.org/10.1016/j.carbon.2013.03.006>

ACKNOWLEDGMENTS

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

11:40am **TR+SE-TuM12 Scaling of Structural Lubricity**, D. Dietzel, M. Feldmann, University of Giessen, Germany, U.D. Schwarz, Yale University, H. Fuchs, University of Muenster, Germany, A. Schirmeisen, University of Giessen, Germany

In an effort to reduce the friction between sliding components scientists and engineers have developed a multitude of lubrication schemes. One of the most intriguing concepts is referred to as 'structural lubricity', where at surfaces are thought to slide past each other virtually frictionless if their atomic structures are incommensurate, i.e. they do not match. Corresponding theories are based on sub-linear power laws for the area-dependence of friction in the structural lubricity regime, but this unusual scaling has never been observed so far. Here, we present experiments that quantify nanoparticle sliding resistance of amorphous antimony particles on crystalline graphite [1,2]. Our results confirm the predicted sub-linear scaling behavior for incommensurate, disordered interfaces, and allow a direct link between mesoscopic friction and atomic principles. Additionally, the case of crystalline incommensurate interfaces is investigated for gold crystals on graphite, pointing towards a more complex scaling behavior that accounts for particle shape and orientation. Our findings point towards a new route to engineer surfaces with unprecedented low friction on the basis of well-defined nanocontacts.

[1] A. Schirmeisen and U. D. Schwarz, ChemPhysChem 10 (2009) 2358

[2] D. Dietzel et al., Physical Review Letters 101 (2008) 125505

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