

## Tribology Focus Topic

### Room 10 - Session TR+AC+TF+VT-ThM

#### Lubricant, Coatings, and Biotribology

Moderator: J. David Schall, Oakland University

#### 8:00am TR+AC+TF+VT-ThM-1 Superlubricity of Hard Compliant Carbon Coatings with Green Lubricants: Role of Surface Chemistry and Structural Changes, *Maria-Isabel De Barros Bouchet*, Ecole Centrale de Lyon - LTDS, France

INVITED

Reduction of energy loss by mechanical friction has been strongly required in recent years for improving fuel efficiency especially for automotive engine. Even at a modest rate, it is of primary importance to reduce parasitic energy losses and provide environmental sustainability. An approach to achieve this target is the development of new lubrication technologies, combining new lubricant formulations and cutting-edge coatings transferable to industrial applications. Since superhard carbon material like tetrahedral amorphous carbon (ta-C) and Nano-Crystalline Diamond (NCD) coatings combine both crucial properties, high hardness with an ultra-smooth surface roughness, they have attracted a growing interest in the last decade. While the friction coefficient is generally extremely high under ultra high vacuum conditions, in the earlier years we have discovered the ability of these coatings to be lubricated by selected biodegradable green molecules like fatty acids, glycerol mono-oleate GMO and polyols, as well as their mixture with synthetic base oil such as Poly-Alpha Olefines (PAO). Some of these compounds are able to lubricate ta-C and NCD coatings with a friction coefficient below 0.01 (so-called superlubricity) in thin-film EHL/mixed regime and below 0.03 in severe boundary regime without significant wear<sup>1</sup>. As this case of superlow friction is extremely promising for many applications fields, the related mechanism has been investigated and a special attention has been paid to the surface chemistry and structural changes of the carbon coatings. By coupling advanced extreme surface analyses (PES and XANES), we show that the mechanism of friction reduction is related to the tribo-formation of quasi-2D planar graphene-like structures at the top of the colliding asperities (thickness about 1 nm). Eventually, the graphene can be slightly oxidized by the OH-groups coming from the tribo-decomposition of the lubricant molecules trapped between asperities. Moreover, the rubbed sub-surface is enriched with sp<sup>2</sup>-hybridized carbon, such as in a soft a-C material, during the friction<sup>2</sup>. These strong structural changes certainly ease the tribochemical-formation of the carbon rings present in the graphene-like structure as pointed out by atomistic computer simulations.

1. M. Kano, J. M. Martin, K. Yoshida, M.I. De Barros Bouchet, *Friction*, 2 (2) (2014) 156.

2. M.I. De Barros Bouchet, J.M. Martin, J. Avila, M. Kano, K. Yoshida, T. Tsuruda, S. Bai, Y. Higuchi, N.i Ozawa, M. Kubo and M. C. Asensio, *Scientific Reports*, 2017 (DOI: 10.1038/srep46394).

#### 8:40am TR+AC+TF+VT-ThM-3 Role of Deuterium and Hydrogen in the Physical Understanding of Nano-friction in a-C:H/D Thin Films, *F Echeverrigaray, S Sales de Mello, A Michels*, UCS, Brazil; *F Alvarez*, UNICAMP, Brazil; *Carlos Figueroa*, UCS, Brazil

The friction phenomenon is a complex manifestation of the nature. In spite of phenomenological laws can describe the friction force at different scales, the fundamental physical understandings of such a phenomenon do not have consensus. Phenomena such as phononic, electronic, magnetic, and also electrostatic effects and models were developed in order to explain the meta- and nano-friction behavior of materials. In this work, we report the friction behavior of a diamond spherical dome sliding on different amorphous carbon thin films containing different amounts of hydrogen and/or deuterium inspecting at the meta-nanoscale indentation. Two important situation are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film bulk, the friction coefficient decreases for increasing *deuterium* included in the carbon underneath structure. Secondly, for samples where hydrogen content is increased on the surface, the friction coefficient decreases with the increasing of the ratio H/C at the surface. In this paper, we discuss two different physical mechanisms describing these peculiar experimental results: dissipation effects associated with phonon coupling and van der Waals forces contributions coexisting and determining the friction behaviour of a-C:H/D for the cited studied situations.

#### 9:00am TR+AC+TF+VT-ThM-4 Imaging X-Ray Absorption Spectroscopic Investigation of the Mechanisms Behind the Environmental Dependence of the Tribological Properties of Amorphous Carbon Surfaces, *Filippo Mangolini*, University of Leeds, UK; *M Koshigan*, Ecole Polytechnique Montréal, Canada; *M Van Benthem, J Ohlhausen*, Sandia National Laboratories; *B McClimon, J Hilbert*, University of Pennsylvania; *J Fontaine*, Ecole Centrale de Lyon, France; *R Carpick*, University of Pennsylvania

Among the variants of diamond-like carbon films developed for the ever-increasing performance and durability requirements of tribo-mechanical applications, silicon oxide-containing hydrogenated amorphous carbon (a-C:H:Si:O) is of interest as it exhibits good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon, and higher thermo-oxidative stability. However, the scientific basis for this improved behavior is not established. In this work, we develop a fundamental understanding of the structural transformations occurring in a-C:H:Si:O when sliding against steel in different environments (from high vacuum to controlled hydrogen and oxygen pressures). The results of tribological experiments revealed that upon increasing the oxygen pressure in the experimental chamber from 10 mbar to 1000 mbar, the coefficient of friction increased from 0.02±0.01 to 0.06±0.01, whereas upon increasing the hydrogen pressure from 50 mbar to 2000 mbar, the coefficient of friction decreased from 0.08±0.01 to 0.02±0.01. The subsequent near edge X-ray absorption fine structure (NEXAFS) spectroscopic measurements and X-ray photoelectron spectroscopy (XPS) analyses provided insights into the structural transformations and chemical reactions occurring in a-C:H:Si:O upon sliding. Independently of the gas, a stress-induced conversion from sp<sup>3</sup>- to sp<sup>2</sup>-bonded (disordered) C-C bonds occurs. When sliding in hydrogen, the newly-generated, strained sp<sup>2</sup> carbon layer reacts with hydrogen molecules to form a hydrogenated amorphous carbon interfacial material. Upon increasing the hydrogen pressure, the fraction of C-H bonds increases in the near-surface region of the wear tracks formed on a-C:H:Si:O. This is proposed to progressively lower the shear strength of the material at the sliding interface, thus resulting in a decrease of friction with hydrogen pressure. When sliding in oxygen, the dissociative reaction of oxygen molecules with strained sp<sup>2</sup> C-C bonds leads to the formation of C=O groups. Additionally, increasing the oxygen pressure during tribological testing leads to an increase in oxygen concentration in the near-surface region of a-C:H:Si:O together with an increase in the fraction of Si atoms in high oxidation states. These surface chemical changes and structural transformations are proposed to increase friction with oxygen pressure by progressively increasing the shear strength of the material generated at the sliding interface.

#### 9:20am TR+AC+TF+VT-ThM-5 Structure Evolution in Tribological Interfaces Studied by Multilayer Model Alloys, *Martin Dienwiebel, E Cihan*, Karlsruhe Institute for Technology (KIT), Germany

INVITED

During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called "third body" or "tribomaterial" forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-steady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS. During sliding of surfaces the near surfaces undergo significant changes in terms of topography, composition and microstructure and a so-called "third body" or "tribomaterial" forms which differs strongly from the bulk materials in terms of topography, composition and microstructure. Initially we use multilayer model alloys of an Au/Ni layer system to study effects of grain size on steady-steady friction by varying the layer spacing and the number of layers. Experiments are performed in a UHV microtribometer, the analysis of microstructure before and after tribological stressing is done by FIB and STEM and the chemistry is investigated by XPS.

#### 11:00am TR+AC+TF+VT-ThM-10 Carbon, Carbon Everywhere, from Catalysts to Hip Implants, *Laurence Marks*, Northwestern University

INVITED

Friction is a pervasive problem, by some estimates consuming about 5% of the GDP of the economies of the developed world, and a recent analysis has indicated that about one third of the fuel energy in automobiles goes to overcoming frictional losses. While the importance of minimizing friction can be traced back at least as far as the tomb of Tehuti-Hetep, circa 1880 B.C, where a man can be seen pouring a lubricant to assist moving a statue, there are still many unknowns in the field of tribology which encompasses

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friction as well as other critical processes such as wear and lubrication. For many of the phenomena in tribology there are still numerous unknowns. When it comes to biological systems most work to date has assumed that different mechanisms are taking place than occur for inorganic systems. While there are differences, there are also significant similarities particularly in implants when inorganic and biological meet. We have recently shown that for metal implants in-vivo the same type of graphitic materials that appear in many areas ranging from heterogeneous catalysis to oil lubrication are present. Beyond just lubrication, corrosion of these materials is not special to biological systems, but has strong similarities to established factors such as grain boundary precipitation and a significant role for molybdenum as reducing the occurrence of breakdown of the protective oxide film via complex processes involving solute trapping. These and related recent results will be described.

11:40am **TR+AC+TF+VT-ThM-12 Tribology of Cellular Interfaces, *Angela Pitenis, J Urueña, S Hart, T Hormel, C O'Bryan, S Marshall, K Schulze, P Levings, T Angelini, W Sawyer***, University of Florida

**INVITED**

Human health, mobility, and quality of life critically hinge on the body's ability to provide adequate lubrication between most contacting and sliding biological interfaces. Soft, aqueous, and mucinated biopolymer networks lining all moist epithelia enable the body to provide lubricity over a wide range of contact pressures and sliding speeds. The exquisite slipperiness and softness of biological sliding interfaces present significant experimental challenges for fundamental studies on their tribological performance. Physiological contact pressure conditions must be matched in in vivo, ex vivo, and in vitro studies that aim to acquire physiologically-relevant friction measurements. While biotribological investigations using living cells, cell layers, and tissues necessitate low contact pressure measurements, such studies frequently rely on the application of low forces to achieve accommodating contact pressures (kPa range), and traditional methods can decrease the contact area below a physiologically-relevant threshold. The softness of a cell layer ( $E \sim 10$  kPa) provides an order-of-magnitude estimate for the amount of mechanical pressure that may be applied to cells during tribological testing; contact pressures about 5 kPa and shear stresses in excess of 200 Pa are sufficient to wreak significant damage to a cell layer. Recently, direct contact tribological experiments on a living cell layer without incurring any measurable cell death in the sliding path has become possible through the application of a soft, thin, spherically-capped membrane hydrogel probe. With this experimental configuration, in vitro tribological experiments were performed against a monolayer of mucin-producing human corneal epithelial cells (hTCEpi) for 10,000 reciprocating cycles at physiologically-relevant contact pressures and challenging sliding speeds. The gel-cell sliding interface under applied normal loads of  $\sim 200$   $\mu$ N resulted in measured friction coefficients of  $\mu \sim 0.06$  and achieved shear stresses on the order of 60 Pa, which is below the critical shear stress for inducing cell death; excellent cell survival rates ( $\sim 99.8\%$ ) were measured after extended duration tribological experimentation.

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