Tribology and Mechanical Behavior of Coatings and Engineered Surfaces

Room San Diego - Session E1-2-ThA

Friction, Wear, Lubrication Effects, and Modeling III

Moderators: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Carsten Gachot**, Vienna University of Technology, **Tomas Polcar**, Czech Technical University in Prague, Czech Republic

1:40pm **E1-2-ThA-2 Exploring the Nanomechanical Properties of Transition Metal Dichalcogenides using Density Functional Theory**, ***Benjamin Irving***, *P Nicolini,* Czech Technical University in Prague, Czech Republic*; T Polcar,* University of Southampton, UK

Low-dimensional materials have recently attracted immense interest due to their fascinating physical properties and potential for application in diverse fields such as (opto)electronics, energy harvesting and dry lubrication. Transition metal dichalcogenides (TMDs), of general form MX_2 (M = Mo, W; X = S, Se, Te), are posited as being some of the best solid-state lubricants currently available. They exhibit a lamellar structure in which covalently-bonded MX_2 layers are held together by weak van der Waals forces, which, together with very low ideal shear strengths (i.e., the maximum load applied parallel to the face of the material that can be resisted prior to the onset of sliding) render them suitable for use in the mitigation of friction. Our extensive density functional calculations highlight the dependence of important nanomechanical properties of TMDs on their chemical composition and bilayer orientation (sliding direction); in particular, our calculations underscore the intrinsic relationship between incommensurate layers and superlubricity.[1] Our latest calculations have focused on TMD-based van der Waals heterostructures (e.g. WS_2 sliding on MoS_2), with the aim of formalizing the relationship between fundamental quantum chemical parameters of the constituent elements and the nanomechanical properties of the material. Ultimately, we wish to improve the predictive capabilities of *in silico* methods during the material design process.

[1] B. Irving, P. Nicolini and T. Polcar, *Nanoscale*, 2017, 9, 5597-5607

2:00pm **E1-2-ThA-3 Mechanics, Materials, and Design Problems in Medical Device Technology and Information Storage**, ***Frank E. Talke***, University of California, San Diego, USA **INVITED**

Current research in medical device technology and information storage at the Center for Memory and Recording Research will be discussed with emphasis on mechanics and materials issues.

In the area of medical device technology, the design of a minaturized pressure sensor for implantation in the eye will be discussed to help in the understanding and treatment of glaucoma. The sensor is a passive devise, based on interferometry, and does not require a power source to be implanted in the eye. Another materials related topic is concerned with the design and development of a 3-d printed disposable endoscope to avoid spread of antibiotic resistant superbugs, a serious medical infection and contamination problem. Materials and manufacturing isues will be discussed. In the area of information storage on hard disks, mechanics and materials problems will be discussed that are encountered during flying of a magnetic recording head at a head disk separation on the order of 1 nano meter. In order to increase the storage density further, the flying height of the read/write element must be reduced to less than 1 nm, and the track width to less than 20 nm (500,000 tracks per inch). To achieve sub-nano meter head disk spacing, the flying height of the head disk interface is controlled using the so-called thermal flying height control technology. In this approach, a controlled thermal deformation of the slider is achieved in the read write area of the slider by energizing a miniaturized resistance heater, causing a reduction in the flying height of the read write element to the order of 1 nm. Voltage biasing will be descussed to minimize materials transfer at the head disk interface. Another approach to achieve higher storage densities is the use of heat assisted magnetic recording where the magnetic medium is heated up to the Curie temperature just prior to recording using a laser beam. Current and future problems in the mechanics and materials area of information storage on hard disks will be presented.

2:40pm **E1-2-ThA-5 Frictional Anisotropy of MoS_2 During Sliding: A Molecular Dynamics Study on the Atomistic Understanding of Frictional Mechanisms**, ***Victor Claerbout***, *P Nicolini,* Czech Technical University in Prague, Czech Republic

The tribological characteristics of molybdenum disulfide (MoS_2) as solid lubricants are well-described starting from the discovery of the super low friction behavior of MoS_2 by Martin et al. in 1993 [1]. However, despite numerous experimental and theoretical efforts, a fundamental understanding of the frictional mechanisms at the nanoscale is lacking.

In this contribution, we aim to elucidate the phenomena taking place at the nanoscale when several layers of MoS_2 slide atop another. In particular, by means of molecular dynamics simulations, we studied the effect of rotational sliding anisotropy [2] (i.e., the changing frictional behavior upon introducing a misfit angle between the layers or by varying the relative sliding angle) on the energy dissipation due to friction. We simulated different sliding conditions (varying e.g. normal load) in order to highlight their effect on the lubricating properties. These results will help on the one hand to identify the fundamental mechanisms that govern friction at an atomistic level, as well as providing guidelines for the design of novel layered materials with improved tribological properties.

[1] J.M. Martin et al., Phys. Rev. B, 48, 10583(R) (1993). [2] Onodera et al., J. Phys. Chem. B, 114, 15832 (2010).

3:00pm **E1-2-ThA-6 Effect of the Presence of Small Molecules on the Entangled Electronic and Dynamic Features in Layered MX_2 Transition Metal Dichalcogenides: Systematic Quantum Mechanic Ab Initio Smulations**, ***Jamil Missaoui***, *A Cammarata,* Czech Technical University in Prague, Czech Republic

Great attention has been paid to the problem of friction in materials because of its enormous practical and technological importance in a vast range of scales including nanomaterials. In particular, control of intrinsic friction is mandatory in nano-electro mechanical devices (NEMS), mainly based on multi-layered Transition Metal Dichalcogenides (TMD). In this perspective, the present work is aimed to study the entangled electronic and dynamic features of selected TMD in the presence of small molecules of contaminants from the atmosphere.

We conducted systematic quantum mechanic ab initio simulations on prototypical layered MX2 (M = transition metal, X = chalcogen anion) TMDs with hexagonal structure in the presence of small molecules in the inter-layer region. We combined group theoretical analysis and phonon band structure calculations with the characterization of the electronic features using non-standard methods such us orbital polarization and the recently formulated bond covalency and cophonicity analyses. We will then study how the vibrational frequencies of the pristine material are shifted in the presence of the contaminant, by relating such shift to the nanoscale friction between adjacent MX2 layers. Finally, we will present guidelines on how to engineer intrinsic friction in TMDs at the atomic level.

Thanks to the generality of the used simulation protocol, the outcomes of the present study can be exploited to harness the macroscopic response of electro-dynamic entangled systems; the latter find application in fields beyond tribology based on physical phenomena like metal-insulator transition, second harmonic generation, and exciton effects (optoelectronics), among others.

3:20pm **E1-2-ThA-7 Nanoscale Frictional Properties of Ordered and Disordered MoS_2**, *E Serpini, A Rota,* Università di Modena e Reggio Emilia, Italy*; S Valeri,* Istituto CNR-NANO S3, Italy*; E Ukraintsev,* Academy of Science of the Czech Republic, Czech Republic*; B Rezek,* Czech Technical University in Prague, Czech Republic*; T Polcar,* University of Southampton, UK*;* ***Paolo Nicolini***, Czech Technical University in Prague, Czech Republic

One third of energy produced by industrial countries is lost as friction. High wear caused by friction means approx. 35% of industrial production is used to replace degraded products, whilst causing the breakdown of machinery, resulting in safety risks and environmental pollution. Controlling and reducing friction is a fundamental step in attaining the sustainable development of our society, as detailed in the Brundtland report. In this contribution I will present the results of a study on the nanometric sliding of molybdenum disulfide against itself both from the experimental and from the computational point of view. The differences between ordered material (single crystal) and disordered material (sputtered coating) were investigated. Tribological experiments were performed using Lateral Force Microscopy. Atomic Force Microscopy tips modified by sputter deposition of molybdenum disulfide were used for the first time. This feature opened up the possibility for close comparison with classical molecular dynamics

simulations. In both cases, the coefficient of friction for the ordered system in inert conditions was found to be smaller than for disordered system. This result demonstrates the impact of morphology at the nanoscale and highlights the importance of molecular dynamics as a diagnostic and predictive tool in nano-friction. Furthermore, experiments show that the effects of the environment on nanoscale friction are reduced with respect to the macroscale case. These findings can expedite the process of fabricating molybdenum disulfide-based coatings with superior tribological properties, with the ultimate aim of reducing the energy dissipation due to friction.

3:40pm **E1-2-ThA-8 Electrical Tuning of Vibrational Modes in Transition Metal Dichalcogenides***, **Florian Belviso**,* Advanced Material Group, Czech Technical University in Prague, Czech Republic

Transition metal dichalcogenides (TMDs) have been shown to be a promising source of applications in multiple fields, such as nanoelectronics, photonics, sensing, energy storage, and opto-electronics.

We investigated the atomic scale tribological properties of TMDs, using ab-initio techniques. Such compounds are formed by triatomic layers with MX2 stoichiometry (M: transition metal cation, X: chalcogen anion) held together by van der Waals forces.

We considered 6 prototypical MX2 TMDs (M=Mo, W; X=S, Se, Te) with hexagonal P63/mmc symmetry, focusing on how specific phonon modes contribute to their intrinsic friction. Within the DFT framework, we described the exchange-correlation interaction energy by means of the PBE functional, including long range dispersion interactions in the Grimme formulation (DFT-D3 van der Waals).

We identified and disentangled the electro-structural features that determine the intra- and inter-layer motions affecting the intrinsic friction by means of electro-structural descriptors such as orbital polarization, bond covalency and cophonicity.[1]

We show how the phonon modes affecting the intrinsic friction can be adjusted by means of an external electrostatic field. In this way, the electric field turns out to be a knob to control the intrinsic friction.

We also show the structural distortion induced by some various cation substitution.

The presented outcomes are a step forward in the development of layer exfoliation and manipulation methods, which are fundamental for the production of TMD-based optoelectronical devices and nanoelectromechanical systems.

[1] Cammarata, Antonio and Polcar, Tomas (2015) DOI 10.1039/C5RA24837J

4:00pm **E1-2-ThA-9 On the In-situ Formation of Transition Metal Disulphides in Lubricated WN or WC Coating Contacts***, **Bernhard Kohlhauser**,* TU Wien, Institute of Materials Science and Technology, Austria*; M Rodríguez Ripoll,* AC2T research GmbH, Austria*; H Riedl, C Koller, N Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; G Ramirez, A Erdemir,* Argonne National Laboratory, USA*; C Gachot,* TU Wien, Institute for Engineering Design and Logistics Engineering, Austria*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

In recent years, solid lubricants such as transition metal dichalcogenides have attracted attention in form of nanoparticle additives for conventional oil-based lubricants. Those nanoparticle additives entail several disadvantages, including the need to compose a stable dispersion. An in-situ formation of lubricating solid compounds via a tribochemical reaction path between a coating and conventional S containing extreme pressure additives could prove to be much more advantageous.

While MoS_2 can easily be formed on metallic Mo surfaces, the conditions in lubricated tungsten contacts are not severe enough to produce WS_2. A new generation of functional coatings is helping to overcome this energetic barrier, which is linked to the formation of intermediate tungsten oxide phases. WN and WC based coatings are able to facilitate this in-situ formation of WS_2 and combine excellent mechanical properties with an optimization of friction and wear via the formation of a low friction tribofilms.

The coatings were prepared by magnetron sputtering and their mechanical, structural and chemical properties were investigated with nanoindentation, energy dispersive x-ray spectroscopy, X-ray diffraction, and transmission electron microscopy.

The tribofilms, resulting from lubricated pin on disk tests, were studied in detail and consist of a fraction of amorphous WS_2 and C based oil derived debris, but also of nanocrystalline WS_2 domains along the surface. These lubricating WS_2 sheets lead to a low coefficient of friction around 0.05 and the tribofilm protects coating and counter body from any wear, even after 100 h of testing.

4:20pm **E1-2-ThA-10 Tribological Investigations of Coated Roller Finger Followers using Application Oriented Valve Train Test***, **Ricardo H. Brugnara**, E Schulz, L Dobrenizki, N Bagcivan, C Geers,* Schaeffler AG, Germany

Due to the increasing demand to reduce emissions, friction reduction is an important topic in the automotive industry. Among the various possibilities to reduce mechanical friction, the usage of a low-viscosity lubricant in the engine is one option. Thus, continuously lower viscosity lubricants are being developed and offered on the market. Other approach is to adjust the properties of the components using surface technology in order to minimize friction losses and meet the more stringent environmental requirements. Coated components using thin film vacuum technology offers the possibility to reduce CO_2-emissions and fuel consumption of the vehicle by mandatory lightweight design, reducing friction losses in tribological contacts. In present study, uncoated and DLC (Diamond-like Carbon) coated roller finger followers were investigated for the first time using application oriented driven cylinder head tests with 0W20 low viscosity oil under relevant conditions. The results show a significant friction reduction in rolling contact with coated cam rollers compared to the uncoated refence.

4:40pm **E1-2-ThA-11 Physical Understanding to Nano-friction of C:H/D Thin Films: Coupling Mechanism by Atomic-scale Vibration Damping***, F Echeverrigaray, S de Mello,* Universidade de Caxias do Sul, Brazil*; F Alvarez,* Universidade Estadual de Campinas, Brazil*; A Michels, **Carlos Figueroa**,* Universidade de Caxias do Sul, Brazil

Friction phenomenon is a complex manifestation of the nature originated in energy dissipation events owing to the lost work of non-conservative forces. In spite of phenomenological laws describe the friction force at different scales, the fundamental physical understanding of such a phenomenon still did not achieve consensus. Phononic, electronic, magnetic and electrostatic effects were considered and theoretical models were developed in order to explain the nano-friction behavior of materials. The surface structure of deuterated and/or hydrogenated amorphous carbon (a-C:D/H) thin films in air, which plays an important role in nanoscale friction research, is constituted by deuterium and/or hydrogen terminated bonds and physisorbed oxygen, nitrogen and water molecules. There are well established models to explain the tribological behavior of carbon-based thin films in different atmospheres, however, the fundamental physical mechanism at the interfacial atomic-scale remains open. In this study, we report the friction forces at the nanoscale on amorphous carbon thin films with different [D]/[C] and [H]/[C] contents by nanoindentation followed of unidirectional sliding (NUS) and friction force microscopy (FFM). Two different experimental setups are reported. Firstly, for samples where hydrogen was replaced by deuterium in the thin film the friction force decreases with the increasing of deuterium content, this behavior is associated to a fononic phenomenon owing to isotope effect. Secondly, for samples where hydrogen content is increased at the surface, the friction force decreases with the increasing of the ratio H/C at the surface, which is explored by an electronic interaction analysis. We discuss these two different frictional damping mechanisms by dissipation effects associated with phonon/van der Waals (vdW) coupling by sliding interface polarizability.

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