## Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
### Room Town & Country B - Session E1-2-WeM
### Friction, Wear, Lubrication Effects, and Modeling II

**Moderators: Noora Manninen**, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein, **Andreas Rosenkranz**, Andreas Rosenkranz, Universidad de Chile

8:00am **E1-2-WeM-1 MXenes: A Model Material for Solid Lubricants**, ***Philipp Grützmacher (philipp.gruetzmacher@tuwien.ac.at)***, Vienna University of Technology, Austria; *C. Gachot,* TU Wien, Austria; *S. Suarez,* Saarland University, Germany; *A. Rosenkranz,* University of Chile

Typically, liquid lubricants are introduced between rubbing surfaces in machine elements and mechanical systems, thus minimizing friction and wear. Diminishing oil resources, the need for ever lower frictional losses, as well as higher demands on the lubricants in terms of resistance against extreme conditions such as high temperatures or low environmental pressures push liquid lubricants to their limits. Therefore, focus turns to solid lubricants. Two-dimensional materials with graphene-like structure have gained remarkable attention, because they have demonstrated excellent tribological properties, even when applying only one or a few atomic layers of the material to the contact zone. There are even several studies, which reported friction coefficients (COFs) below 0.01 and, therefore, superlubricious performance. However, the mechanisms of friction reduction and the influence of the materials' structural and mechanical properties on the latter are still not well understood. One of the newest members of the class of 2D materials are so-called MXene, which were discovered in 2011. MXenes, which are 2D transition metal carbides, nitrides, and carbonitrides, with layers a few atoms thick and, thus, represent an entire class of 2D materials. Single flakes of MXene can be described by the chemical formula $M_{n+1}X_nT_x$ (n = 1 to 4). MXenes offer an extreme versatility in terms of composition, layer thickness, and surface terminations. This makes them ideal model materials to study the influence of theses parameters on tribological behaviour. Despite a still small number of publications on the tribological prosperities of MXenes the field is rapidly growing. First studies have already shown very promising results in terms of wear resistance and friction reduction, even reaching the superlubric regime.

8:20am **E1-2-WeM-2 Structural and Nanomechanical Properties of Manganese Phosphate Coatings**, ***Esteban Broitman (esteban.daniel.broitman@skf.com)***, *Y. Kadin, P. Andric,* SKF B.V. - Research and Technology Development (RTD), Netherlands; *V. Ott, M. Stüber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Manganese Phosphate (MnPh) coatings are nowadays used in rolling bearings applications due to their advantages such as wear resistance, corrosion resistance, improved fatigue life, and anti-fretting performance.

In this work, MnPh coatings with a thickness of about 5 µm were deposited by a chemical conversion process. AISI 52100 steel substrates were placed in a phosphoric acid bath, where an acid-metal reaction took place locally depleting the hydronium ($H_3O^+$) ions, raising the pH, and causing a manganese phosphate dissolved salt to fall out of the solution and be precipitated onto the steel surface. Analysis of the surface microstructure and composition of the coatings by X-ray diffraction (XRD), Optical Microscopy (OM), Scanning Electron Microscopy (SEM), and Electron Dispersion Spectroscopy (EDS) has revealed a polycrystalline coating with prismatic-shaped crystals, and about 20% content of Mn. The nanomechanical properties, studied by nanoindentation, exhibit a surface with hardness $H_{IT}$ ~ 1 GPa and Young's modulus $E_{IT}$ ~ 50 GPa. A nanoindentation statistical method was used to obtain $H_{IT}$ and $E_{IT}$ value frequencies over a large area of the coating. We demonstrate that the nanoindentation frequency peaks can be correlated to the coating crystalline orientation revealed by XRD.

8:40am **E1-2-WeM-3 Nanoscale Materials for Macroscale Applications: Zero-Friction and Zero-Wear Carbon Films (Virtual Presentation)**, ***Diana Berman (diana.berman@unt.edu)***, University of North Texas, USA **INVITED**

Friction and wear-related failures remain the greatest problems in today's moving mechanical components, from microelectromechanical devices to automotive assemblies and to biological systems. The critical need to reduce and eliminate the tribological failures constitutes the necessity for continuous search of novel materials and lubrication solutions. In this presentation, we overview recent advances in establishing the fundamental understanding of materials interactions at sliding interfaces and use this knowledge as a guide to developing nanomaterials solutions that enhance reliability and efficiency of tribological systems. We evaluate tribological performance of carbon nanomaterials and demonstrate realization of superlubricity regime at macroscale in carbon-based systems. To extend the lifetime of the tribological materials, we demonstrate tribochemically-driven self-replenishment of carbon-based materials inside the contact interfaces, thus, in addition to the superlubricity, enabling a zero-wear sliding regime.

Overall, the findings have not only allowed us to solve some long-standing puzzles, but could also open a new avenue for the development of new concepts and design strategies for next generation of tribologically efficient materials systems.

9:20am **E1-2-WeM-5 Self Lubricant TiSiN/TiAgN Coatings: Room and High Temperature Tribological Behavior**, *F. Fernandes, A. Al-Rjoub,* University of Coimbra, Portugal; ***Albano Cavaleiro (albano.cavaleiro@dem.uc.pt)***, Instituto Pedro Nunes, Portugal

Increasing requirements on high speed and dry cutting applications open up new demands on the quality of cutting tool materials. This is particularly important in the aerospace and automotive industries where easy and premature degradation of the cutting tools is observed during the machining of hard-to-cut materials. Several solutions have been tried to improve the machinability of these alloys, being the application of thin solid films by sputtering techniques the most promising. However, so far, such solution does not yet allow meet the need for high speed machining and green manufacturing required for machining those materials. In this study, novel multilayered TiSiN/Ti(Ag)N with different Ag concentrations were developed with potential to protect the surface of machining tools under the absence of lubrication. In order to estimate their wear resistance at high temperature the coatings were tribologically tested in a pin-on-disc equipment at different temperatures against two different counterparts (Al2O3 and TiAl6V4 balls). For Al2O3 balls, the hardness and reduced modulus determine the tribological performance of the coatings for tests conducted at room temperature (RT). At 550 ºC, the TiSiN/TiN coating failed, whereas the Ag-containing coating performed better due to the presence of Ag in the contact, which decreased the shear stress and, consequently, the friction. For tests against TiAl6V4 balls, the Ag-containing coating was always better than the TiSiN/TiN one. At 550 C, Ag in the wear track prevented the adhesion of the oxidized Ti-alloy wear debris in the contact, favoring the adhesion of wear debris from the coating to both the coating and counterpart surfaces. No wear could be measured for the 700 ºC tests for both coatings due to different reasons: (i) the presence of oxidized adhered material from the ball to the reference TiSiN/TiN coating surface protected from wear and (ii) the presence of Ag-agglomerated particles decreased the friction and minimized the adhesion wear of the counterpart for the TiSiN/TiN(Ag) coating.

9:40am **E1-2-WeM-6 Design and Tribological Characterization of Self-Lubricating Alloys for Laser Deposition Processes**, *H. Torres,* AC2T Research GmbH, Austria; ***Carsten Gachot (carsten.gachot@tuwien.ac.at)***, TU Wien, Austria; *M. Rodriguez Ripoll,* AC2T Research GmbH, Austria

This work presents the development of self-lubricating metallic alloys for laser deposition processes. Laser deposition processes such as laser metal deposition or direct energy deposition are additive manufacturing techniques that offer a great flexibility and efficiency compared to traditional subtractive manufacturing processes. However, the extreme thermal conditions during deposition and the rapid cooling times pose great challenges in the alloy design. This work illustrates these challenges using metals, such as iron and nickel-base alloys, incorporating lubricious soft metals and metal sulfides.

The microstructure and phase composition of the deposited self-lubricating alloys are characterized using X-ray diffraction, scanning and transmission electron microscopy, showing the importance of having the soft metal as single phase without forming intermetallic compounds or being in solid solution. Additionally, the role on friction of the metal sulfide composition and stoichiometry formed during the laser deposition process is discussed. Afterwards, their friction and wear performance are evaluated using high temperature tribological tests in air and vacuum.

The results reveal that the self-lubricating laser deposited alloys are able to control friction from room temperature to 600 °C in ambient air and at least until 300 °C in vacuum. In ambient air, the friction reduction mechanism is determined by the soft metal and the metal sulfides. At higher temperatures, the contribution of the soft metal diminishes due to oxidation so that the role of metal sulfides to self-lubrication is dominant. In vacuum conditions, the laser deposited self-lubricating alloys can effectively reduce friction down to 0.25 without the aid of an additional lubricant against martensitic stainless steel at 300 °C. This overall tribological performance makes the presented self-lubricating alloys potential candidates for high temperature forming and space applications.

11:00am **E1-2-WeM-10 On the Tribological Performance of Magnetron Sputtered W-S-C Coatings With Conventional and Graded Composition***,* ***Todor Vuchkov (todor.vuchkov@ipn.pt)****,* Instituto Pedro Nunes, Laboratory for Wear, Testing and Materials, Portugal*; A. Cavaleiro,* University of Coimbra, Portugal

Nanocomposite coatings consisting of an amorphous carbon matrix (a-C) with nanocrystallites of transition metal dichalcogenides (TMDs) embedded in it can provide protection against friction and wear in different operating environments, from vacuum to humid ambient air conditions. Magnetron sputtered W-S-C coatings are part of this group of coatings which shows good adaptive tribological behaviour. One potential issue is the running-in behaviour of these coatings as the formation of lubricious tribofilms is crucial for a good tribological response. These tribofilms are most often rich in $WS_2$, a lubricious compound that is an exceptional lubricant in inert environments (dry $N_2$, vacuum). A way to improve the running-in behavior would be to change the chemical composition of the coatings across their thickness. Therefore, we deposited a W-S-C coating with varied carbon content across its thickness. The bottom layers of the film were rich in carbon which improved the hardness and thus the load-bearing capacity. The carbon content was gradually reduced towards the top-most layers and finally, a pure $WS_2$ layer is deposited. In comparison, coatings with a constant composition of ~30 at. % and 50 at. % of carbon were also deposited. The characterization of the coating included scanning electron microscopy with wavelength dispersive spectroscopy for morphological and a study of the chemical composition. X-ray diffraction for structural analysis. Nanoindentation and scratch testing for hardness and adhesion studies respectively. Finally, tribological studies were performed in ambient conditions, dry $N_2$ environment and at elevated temperature. The correlation between the tribological results and the physico-chemical properties of the coatings revealed that every coating has an advantageous sliding environment.

11:20am **E1-2-WeM-11 Revising the Role of Oxygen "Impurities" in Tribological and Mechanical Performance of $MoS_2$ Coatings Under Vacuum and Ambient Air Conditions***,* ***Andrey Bondarev (bondaan2@fel.cvut.cz)****, T. Polcar,* Czech Technical University in Prague, Czech Republic

The $Mo_{32}S_{66}O_2$, $Mo_{33}S_{58}O_9$, $Mo_{24}S_{38}O_{38}$ and $Mo_{24}S_5O_{71}$ coatings were fabricated by unbalanced magnetron sputtering. The increase of oxygen concentration in the Mo-O-S system from 2 to 38 at.% displace sulfur, and changes the structure from columnar crystalline to dense amorphous Mo-O-S. Hardness and Young modulus rise with an increase of O concentration from 2 to 38 at.%. These changes are accompanied by enhancement of the tribological performance both under vacuum and humid air. The triboactivated formation of the crystalline $MoS_2$ tribolayer from amorphous Mo-O-S occurs inside the wear track as well as on the counterpart surface. In the case of the low amount of S for $MoS_2$ formation,the tribofilm is preferentially formed on the counterpart surface. In the case of the $Mo_{24}S_5O_{71}$ coating with low S content, the lubricious $MoS_2$ tribolayer is not formed and the coatings fail the tribotests both under vacuum and humid air. Under vacuum, the lowest CoF of 0.02 is observed for the $Mo_{33}S_{58}O_9$ coating and associated with interfacial sliding between $MoS_2$ transfer film and wear track. For the $Mo_{32}S_{66}O_2$ and $Mo_{24}S_{38}O_{38}$ coatings, CoF values of 0.05 and 0.04 are recorded, this slightly higher CoF is associated with mixed interfacial sliding/transfer film shearing mode of friction. In humid air the CoF values of the coatings were 0.27, 0.29, and 0.18 for the $Mo_{32}S_{66}O_2$, $Mo_{33}S_{58}O_9$, and $Mo_{24}S_{38}O_{38}$ coatings,respectively. Probably, the friction is controlled by physisorbed water between the $MoS_2$ tribolayers that forms hydrogen bonds with S atoms which increases the interlayer binding energy, and CoF, respectively. Wear resistance under vacuum is governed by the ability of the coatings to form continuous and stable $MoS_2$ tribolayer and their mechanical properties. Wear resistance in humid air is governed by cohesive wear that probably takes a place because of increased interlayer binding energy. Important, that in the case of a moderate concentration of O in the coatings composition ($Mo_{33}S_{58}O_9$) the water physisorption can be suppressed, and that improves wear resistance.

11:40am **E1-2-WeM-12 Understanding Ultra-Low Coefficient of Friction of a-C Coated Surfaces Under High Contact Pressure and Humidity Levels***,* ***Newton K. Fukumasu (newton.fukumasu@usp.br)****, A. Tschiptschin, I. Machado, R. Souza,* University of São Paulo, Brazil

Carbon-based coatings have attracted significant attention of aerospace, automotive and energy industries, due to low friction and high wear resistance. Usually, these tribological characteristics can be tailored based on different levels of $sp^2$ to $sp^3$ carbon bond ratios induced by the presence of hydrogen/dopants or deposition process variables, such as power, substrate bias and sample to target distance. Literature reports that ultra-low friction and superlubricity behavior of carbon-based coatings are influenced by the presence of hydrogen and water molecules at the contact during the tribological test. In this work, experimental and numerical analyses were carried out to understand the conditions of the a-C contacting surfaces that promote ultra-low friction states under high contact pressures. The experimental analyses consisted of ball-on-disk reciprocating tests to evaluate friction and wear of non-hydrogenated amorphous carbon (a-C) coatings, deposited by pulsed-DC magnetron sputtering technique. A polycrystalline graphite target was used to deposit the a-C coating over AISI H13 disks and AISI 52100 balls. Scanning Electron Microscopy (SEM), Raman spectroscopy, optical profilometry and instrumented indentation were applied to characterize tested surfaces. Tribological tests were carried out under dry contact conditions at room temperature, high relative humidity (>60%) and high Hertzian contact pressures (>2 GPa). Results indicated a correlation of the G band peak position (GBPP) with the coefficient of friction. When both surfaces were coated, results showed a stable ultra-low coefficient of friction, stabilized down to 0.03 for the highest GBPP. The digital tribology platform TriboCODE was applied to observe the stress distribution in coated surfaces under tribological applications, in which multiscale numerical simulations suggested a possible whole of water molecules, between carbon surfaces, that induces localized changes on carbon bonds, forming structured tribo-films, promoting both reduction of friction coefficient and improved wear resistance.

# Author Index

## Bold page numbers indicate presenter


— A —
Al-Rjoub, A.: E1-2-WeM-5, 1
Andric, P.: E1-2-WeM-2, 1
— B —
Berman, D.: E1-2-WeM-3, **1**
Bondarev, A.: E1-2-WeM-11, **2**
Broitman, E.: E1-2-WeM-2, **1**
— C —
Cavaleiro, A.: E1-2-WeM-10, 2; E1-2-WeM-5, **1**
— F —
Fernandes, F.: E1-2-WeM-5, 1
Fukumasu, N.: E1-2-WeM-12, **2**
— G —
Gachot, C.: E1-2-WeM-1, 1; E1-2-WeM-6, **1**
Grützmacher, P.: E1-2-WeM-1, **1**
— K —
Kadin, Y.: E1-2-WeM-2, 1
— M —
Machado, I.: E1-2-WeM-12, 2
— O —
Ott, V.: E1-2-WeM-2, 1
— P —
Polcar, T.: E1-2-WeM-11, 2
— R —
Rodriguez Ripoll, M.: E1-2-WeM-6, 1
Rosenkranz, A.: E1-2-WeM-1, 1
— S —
Souza, R.: E1-2-WeM-12, 2
Stüber, M.: E1-2-WeM-2, 1
Suarez, S.: E1-2-WeM-1, 1
— T —
Torres, H.: E1-2-WeM-6, 1
Tschiptschin, A.: E1-2-WeM-12, 2
— V —
Vuchkov, T.: E1-2-WeM-10, **2**