Thin Films
Room Naupaka Salon 5-7 - Session TF-TuE
Next-generation Protective Coatings and Tribological Applications
Moderator: Hisao Ishii, Chiba University

5:40pm **TF-TuE-1 Functional Coatings for Aerospace Applications – Perspectives and Sustainable Development***, **Jolanta-Ewa Klemberg-Sapieha**,* Polytechnique Montréal, Canada **INVITED**

Materials exposed to harsh environments continue to face ever-increasing technological, environmental, and economic challenges. Consequently, the field of coating and surface engineering (CSE) technologies has been extremely active, addressing numerous challenges related to the increasingly stringent requirements for the performance of coatings and surface engineering solutions. This frequently includes a controlled combination of several functional properties and long-term environmental stability and durability (multifunctional character of the coatings).

These requirements call for novel thin film fabrication processes and new materials with a synergistic combination of tailored characteristics, while solutions must fit into a sustainable (green) development approach including new “clean” (environmentally friendly) fabrication technologies, and life cycle compatible with economic and environmental constraints.

Protection against materials deterioration is particularly important in the context of aircraft components as operation conditions can vary very widely from severe erosive wear to exposure to hot oxidative gases, extreme thermal loads, or even instant icing of critical surfaces. The reduction of emissions through better engine efficiency can be achieved by using lighter structural materials while preserving the integrity of gas path aerodynamic characteristics; this can be accomplished by surface engineering and application of coatings resulting in the reduction of friction, erosion, wear, and corrosion.

In response, our Functional Coating and Surface Engineering Laboratory (FCSEL, www.polymtl.ca/larfis) has proposed, a comprehensive approach to surface engineering problems. This is based on a simultaneous action of the following key elements: (i) in-depth understanding of the technological problem, (ii) availability of the appropriate metrology tools (testing methods) that allow one to seek appropriate solutions in terms of (iii) nanostructured coating materials, and (iv) their integration in specific coating architectures while applying (v) suitable fabrication processes.

In this presentation, the global approach described above will be illustrated by examples related to the development of protective coating systems against solid particle erosion, high-temperature oxidation, and ice accumulation, as well as our work on the next-generation low-emissivity thermal barrier coatings.

6:20pm **TF-TuE-3 How to Manage Friction and Wear of Diamond-Like Carbon Coatings Lubricated with ZDDP Additive by Tuning Their Mechanical Properties***, **Maria Isabel De Barros Bouchet**,* LTDS - Ecole Centrale de Lyon , France

HoIn various industrial applications, friction and wear reduction by diamond-like carbon (DLC) can be severly affected by the presence of zinc-dialkyldithiophosphate (ZDDP) additive in formulated oils. Tribological experiments show that DLCs friction and wear behaviour in the presence of ZDDP-additivated oils can be managed by tailoring their stiffness, surface nano-topography and hydrogen content. An optimal combination of ultralow friction and negligible wear is achieved using hydrogen-free tetrahedral amorphous carbon (ta-C) with moderate hardness. Softer coatings exhibit similarly low wear and thin ZDDP-derived patchy tribofilms but higher friction. Conversely, harder ta-Cs undergo severe wear and subsurface sulphur contamination. It appears that high local contact pressures caused by the contact stiffness and average surface slope of hard ta-Cs favour ZDDP fragmentation, inducing free sulphur release and its penetration in coating subsurface. Plastic deformation and the formation of graphitic regions and onion-like structures are observed in the weakened sulphur-rich zones by HRTEM[1].

The effect of sulphur element was further investigated by testing other sulphur-containing and sulphur-free additives. Similar tribochemical wear and high friction were observed for hard ta-Cs lubricated with Sulphur-containing molecules. On the contrary, no wear was observed with the sulphur-free additive. This work sheds light on the underlying micro/nano-scale mechanisms that are responsible for macroscopic tribological behaviour of DLC coatings lubricated in the presence of ZDDP and similar sulphur-containing additives.

[1] Valentin R. Salinas Ruiz, Takuya Kuwahara, Jules Galipaud, Karine Masenelli-Varlot, Mohamed Ben Hassine, Christophe Héau, Melissa Stoll, Leonhard Mayrhofer, Gianpietro Moras, Jean Michel Martin, Michael Moseler & Maria-Isabel de Barros Bouchet, NATURE COMMUNICATIONS (2021), https://doi.org/10.1038/s41467-021-24766-6.

6:40pm **TF-TuE-4 Corrosive Properties of Y_2SiO_5 Environmental Barrier Coatings***, **Byung-Koog Jang**,* Kyushu University, Japan

Silicon-based ceramics such as SiC/SiC_f composites and silicon carbide (SiC) are of interest as candidate materials for the hot-section components of new-generation gas turbines in order to meet future higher fuel efficiency and lower emission goals for enginesbecause of their excellent high-temperature mechanical properties (e.g., retention of high-temperature strength and toughness up to 1400°C). However, since it is prone to hot-corrosion in thermally extreme environments (ex, steam), the development of environmental barrier coatings (EBCs) is mandatory. In the present work, Y_2SiO_5EBCs have been deposited by plasma spray technique as protection layer of SiC substrate from oxidation and steam corrosion. Y_2SiO_5 coatings were exposed at 1400°C for 1~50hr by isothermal heat treatment in the presence of an erosive impurity of calcium-magnesium-aluminosilicate (CMAS). At the interface between the Y_2SiO_5 coatings and CMAS, the coatings were partially dissolved in the CMAS, resulting in the degradation of coatings by the formation of the reacted region. The chemically reacted region from the top surface of the Y_2SiO_5 coatings showed increasing tendency with an increase in isothermal heat-treatment time.In addition, the hardness and elastic modulus ofY_2SiO_5 coatingswere evaluated by nano indentation.

7:00pm **TF-TuE-5 The Effect of Morphology in the Diffusion of Ag Inside Hard Coatings***, **Diogo Cavaleiro**,* University of Coimbra, Portugal*; F. Fernandes,* Instituto Superior Engenharia do Porto, Portugal

One of the most promising solutions for long term lubrication during dry machining operations are self-lubricant coatings. However, the main problem in these kind of coatings is the swift diffusion of the lubricious element and consequent loss of lubricant properties after short periods of time. By combining the mechanically sound TiSiN coating system with its reported anti-diffusion properties of the amorphous SiN a solution to halt the diffusion of the lubricious element can be found. In this work, triple layer coatings constituted by a Ag doped TiN layer sandwiched between two layers of either TiN or TiSiN were deposited by HiPIMS working in deep oscillation magnetron mode (DOMS) with the objective of studying the diffusion of Ag (the lubricious element) in these two different types of matrices (TiN and TiSiN) when exposed to high temperatures. After annealing treatment of the samples at 600ºC and 800ºC for 2 hours, RBS and TEM analyses allowed to observe that the morphology of the coatings had a big impact in the way Ag diffusion occurred. Open columnar structures facilitate Ag movement through surface diffusion of the columns. While, at first, it seemed that the TiN matrix was a better barrier to the diffusion of the silver, the incorporation of Si_3N_4 cap layers allowed to disregard the effect of structure and confirm that with the right morphology, the TiSiN matrix can completely halt the diffusion, thus demonstrating its ability to be applied in tools for dry machining operations.

7:40pm **TF-TuE-7 Comparison of Mechanical and Tribological Properties of Diamond-Like Carbon Coatings Doped with Europium and Gadolinium Produced by HiPiMs***, M. Fontes,* Federal Institute of Education, Science and Technology of Sao Paulo, Brazil*; A. Cavaleiro, **Fábio Ferreira**,* University of Coimbra, Portugal

Hydrogen-free diamond-like carbon (DLC) thin films exhibit properties that make them suitable for a wide range of applications, from biomedical implants to engine components. They have been used as coatings due to their attractive properties including high-temperature stability, high hardness, high wear resistance (wear rate <10-16 m3/Nm), and low friction coefficient (<0.2) even under high load/pressure. One of the major limitations of hard hydrogen-free ta-C coatings applications is related to the low reactivity with oil additives used nowadays. The Ionic liquids (ILs) emerged as a novel class of lubricants that can be used in future lubricated systems due to possesses unique physical properties, including high thermal stability, high thermal conductivity, very low volatility, low melting point, and nonflammability. To improve the lubrication performance of DLC with ILs, it was doped the DLC films with rare earth metals such as Gadolinium (Gd) and Europium (Eu). The working hypothesis is that these non-carbide-forming elements can be introduced in the DLC matrix, incorporated as single atoms, and enhance the surface adsorption and reactivity of phosphorus-based IL, improving, consequently, the lubricating properties of DLC/ILs sliding contacts, with no effect the mechanical and tribological proprieties of DLC films. Therefore, in this work, the mechanical and tribological properties of the doped-DLC films, with different atomic concentrations of Eu and Gd elements, deposited by High Power Impulse Magnetron Sputtering (HiPIMS), were characterized and compared with the pure DLC films. Results show that for samples doped with a low atomic concentration of Eu or Gd (1% to 3%), despite having a friction coefficient higher than pure DLC films (0.45), shows typical values for pure DLC coatings, like low wear rate and high hardness (23GPa), permitting, in the future, the combination of novel nanostructured alloyed-DLCs and ILs needed to achieve the optimal lubrication performance.

8:00pm **TF-TuE-8 Reactive Molecular Dynamics Simulation Study on the Chemical Reactions Induced at the Diamond-Like Carbon/Fe Sliding Interface and Their Effects of Friction and Wear***, **Mizuho Yokoi**, M. Kawaura,* Institute for Materials Research, Tohoku University, Japan*; Q. Chen,* New Industry Creation Hatchery Center, Tohoku University, Japan*; Y. Asano, Y. Ootani,* Institute for Materials Research, Tohoku University, Japan*; N. Ozawa,* New Industry Creation Hatchery Center, Tohoku University, Japan*; M. Kubo,* Institute for Materials Research, Tohoku University, Japan

Understanding wear phenomena is essential to prevent fatal accidents caused by the destruction of machine systems due to wear. Wear amount is usually governed by mechanical factors, however sometimes chemical factors also strongly affect the wear. For example, a previous experimental study has shown that when water is present at the diamond-like carbon (DLC)/Fe sliding interface wear amount increases due to chemical reactions induced at the sliding interface [1]. Therefore, it is important to clarify the atomic-scale wear mechanism in which mechanical and chemical actions are involved.However, the observation of the atomic-scale wear phenomena at the sliding interface from experiments is difficult.In this study, we successfully revealed the tribochemical reactions and their effects on the atomic-scale wear mechanism at the sliding interface of DLC and Fe pair, which is typically used in automobile engines, in the presence of H_2O and $O_2$by using reactive MD simulation.

The sliding simulation model is shown in a supplementary document (SD) Fig.1. To investigate the effects of H_2O and O_2, we prepared the following three models: H_2O model, O_2 model and H_2O+O_2 model. H_2O molecules, O_2 molecules and both H_2O and O_2 molecules were placed at the DLC/Fe sliding interface of H_2O model, O_2 model and H_2O+O_2 model, respectively. In the sliding simulations, the DLC substrate on the Fe substrate was slid along the x-direction at a speed of 100 m/s with the normal load of 1 GPa.

In all sliding simulation models, when the Fe and DLC substrates came into contact with each other, the Fe atoms were scraped off and adhered to the DLC surface with a formation of Fe-C bonds. The amount of atomic-scale wear was smaller in the following order, H_2O+O_2 model < O_2 model < H_2O model. In H_2O model, H_2O molecules were adsorbed on the surface to prevent adhesion (SD Fig.2(a)). However, they were ejected from the contact surface when the high contact pressure was applied, allowing the direct contact. In contrast, in O_2 model O_2 molecules reacted with the Fe surface, forming chemically inert layer, thereby prevented atomic-scale adhesive wear (SD Fig.2(b)) [2]. Moreover, in H_2O+O_2 model, in addition to the above roles of H_2O and O_2, the reaction of H_2O with the oxide layer promotes the formation of Fe-O-H groups which passivate nascent Fe surface (SD Fig.2(c)). Thus, the results indicate that H_2O and O_2 play the different role to reduce atomic-scale wear. Moreover, when H_2O and O_2 coexist at the sliding interface they play a collaborative role to reduce atomic-scale wear.

[1] A. Alazizi, *et al.*, Langmuir, 32, 1996 (2016).

[2] M. Yokoi, M. Kubo, *et al.*, J. Comput. Chem. Jpn. in press

8:20pm **TF-TuE-9 High-Entropy Configuration Strategy for the Synthesis of Oxide, Glycerate, and Sulfide Catalysts for Oxygen Evolution Reaction in Water Splitting***, **Jyh-Ming Ting**,* National Cheng Kung University (NCKU), Taiwan*; T. Nguyen,* National Cheng Kung University (NCKU), Taiwan, Viet Nam*; Y. Liao, C. Lin, Y. Su,* National Cheng Kung University (NCKU), Taiwan

INVITED

High entropy material provides an unlimited compositional space that allows an unparallel possibilities for tailoring the electronic structure favorable for catalysts reaction.We report herein two advanced high entropy electrocatalysts having earth-abundant metals for oxygen evolution reaction (OER) in water splitting.The first one is a high entropy perovskite oxide (HEPO) and the second one is high entropy sulfide (HES).The B-site lattice in the HEPO consists of 5 consecutive first-row transition metals, including Cr, Mn, Fe, Co, and Ni, which have quite similar ionic radii.Equimolar and five non-equimolar HEPO electrocatalysts have been studied for their OER electrocatalytic performances.Optimized HEPO having outstanding OER activity is demonstrated.The metals used in the HES are Fe, Ni, Co, Cr, and X where X = Mn, Cu, Zn, or Al.We show that the obtained sulfate-containing $FeNiCoCrMnS_2$ exhibits superior OER activity with exceptionally low overpotential of 199, 246, 285, and 308 mV at current densities of 10, 100, 500 and 1000 mA cm^{-2}, respectively.The electrocatalyst yields exceptional stability after 12000 cycles and 55 h of durability even at a high current density of 500 mA cm^{-2}.Various *in-situ* and *ex-situ* analyses were used to investigate the self-reconstruction of the sulfides during the oxygen evolution reaction (OER) for the first time.Density function theory calculation is in a good agreement with the experimental result.The result demonstrates a viable strategy that leads to the development of new catalyst materials with excellent OER performance.It also opens a new avenue to explore novel, outstanding high entropy materials for various applications.

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