## Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
## Room Town & Country B - Session E3-1-TuM
## Tribology of Coatings and Surfaces for Industrial Applications I

**Moderators: Dr. Nazlim Bagcivan**, Schaeffler Technologies GmbH & Co. KG, Germany, **Dr. Rainer Cremer**, KCS Europe GmbH, Germany, **Dr. Philipp Grützmacher**, Institute of Engineering Design and Product Development, Austria

8:00am **E3-1-TuM-1 Carbon Based Coatings Deposited Over Aisi 4140 to Improve Wear Resistance in Machine Components***, F. Delfin,* UTN, Argentina*; D. Heim,* Upper University of Applied Sciences, Wels Campus, Austria*; **Sonia Brühl,*** UTN, Argentina **INVITED**

Carbon based coatings or DLC are well known to have a low friction coefficient, chemical stability at room or low temperatures, high hardness and also corrosion resistance. Three different carbon-based coatings were deposited over plasma nitrided or non nitrided AISI 4140 mild steel to improve hardness and wear resistance so as tribological properties.

One of them is an amorphous hydrogenated thick Si doped DLC (a-C:H:Si) deposited by PACVD, in a Rübig facility in Austria using a DC pulsed discharge, with acetylene and HMDSO as carbon and silicon precursors, respectively. It will be compared with a Si-free DLC (a-C:H) deposited in the same conditions. The third one is a multilayer film with DLC as top coating deposited by the PVD PEMS technique in a Cemecon facility in Argentina. In this case, the anchor layer consists of CrN and the top layer is a chromium-dopped hydrogenated amorphous carbon (a-C:H:Cr).

Full characterization was carried out by SEM, Raman Spectroscopy and XRD. Mechanical properties were obtained using nanoindentation. Tribological behavior was study with Pin-on-Disk tests, evaluating wear loss and friction coefficient, and complementary SEM/EDS analysis on the wear track and on the counterpart. Adhesion was assessed with variable load Scratch Test and Rockwell C indentation method. Abrasion tests following ASTM G65 standard were also conducted.

All coatings contain hydrogen and a combination of $sp^3$-$sp^2$ bonding, with high disorder level caused mainly by the dopants. Low coefficients of friction were obtained with the films, between 0.1 and 0.3, being the lowest the Si-free thick DLC reaching 0.06. Regarding the wear rates with alumina as counterpart, only the Si-free DLC and the duplex nitrided steel plus a-C:H:Cr presented a low volume loss. Adhesion was also improved by the plasma nitriding pre-treatment in this coating, which provided a hardness gradient in the substrate to support the load applied. Meanwhile, Si doping improved DLC wear resistance in the case of abrasion tests.

As a conclusion, the thick and Si-free DLC coating has the lowest CoF and wear rate when deposited over mild steel. On the other hand, the thin PVD Cr doped DLC coating presented the best performance when deposited over nitrided steel. This also improved the adhesion comparing to the other two PACVD coatings. The Si-doped DLC failed in the pin-on-disk test because of the adhesion with the counterpart, but it presented a good wear resistance in abrasion.Tribological mechanisms, and applications of each type of coating will be discussed.

8:40am **E3-1-TuM-3 Tribological Behaviour of Diamond Coated Reaction-Bonded Silicon Carbide Under Dry and Seawater Environment***, R. Kannan, N. C,* Indian Institute of Technology Madras, India*; R. Ganguly, S. Mandal, S. Rao,* Carborundum Universal Limited, Industrial Ceramic Division, India*; **M.S Ramachandra Rao,*** Indian Institute of Technology Madras, India

Ceramic seal materials such as silicon carbide (SiC) and Reaction-Bonded SiC (89%SiC and 11% free Silicon) are widely used in mechanical pumps, compressors, and feed water pumps to prevent the fluid leakage between the two rotating shafts. In a continuously harsh environment, these mechanical seal materials undergo high friction and wear due to the high asperity-to-asperity contact between the two mating parts and generate high frictional heat at the interface. This scenario induces seal failure under high operating conditions. Especially in the corrosive medium such as acids, high pH value solutions and hard abrasive media can cause aggressive seal failure. To reduce production downtime and improve the longevity of the mechanical seal, the surface of the seal material needs to be engineered with a suitable coating that will satisfy the required properties of high hardness, chemically inertness, and low friction coefficient. In this regard, we have come up with a super hard coating material such as diamond (Micro-crystalline) on the surface of Reaction-Bonded SiC using the hot filament CVD (HFCVD) method to meet the above-required properties. In this work, we have carried out a systematic study on the tribological effect of uncoated and diamond-coated seal material against silicon nitride ceramic under a dry and seawater environment. The initial physical characteristics such as surface morphology, surface roughness, and Raman analysis were performed on the samples before and after coating. To understand the friction and wear characteristics, the linear reciprocating tribometer test (Ball on Flat) was conducted on the uncoated (18,000 cycles) and diamond-coated (36,000 cycles) samples using a universal tribometer. The experimental results show that the diamond-coated sample exhibits a low friction coefficient (0.05 ± 0.01) compared to the uncoated sample (Friction coefficient (CoF) = 0.24 ± 0.037) at a normal load of 10 N with a frequency of 10 Hz under a seawater environment. Similarly, under dry conditions for the same tribo-test parameters, the diamond-coated sample (CoF = 0.06 ± 0.02) outperforms compared with the uncoated sample (CoF = 0.42 ± 0.17) at a percentage improvement of 85%. From the observed results, we conclude that diamond-coated ceramic seals are considered a suitable alternative to commercially available seals in terms of high operating conditions and durability under both wet (Sea water) and dry running operation. All these results will be presented.

9:00am **E3-1-TuM-4 Friend or Foe? The Role of Oxygen in the Tribological Performance of Solid Lubricant $MoS_2$***, **Andrey Bondarev,*** Czech Technical University in Prague, School of Engineering, Bernal Institute, University of Limerick, Ireland*; I. Ponomarev, T. Polcar,* Czech Technical University in Prague, Czechia

$MoS_2$ is a solid lubricant used in various forms, such as a dry lubricant by itself, or as a component of a more complex coating. In both these forms, the effect of oxygen contamination on the sliding properties of $MoS_2$ coatings is traditionally considered detrimental, resulting in expensive technological processes to produce pure $MoS_2$.

The interaction of the film with oxygen can be split into three phases. First, during magnetron sputtering, oxygen is incorporated into the growing film from the residual atmosphere. Then, storing the film in the open air can cause oxidation. Finally, the coatings experience a negative influence of molecular or atomic oxygen from the surrounding atmosphere on their tribological properties. Despite the origin, a formation of a noticeable amount of molybdenum oxides on the sliding surface has been reported as the reason behind the poorer tribological properties.

The Mo-S-O coatings were fabricated by unbalanced magnetron sputtering. It was found that hardness, elastic modulus, and wear resistance can all be enhanced with the addition of oxygen. The Mo-S-O coatings were tribologically tested under vacuum, ambient air, and nitrogen. A high oxygen content, up to 38 at.%, does not prevent the formation of a lubricious crystalline $MoS_2$ tribofilm, which is formed through triboactivated segregation of the deposited Mo-S-O amorphous coatings into a crystalline $MoS_2$-based phase and an amorphous S-depleted Mo-S-O phase. By means of advanced TEM and EELS studies, it was shown that an ultra-thin crystalline $MoS_2$ tribolayer incorporates some amount of oxygen. Such an imperfect tribolayer was found to reduce the coefficient of friction to 0.02, a value lower than that of pure MoS2 under vacuum (0.05). Molecular dynamics simulations performed using a newly developed Mo-S-O force field confirmed that such an imperfect tribolayer can mitigate friction in a manner comparable to $MoS_2$. Results of DFT simulations support the experimental findings and show that partial substitution of S atoms to O atoms in the $MoS_2$ crystal structure does not increase shear modulus. Tribological tests of the Mo-S-O coatings after 1-year storage under ambient air (RH = 35 ± 5%) revealed the same trends as freshly deposited samples – the Mo-S-O coatings outperform pure $MoS_2$ coatings demonstrating lower values of friction coefficient.

In this work it is shown that contradictory to common knowledge, adding oxygen to a solid lubricant $MoS_2$ coating could be beneficial. Since eliminating oxygen in MoS2-based solid lubricants is extremely costly, our findings can significantly reduce the production and storage cost for aerospace and other vacuum applications.

9:20am **E3-1-TuM-5 Tribological Properties $MoS_2$-WC Duplex Coatings in Low Viscosity Hydrocarbons***, **Euan Cairns,*** University of North Texas, USA*; S. Dixit,* Plasma Technology Inc., USA*; D. Berman, S. Aouadi, A. Voevodin,* University of North Texas, USA

Emerging applications using low-carbon emission fuels, such as ethanol and dodecane, lead to a growing need for lubricious materials that can improve the tribological behavior and increase the wear life of fuel pump components. In our previous studies we found that $MoS_2$ spray-coat on

52100 steel had the potential to be used in low-viscosity hydrocarbon fuels as a protective coating. The best results were observed in dodecane fuel, where a coefficient of friction of less than 0.1 was maintained for 100 m of sliding. In this report, we extend the understanding of $MoS_2$ spray coating performance in low viscosity hydrocarbons to a duplex coating with a hard, wear-resistant underlayer made of coated and ground finished High Velocity Oxygen Fuel (HVOF) thermal spray tungsten carbide (WC) combined with the lubricious $MoS_2$ top layer to create synergistic tribological protection of 52100 steel substrates from the sliding wear. Tribological tests were performed under the reciprocating sliding condition in dodecane and ethanol, followed by investigations with scanning electron microscopy equipped with an energy dispersive spectrometer, Raman microscopy, and x-ray photoelectron spectroscopy for microstructural and compositional analysis.The effects of substrate roughness and composition on the wear life of the coatings were examined using optical profilometry and microscopy of wear tracks. The results were used to identify lubrication and sliding wear protection mechanisms when using $MoS_2$-WC duplex coatings prepared by spray methods.

9:40am **E3-1-TuM-6 Modification of Diamond Like Carbon (DLC) to Improve Specific Tribological Characteristics for Automotive Applications***,* ***Denis Romagnoli****, F. Lavalle,* STS srl, Italy **INVITED**

Carbon-based materials play an important role in today's science and technology. Carbon is a very versatile element whose two most interesting allotropic forms are Diamond (sp3) and Graphite (sp2). In recent years, there have been continuous and important advances in carbon science, such as the chemical vapor deposition of diamond, the discovery of fullerenes, carbon nanotubes, and the single layer of graphene. At the same time, the DLC has consolidated all its applications in the automotive, mechanical in general but also fashion sectors. An amorphous carbon layer can have different ratios between diamond C and graphitic C. The management of these fractions but above all the architecture of the layer generates different types of DLC that allow to enhance the hardness, contain friction and improve the corrosion resistance of the component.

The demand for the application of DLC on components for endothermic and hybrid engines (pins, valves, camshafts) is constantly growing; about the novelties in the field of mobility, the need to protect the gears of electric motors from wear or corrosion the bipolar plates of hydrogen propellers are increasingly pressing. DLC can increase surface hardness, reduce friction and protect against corrosion; for racing this means an improvement in terms of overall engine performance, and for the automotive sector an improvement in yield with the consequent possibility of reducing emissions into the atmosphere, allowing the use of certain components in non-standard conditions (e.g. rotation constantly at a maximum number of revolutions in an electric motor) and use different materials (for example steel compared to graphite in a Fuel Cell). The possibility therefore of being able to manage hardness, coefficient of friction, and corrosion resistance in the same DLC layer is determined for the application.

In this presentation, the DLC deposited with hybrid technology PVD-PaCVD (Physical Vapor Deposition- Plasma assisted Chemical Vapor Deposition) will be examined. The modification of the layers, the thicknesses, the compositions, and the containment of surface defects allow enhancing the characteristics of hardness, reduction of friction, and resistance to corrosion of the layer. These characteristics can therefore be objectified with laboratory instruments such as nanoindenter, contact tribometer, and salt spray chamber. The next step is the bench test to then move on to the final validation and production launch.

10:20am **E3-1-TuM-8 Fabrication and Tribological Behaviors of DLC Coatings Embedded with Graphene Nanoplatelets***,* ***Guizhi Wu****, R. Brittain, A. Morina,* University of Leeds, UK*; E. Broitman,* SKF Research & Technology Development Center, Netherlands*; L. Yang,* University of Leeds, UK

Graphene has garnered widely interests in tribology due to its nature of reducing friction. The lamellar structure endows graphene a weak shearing stress, and thus a low friction. Utilizing graphene platelets to wrap around nanodiamond particles to form nanoscrolls at a sliding interface would decrease coefficient of friction (COF) significantly by achieving an incommensurate contact on diamond-like carbon (DLC) coatings. However, such complicated design containing too many additives will reduce the stability of the system. COF of TiN ceramic film will decrease by simply driping down a graphene aqueous dispersion on the slding interface, by which a smooth sliding interface promoted by graphene are formed. Nevertheless, the most concern is that graphene might be easily pushed out of the friction interface at the beginning of sliding, thus may not affect the friction test. Graphene nanocrystallites can also be fabricated by vapor deposition method and embedded in the carbon film matrix to form a nanocomposite carbon film, of which the COF decreases significantly. But it remains to be further demonstrated whether the synthesized carbon crystallites is graphene.

In this study we report the synthesis and tribological behaviors of DLC coatings embedded with Graphene nanoplatelets (GNP), namely DLC-GNP nanocomposites. GNP layer was deposited by two methods, namely, spin-coating and spray-coating. The DLC layer was deposited on top of the GNP coated coupon by plasma enhanced chemical vapour deposition. The effect of GNP on the lubricated tribological response under elevated temperature was discussed. The results show that GNP has a tendency to agglomerate for higher GNP coverages by using spin-coating, which would lead to removal of the GNP more easily and negate the friction reduction effect of the GNP. The tribotests show decrease in friction and wear of the DLC-GNP nanocomposites in various GNP coverages, with the lowest friction (COF ~0.03) and wear (~$1.6 \times 10^{-19}$ $m^3/Nm^{-1}$) achieved, which might be due to a highly graphitic transfer film featuring low shearing stress formed in the friction interlayer. This study might contribute to energy conservation and emission reduction, and also promote the development of green tribology under the global ‘Carbon net zero’ aim.

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