Surface Engineering - Applied Research and Industrial Applications
Room Pacific Salon 1 - Session G4+G5+G6-ThA

Pre-/Post-Treatment and Duplex Technology/Hybrid Systems, Processes and Coatings/Application-Driven Collaborations between Industry and Research Institutions

Moderators: Heidrun Klostermann, Fraunhofer FEP, **Kumar Yalamanchili**, Oerlikon Balzers, Oerlikon Surface Solutions AG, **Tobias Brögelmann**, Surface Engineering Institute - RWTH Aachen University, **Hana Barankova**, Uppsala University, Sweden

1:20pm **G4+G5+G6-ThA-1 From Detailed Understanding to In Operando Studies of Coated Cutting Tools: A Successful and Long Term Collaboration between Industry and Universities***, Jon Anderson,* Seco Tools AB, Sweden **INVITED**

The truth is in the details when it comes to development of materials, so also for cutting tool coatings. For example, two coating materials CVD Al_2O_3 and PVD TiAlN have been the dominating commercial wear resistant coatings for the last 20-30 years. Over the same period, both the coating properties and their performance during machining have improved dramatically. This has been made possible by paying attention to the details of the coating synthesis coupled to its structure, properties and performance during service. The key to finding these details as well as deciding which to focus on to achieve the desired results is advanced characterization and an in-depth analysis combined with the feedback from focused material, process or functional modeling studies. At Seco Tools we have a long and fruitful experience of collaborating with universities around these issues with an open and creative mindset. Here we will present the outcome of a few case studies, ranging from fundamental arc plasma studies vs. coating synthesis including particle-in-cell (PIC) simulation of the same, correlated to coating structure and properties, to atomic-level materials characterization and in operando synchrotron investigations of the tool/chip contact during metal cutting.

2:00pm **G4+G5+G6-ThA-3 Electrolytic Plasma Polishing of Titanium Alloys***, **Nicolas Laugel**, A Yerokhin, A Matthews,* University of Manchester, UK

Electrolytic plasma polishing (EPPo) is a method for metals surface finishing. Its applications see a fast growing interest in line with its advantages over more established competing methods, in particular in the field of additive manufacturing. The promises of additive manufacturing include a disruptive impact on metals manufacturing in virtually all high value applications, from aerospace to automotive and medical industries. However it suffers to this day from entirely unsatisfactory surface states, both for direct use or for subsequent surface treatment or coatings. The most promising approach to the issue is arguably contactless post-treatment and EPPo as one of the best fitting contenders.

EPPo consists in setting a workpiece as the anode in an electrolytic cell, and apply voltages in the hundreds of volts. The energy liberated due to this strong polarization is transferred primarily through the production of large quantities of electrolysis gases and of water vapor, resulting in a relatively stable isolating sheath. This envelope hinders dramatically the passage of current, ultimately mediating the electrochemical dissolution of the metallic workpiece. Compared to traditional electropolishing, EPPo notably features slower material removal for more control over geometry conservation and electrolyte compositions much more benign to the workplace and to the environment. Yet it retains all the advantages of contactless, geometry-independent polishing.

Titanium and its alloys are of notorious interest to a wide range of industries and as such are a particularly valuable application for EPPo. The electrodissolution of titanium, and of some of the elements commonly alloyed to it like aluminum, proves however significantly more difficult to control than that of other EPPo metals. These difficulties are rooted in a strong competition against the formation of insoluble oxides into a compact and process-blocking layer. A range of electrolytes and Ti-complexing agents were combined with different electrical and thermodynamical parameters to investigate this race between electrodissolution and oxide formation. *In situ* measurements of the electric response from the system and of the glow light emitted by the process were collected and analyzed. Characterization of the treated surfaces was performed, in terms of elemental and chemical composition, morphology and topography, to help elucidate the interactions at play during EPPo. The range of surface states that can be produced by the method is explored, both in topological and chemical terms, with the ultimate goal of enabling pathways to subsequent surface treatment and coating.

2:20pm **G4+G5+G6-ThA-4 Characterization of Surface Modification Mechanisms for Boron Nitride Films under Plasma Exposure***, T Higuchi,* Kyoto University, Japan*; M Noma,* Shinko Seiki Co., Ltd, Japan*; M Yamashita,* Hyogo Prefectural Institute of Technology, Japan*; K Urabe,* Kyoto University, Japan*; S Hasegawa,* Osaka University, Japan*; **Koji Eriguchi**,* Kyoto University, Japan

Boron nitride (BN) film has attracted much attention recently because of the superior mechanical properties (hardness) and the unique electronic structure. [1][2] In addition, BN films have potential applications to the usage in harsh environment such as space, *e.g.* (1) solid lubricant material with a low friction coefficient in ultra-high vacuum [3] and (2) coating material on the inner wall of an electric propulsion system for a long-term mission. [4] Recently, we proposed a reactive plasma-assisted coating (RePAC) system [5] and fabricated high-hardness (cubic) BN stack structures on a Si substrate with anti-delamination feature. Regarding the application to solid lubricant, we showed friction coefficient lowering phenomena in BN films under ultra-high vacuum (~10^{-6} Pa), which is in sharp contrast to usually-observed "friction coefficient increase". [6] In this study, we focus on the other issue, the surface modification mechanisms under plasma exposure. A (cubic) BN film consisting of the surface (35 nm) and bulk regions was formed on a Si substrate using the RePAC system. The mechanical property degradation after low-pressure Ar plasma exposure was investigated in detail. The energy of incident ions was controlled to be 170 or 690 eV with a constant ion flux (4.5×10^{13} cm^{-2}s^{-1}). A nano-indentation test identified a plasma-damaged layer in the vicinity of the surface region (a few nm thick), where the indentation hardness (H_{IT}) was modified. On the basis of a three-layer BN structure model, we revealed that the H_{IT} of the damaged layer increased in the case of 170 eV, while the H_{IT} decreased in the case of 690 eV. We performed a molecular dynamics (MD) simulation to predict the surface structure change by particle impacts, where the Tersoff- and Wilson-type potential models [7][8] were used for B–N and Ar–(N or B) systems, respectively. The MD simulation clearly assigned that a change of the cubic BN fraction in the rhombohedral-/hexagonal-BN background within the surface region leads to the H_{IT} change. The present findings should be implemented in designing BN films for harsh environment applications.

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[7] K. Albe and W. Moller, Computational Mater. Sci. **10** (1998) 111.

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2:40pm **G4+G5+G6-ThA-5 Ultra-fast Decoating Method for PVD Coatings***, B Wittel, C Buechel, T Cselle,* Platit AG, Switzerland*; **Bo Torp**,* Platit Scandinavia, Denmark*; A Lümkemann, D Bloesch,* Platit AG, Switzerland

Production of cutting tools requires energy and materials which are getting scarce and thus, more expensive. To save these resources, repeated use of a refurbished cutting tool is an important issue. A PVD coated cutting tool can be decoated, reground and recoated. The conventional ways to remove a worn PVD coating from a cutting tool are slow and expensive. This paper introduces a fast electrochemical decoating system with computer control, using pulsed voltage and end-point detection. The decoating times are in the range of minutes. A thin TiN adhesion layer is used under the coating to be removed. Cobalt leaching is prevented. A PVD coating applied after decoating shows excellent adhesion.

3:00pm **G4+G5+G6-ThA-6 Development of an Omni-phobic Spray Coating for the Oil and Gas Industry***, **Carol Ellis-Terrell**, R Wei, R McKnight,* Southwest Research Institute, USA*; X Huang, K Lin,* Beijing Sanju Environmental Protection & New Materials Co., Ltd., China

In the oil and gas (O&G) industry, low surface energy coatings are of great interest. In the upstream industry, specifically in crude oil exploration and production, where the accumulation of asphaltenes and paraffin wax can clog production tubing completely. Clogging of the tubing may result in the abandonment of the upstream exploration and a significant loss in a multimillion dollar investment. In the downstream petrochemical refinery, the accumulation of carbon deposits, known as coking, is regularly encountered on the walls of reactors. The periodic cleaning of the reactor vessel is not only a very costly process due to the interruption in production; it is also an unsafe operation because manual operation is still heavily involved.

Low surface energy coatings are crucial to prevent foreign substances from sticking to the surface. Water contact angle (WCA), or oil contact angle (OCA) measurements are commonly used to characterize the surface energy. When both the WCA and OCA are >90°, the surface is termed as omni-phobic, reducing/inhibiting the adhesion of oil or water to the surface. Even though, there are a number of techniques used to fabricate omni-phobic surfaces, many are very expensive, short-lived, and impractical for real-world applications. In this study, we will discuss the solution-based spray coating, which is generated by synthesizing and functionalizing nanoparticles. We will present the particle synthesizing process, the chemical composition, the structural and morphological properties, wetting properties, thermal resistance, and the durability. Finally, we will present a few application examples of the omni-phobic coating in the O&G industry.

3:20pm **G4+G5+G6-ThA-7 Hybrid Reactive High Power Impulse Magnetron Sputtering System Combined with Electron Cyclotron Wave Resonance ECWR Plasma used for the Deposition of Semiconducting Thin Films.***, **Zdenek Hubicka**, M Cada,* Institute of Physics CAS, v. v. i., Czech Republic*; S Kment,* Institute of Physics, Academy of Sciences of the Czech Republic, Czech Republic*; V Stranak, R Hippler,* Institute of Physics, Academy of Sciences of the Czech Republic*; J Olejnicek,* Institute of Physics CAS, v. v. i., Czech Republic **INVITED**

A hybride reactive high power impulse magnetron sputtering system (HiPIMS) combined with a RF electron cyclotron wave resonance ECWR plasma (HiPIMS+ECWR) was investigated as a source for the deposition of oxide semiconductor thin films for photoelectrochemical applications as solar water splitting cells and dye sensitized solar cells (DSSC). It includes various forms of TiO_2 thin films working as barrier layers with enhanced electron transport in DSSC perovskite solar cells. Furthermore thin films of Fe_2O_3 and WO_3 working like photoanodes in solar water splitting cells were deposited with this hybride plasma source. The non-stoichiometric oxide thin films have recently gained a huge attention due to their practical applications. These semiconducting materials can have interesting optical, electrical and photoelectrochemical properties with possible applications in various types of optoelectronic devices or different types of solar electrochemical cells working here as the cocatalysts. The defect engineering (DE) has become an attractive research direction for improving the optical and electronic properties of these materials towards highly efficient PEC processes. The main limitation related to the current DE approaches is that they are predominantly realized via a high-pressure high-temperature gas reduction. In the presented work the non-stoichiometric oxide thin films such as WO_{3-x}, TiO_{2-x} were deposited by the HiPIMS+ECWR plasma system. By adjusting the deposition conditions, we can regulate the extent of induced defects and, moreover under significantly reduced temperature. Defined $Ar+O_2$ working gas mixture at different pressures in the range from 0.05- 5 Pa were used for the deposition process with eventual additional substrate annealing in the RF-ECWR reactive plasma after the deposition process. This annealing could further control the stoichiometry of deposited films and change the crystal structure with other semiconducting properties. The plasma was monitored during the deposition process by a time resolved ion mass spectroscopy with energetic resolution, Langmuir probes, RF impedance probe and calorimetric probe. Deposited films were analyzed by XRD, Raman scattering, electrical conductivity and optical absorption measurements. Photoelectrochemical properties of these films in connection with other materials were investigated by photoelectrochemical measurement in three electrode cell.

4:00pm **G4+G5+G6-ThA-9 Pre- and Post-Surface Treatments using Electron Beam Technology for Load-Related Application of Thermochemical and PVD Hard Coatings on Soft Substrate Materials***, **Anja Buchwalder**, R Zenker,* TU Bergakademie Freiberg, Germany **INVITED**

With their specific layer features and properties, surface treatments such as thermochemical treatment (nitriding, boriding) and hard coating (PVD) cover a broad field of application, and in particular for the wear and corrosion protection of steels. Limitations exist, however, when applying these surface treatments to cast irons and aluminum alloys with respect to both their treatability and load-bearing capacity.

The current contribution deals with investigations into duplex surface treatments, where a pre- and post-electron beam (EB) surface treatment (e.g. hardening, remelting, alloying etc.) was combined with one of the above-mentioned treatments. Among other factors, the thermal EB surface treatments were characterized by high heating and cooling rates that facilitated the generation of a variety of non-equilibrium microstructures, which exhibited increased hardness and had minimal thermal effects on the surrounding base material. Furthermore, the layer thicknesses were one or two orders of magnitude higher than those generated by thermochemical treatment or hard coating.

Based on the extensive results, the study should demonstrate (using cast irons as an example) the extent to which duplex treatments can overcome the aforementioned limitations, and how the tribological and/or corrosive load behavior is affected. The property profiles achieved after duplex surface treatment were strongly dependent on the inherent microstructural and chemical processes. These complex processes were influenced by a range of parameters, such as the respective temperature and time of the secondary process, the thermal stability of the EB surface layer generated firstly etc..

The matrix microstructures of cast irons are comparable with those of steels. As is known from steel processing, however, the additional presence of soft graphite and high silicon contents changes the structures and properties of the surface layers generated. This was demonstrated by means of three different treatments and temperature/time regimes: PVD hard coating (575 K/3 h), nitriding (815 K/8-16 h) and boriding (>975 K/3-10 h) performed as both single and duplex surface treatments.

Thus, the focus of the investigations was on comparable investigations of the graphite containing states (single treatment) and the graphite eliminated states after EB liquid surface treatments (duplex treatments).

Hardness measurements, scratch tests and unlubricated pin-on-disc wear tests using different normal loads were realized to facilitate characterization of the different load-bearing capacities of the single- and duplex-treated layers.

4:40pm **G4+G5+G6-ThA-11 Black Oxide and Carbon-Based Coatings for Roller Bearing Applications***, **Esteban Broitman**, X Zhou,* SKF Research & Technology Development Center, Netherlands

It is widely accepted the advantages of using coatings to improve bearings performance. In some applications, they can provide different properties like electrical insulation, low friction, and resistance to corrosion, contact fatigue, abrasive wear, and plastic deformation. Several bearing producers are putting a great effort on coated bearings development as an added value in their product. Among different kind of available industrial coatings, there are two standing out: *"Black Oxide"* and *"Carbon-based"* coatings.

In the first part of the presentation we will introduce two typical carbon-based coatings used by the bearing industry: "diamond-like coatings" (DLC) and WC/C nanostructured coatings. We will show how carbon-based coatings can be deposited at industrial scale on hardened steel bearings and gears which are temperature-sensitive using low deposition temperatures. We will explain how it is possible to deposit films with different amount of sp^2-sp^3 bonding ratios by just changing fundamental deposition parameters, leading to six different microstructures: graphite, non-hydrogenated a-C (amorphous) and ta-C (tetrahedral) carbon coatings, hydrogenated a-C:H and ta-C:H films, and a soft polymeric coatings. We will show films containing nanometric-thick multilayers of different nanostructure that can be tailored according to the applications to obtain coatings with high toughness, high elasticity, and/or very low friction coefficient.

In the second part we will introduce Black Oxide, which is a coating formed by a chemical reaction on the surface of the bearing steel. We will describe the coating process consisting of about 15 steps where the parts to be coated are immersed in alkaline aqueous salt solutions at defined temperatures in the range 130-150 ^{o}C. The reaction produces a dark conversion layer of approximately 1 µm thick formed by mainly magnetite Fe_3O_4. Compared to non-coated bearing steels, we will show experimental results demonstrating Black Oxide benefits: increasing moisture corrosion resistance, steel chemical attack preservation from some aggressive lubricant additives, steel embrittlement protection by hydrogen permeation reduction, enhancing micropitting protection, and improved smearing resistance from bearing sliding during high-load conditions.

In the last part we will present some applications of SKF Black-Oxide and NoWear® carbon-based bearings to extend maintenance and life expectancy of specialized bearings in different areas, like the automotive and wind-energy.

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