Surface Engineering - Applied Research and Industrial Applications

Room Pacific Salon 1 - Session G1+G3-ThM

Advances in Industrial PVD, CVD, and PECVD Processes and Equipment/Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

Moderators: Ladislav Bardos, Uppsala University, Sweden, **Emmanuelle Göthelid**, Sandvik Machining Solutions, **Ali Khatibi**, Oerlikon Balzers, Oerlikon Surface Solutions AG, **Christoph Schiffers**, CemeCon AG, Germany

8:00am **G1+G3-ThM-1 Predicting Coating Uniformity and Cathode Utilization in Magnetron Sputtering Applications using Numerical Simulation**, ***Adam Obrusnik***, *P Zikan,* Plasma Solve, Brno, Czech Republic

In many disciplines of applied science, numerical simulation and computer-aided engineering (CAE) are well established and are being commonly used in process design and utilization. This is not the case in plasma processing science, where numerical simulation is still largely considered an academic endeavour. This is partly due to the complexity of the problem and partly due to the lack of tools available.

In this contribution, we aim to illustrate that numerical models of PVD processes and the codes necessary for implementation of these models have matured enough and are ready to be used on the industrial scale. We provide real-life examples as to how a numerical simulation can be instrumental in optimization of magnetron sputtering processes and low-pressure cathodic arc PVD. To that end, we utilize solvers relying both on continuum plasma models and particle-based models (DSMC, direct-simulation Monte Carlo). These solvers are largely based on open-source computational libraries OpenFOAM and Elmer, which allows for excellent computational scalability and computation in realistic 2D and 3D geometries. The codes presented are capable of predicting application-relevant observables, e.g. magnetron cathode consumption, multilayer structure and coating uniformity on 3D rotating samples.

The contribution illustrates the potential of open-source computational solutions as well as cloud computing, which might be necessary for addressing industrial-scale plasma simulations.

8:20am **G1+G3-ThM-2 Multinary HiPIMS**, *T Leyendecker, W Koelker, S Bolz,* ***Christoph Schiffers***, CemeCon AG, Germany

The almost unlimited choice of materials is one of the biggest strength of HiPIMS. It offers a variety of opportunities for tailoring coatings by alloying of the chemical composition or by using species from certain elements to densify the film by heavy ion bombardment.

Carbon based coatings are mainly used for tribological applications. However, coatings such as TiCN and WC/C are of high relevance for tap tool applications – a market of about 100 Mio tools per year. Commercial coating products for the threading industry are most frequently multilayer designs of an AlTiN with a carbon containing top layer. This gives HiPIMS a new challenge: multinary coatings of materials with rather different properties.

This paper will introduce a new HiPIMS control concept offering for every source an individual set of HiPIMS pulse parameters. Now the coating designer can take the very different ionization potential of different materials into account or select a source for heavy ion bombardment while the other ones are optimized for highest sputtering rate.

All this with full synchronization of the HiPIMS cathodes to the HiPIMS table bias. Hence, the film's designer can actively go for the ionized target species while suppressing the incorporation of sputtering gas into the film.

Data from plasma analysis as well as hardness and stress measurement reveal a huge effect of the pulse parameters such as frequency and pulse length on the film properties.

Multinary HiPIMS gives freedom to coating engineers and broadens the application range of HiPIMS.

Case stories from the thread tool industry underline the industrial relevance of the concept.

8:40am **G1+G3-ThM-3 From Small Parts to Particles – Experiences in Bulk Coating**, ***Heidrun Klostermann***, *F Fietzke, B Kraetzschmar,* Fraunhofer FEP, Germany

Bulk coating seems to be an intriguing variant of vacuum coating for small mass parts. Compared to individual part coating, the handling effort is considerably reduced. This applies to indirect and direct labor such as the production and maintenance of adapted fixtures and the charging and de-charging of individual parts. Furthermore, the utilization of processing volume can be maximized, avoiding void space between the parts. This benefit grows with decreasing part size. However, when it comes to particles, new challenges arise in bulk coating that thwart the fast success.

The surface to be coated per volume increases with decreasing size of the parts/particles. Therefore, high deposition rates are required in order to keep the processing time reasonably low. The economic assessment of bulk vacuum coating has to be made for every individual coating task including a specific substrate, the intended function of the coating, the production volume and the costs. Certainly, for many high volume bulk goods vacuum coating is not an option. However, novel high tech materials are often composites in which bulk materials are included and combined with metals or polymers to result in improved properties and/or reduced weight. Correspondingly, surface functionalization of bulk material becomes more important and more requested.

Fraunhofer FEP has pursued the objective of vacuum bulk coating for several years. We have developed a technology for corrosion resistance coating of rivets. Based on the barrel coating device ALMA 1000, which includes the high rate plasma activated evaporation technique as well as the magnetron sputtering technique, other bulk materials are envisaged for surface functionalization. The challenge starts with the handling of particulate material, its behavior in the rotating substrate drum and its implication for the vacuum process.

First experiences with different particulate materials will be presented that illustrate options and limitations. The contribution is thought to stimulate new ideas for surface functionalized bulk materials that can eventually be solved by vacuum plasma treatment and coating processes.

9:00am **G1+G3-ThM-4 A Novel Industrial Coating System for the Deposition of Smooth Hard Coatings Combining HiPIMS V+ and Rotatable Magnetrons**, ***Herbert Gabriel***, *J Santiago Varela,* PVT Plasma und Vakuum Technik GmbH, Germany*; I Fernandez,* N4E Nano4Energy S.L.N.E, Spain*; N Dams,* PVT Plasma und Vakuum Technik GmbH, Germany*; A Wennberg,* N4E Nano4Energy S.L.N.E, Spain*; J Lu,* PVT Harbin Coating Ltd, China

Multi-layered, nano-structured metal-nitride and carbo-nitride coatings are very well established in the cutting tool industry as well as in other industries. For years most of such coatings have been deposited by arc evaporation despite the badmouthed "droplets", since arc evaporation is an extremely economic process with significant advantages such as high intrinsic ionization which is particularly beneficial during metal etching.

Magnetron sputtering with its low ionization and its deficiencies in adhesion and productivity significantly improved with the development of HiPIMS. An even more significant improvement is the HiPIMS V^+ process where adding positive reverse pulses creates enhanced ion assistance and incorporation to the growing film, thus also increasing the deposition rate .

On the other hand, rotatable magnetrons are well known to provide better material usage, longer operation and higher operation power levels.

The novel industrial system introduced in this paper shows the unique combination of HiPIMS V+ with rotatable magnetrons in a batch coater system, thus enhancing system productivity. This process is applied in a multi-cathode magnetron sputtering system using 4 pieces of 1 m long rotatable cathodes equipped with a strong unbalanced magnetic design allowing high ion-to-neutral ratios to the substrate. The system can be configured to operate in unipolar HiPIMS, Dual Bipolar HiPIMS or DC-Pulsed.

Besides a description of the newly designed coating system, nitride and carbo-nitride nano-structured multilayered coating structures based on Ti, AlTi, AlCr and TiSi deposited in such system are shown and characterized, concerning their micro-structure, adhesion, microhardness and composition.

Wear and performance data are presented.

9:20am **G1+G3-ThM-5 From DCMS to HiPIMS: A Giant Leap for Cutting Tools?**, ***Bastian Gaedike***, Hartmetall-Werkzeugfabrik Paul Horn GmbH, Germany **INVITED**

Carbide cutting tools for machining (e.g. milling or turning) are coated with physical (PVD) or chemical vapor deposition (CVD) to meet the high requirements. Arc and DCMS (Direct Current Magnetron Sputtering) have dominated the PVD sector for decades.

In recent years the PVD process HiPIMS (High Power Impulse Magnetron Sputtering) has moved more and more into the focus of the cutting tools

industry. Research in this area has already progressed considerably. Since the observation of high peak currents by high-frequency pulsing by Kouznetsov in 1999, researchers have published several hundred publications on HiPIMS. While the technical details of the HiPIMS process are highly interesting for researchers and developers, the focus for users and manufacturers of cutting tools is more on the use of coatings.

The machining of new materials for aerospace and medical technology has greatly increased the demands on cutting materials and cutting edge geometries. In general steel and stainless steel processing, there is also an increase in downtimes and cycle times. For the manufacturers themselves, not only the performance of the layers is decisive, but also the economic efficiency in production. The low deposition rates of HiPIMS, which are often reported in publications, are a major topic here.

The main topic of the presentation is the requirements of users and manufacturers of cutting tools and the resulting challenges for research and development. In addition to various applications and problems in machining, the coating of sharp cutting edges and the problem of the deposition rates of HiPIMS are under discussion.

10:00am **G1+G3-ThM-7 Application of Twin-Roll PECVD for Surface Functionalization on Flexible Substrate**, *Y Isomura, Y Ikari,* ***Tadao Okimoto,*** Kobe Steel, Ltd., Japan

Technological development of surface functionalization is of great significance today in the wide field of application. This ranges, for instance, from hard nitride coating for cutting tools to functional transparent electrode on a flexible polymer film. For this purpose, plasma deposition and treatment techniques of cathodic arc, sputtering, Plasma Enhanced CVD (PECVD) are largely used in an industrial production scale. A batch type system is commonly employed in hard coating application where a variety of individual components is deposited by tailor-made coatings while a continuous production with Roll to Roll process, hereafter referred to as R2R, provides a high productivity for surface functionalization on a flexible substrate. Application of R2R has been expanding due to a recent increase in demand for smart devices such as functional display, wearable devices and sensors, energy conversion and storage, contributing towards realization of sustainable smart society in the near future.

We have developed the so-called Twin-Roll PECVD technique integrated into R2R process in an industrial scale. A unique feature of Twin-Roll PECVD is that the winding rolls themselves for flexible substrate serve as the electrode for discharge of PECVD process. This provides a stable discharge for a long time compared to a conventional pulse PECVD since no deposition occurs on the surface of electrode, which often limits productivity of deposition of non-conductive coating such as oxide and nitride. Optimization of magnetic field on the electrode enables to sustain the discharge at a relatively low pressure of 1~10 Pa. The low pressure PECVD process suppresses the formation of dust particles, and hence the film deposition with a low defect density is realized.

In this work we report the basic principle of Twin-Roll PECVD as for a new type of plasma processing as well as some applications of surface functionalization on flexible substrate using this technology. We have deposited and characterized SiOx films exhibiting a high water vapor barrier property, SiOx/SiNx films with a high refractive index, and DLC (Diamond-Like Carbon) films showing a high infrared transmissivity. Spectrophotometry, XPS, TOF-SIM, water vapor transmissivity measurement were mainly used for film characterization. In addition an application of Twin-Roll PECV for deposition of heat-ray reflecting film is demonstrated.

10:20am **G1+G3-ThM-8 A New System Platform for Ultrafast Nitriding and Diamond Like Carbon (DLC) Deposition Based on a Hollow Cathode Discharge**, ***Frank Papa,*** *T Casserly, A Tudhope, S Gennaro,* Duralar Technologies, USA

Diamond Like Carbon (DLC) has become one of the most important coatings in the Physical Vapor Deposition (PVD) industry due to its chemical inertness, hardness and low coefficient of friction. For mass production, these coatings are usually produced in large batch coaters with PVD interlayers for adhesion and load absorption with a Plasma Enhanced Chemical Vapor Deposition (PECVD) DLC layer on top. Typical cycle times for such a batch system are on the order of 6-9 hours. A new PECVD system platform based on hollow cathode technology has been developed for the deposition of DLC (a-C:H) with a complete door to door cycle time of less than 30 minutes for a 2-3 µm DLC coating. In addition to high rate DLC coating (0.5 to 1 µm/minute), ultrafast plasma nitriding can also be done before the DLC process in order to harden and chemically modify the surface before DLC coating. Titanium alloys, stainless, carbon and alloy steels are suitable materials for such processes. In addition to the short cycle times, three dimensional parts with aspect ratios of 15:1 (length:diameter) can also be coated with coating on both external and internal surfaces. DLC coating thicknesses greater than 50 µm can be achieved.

10:40am **G1+G3-ThM-9 Combinatorial Development of Nitride and Oxide Thin Films on an Industrial Scale**, ***Rainer Cremer,*** KCS Europe GmbH, Germany **INVITED**

The ever increasing complexity of modern coatings triggers the need of sophisticated technologies for rapid and commercially advantageous development methods. One possibility to significantly increase the speed of materials development is the use of combinatorial approaches.

In this paper, the applicability of such combinatorial methods in industrial development of advanced materials is illustrated presenting various examples for the deposition and characterization of one- and two-dimensionally laterally graded coatings. These coatings were deposited by means of magnetron sputtering, arc ion plating and plasma-enhanced chemical vapor deposition.

To illustrate the advantages of this approach for the industrial development of advanced materials, the multi-component metastable hard coatings (Ti,Al)N, (Ti,Al,Cr)N and (Ti,Al,Si)N as well as various non conductive oxides and nitrides were investigated with respect to the relations between structure and composition on one hand and physical properties like hardness, erosion resistance, cutting performance and oxidation behavior of these coatings on the other.

11:20am **G1+G3-ThM-11 Protective, Tribological and Decorative PECVD Coatings Deposited with a New Microwave Source: Plasma and Layer Characterization for Appropriate Applications**, ***Rolf Schäfer,*** *T Radny, K Nauenburg,* robeko GmbH & Co.KG, Germany*; S Ulrich,* Karlsruhe Institute of Technology (KIT), IAM, Germany

The KIT designed a novel MW source with a parabolic reflector to focus the high microwave plasma density directly onto the substrates during the deposition of scratch, corrosion and wear protective, tribological, biocompatible and decorative coatings by a PECVD processes using e.g. siloxane and hydrocarbons as precursor compounds. A number of MW sources can be arranged in line or even lateral to form a larger coating area to be used in Inline coaters or larger batch coating systems, also being easily combined with other PVD sources e.g. planar and rotatable sputter magnetrons, both with the option to be driven with a HiPIMS generator to create new and promising combination of diverse plasma effects. At the very first it is necessary to characterize the plasma by different diagnostic methods, e.g. Langmuir probe measurements, OES, RFA and others, but also work out the influence of the plasma parameter settings for the properties of the deposited layers, e.g. diamond - or quartz-like-coatings. At least the design has to be optimized in details to ensure a long-lasting reliable stability of process conditions and product properties in industrial production. First results for all issues will be presented.

11:40am **G1+G3-ThM-12 Complex Coating Technique for Smallest Part of Advanced Powertrain Fuel System**, ***Sung Chul Cha,*** *H Park, J Lee,* Hyundai Motor Group-Hyundai Kefico, Republic of Korea*; K Ko, C Shin,* Dongwoo HST Co. Ltd., Republic of Korea

The objective of this paper is to achieve the high quality SiO-DLC (Diamond Like Carbon) coating on small spherical part with diameter of 2-4 mm applied to the advanced powertrain fuel system. Silicon and oxygen incorporated DLC reduces internal residual stress and improves high temperature stability compared to DLC. The spherical part moves continuously up and down and hits their counterpart. Therefore this part is required to have high hardness and wear resistance. Conventional process, this part firstly welded with bar shaped part and then assembled with further parts, finally coated as assembled state. However in this manner, the maximum amount of charging in one coating batch of coating machine is limited due to big size of whole component, causing cost increasing. Furthermore the assembled component can be contaminated by alkali cleaning agent during cleaning process before and after coating and discolored by the process gas during coating process. Therefore the spherical part is to be coated before welding on the bar shaped part.

One of the challenges of this work was mounting the spherical parts in the coating jig. To maximize the production amount, parts shall be mounted in vertical direction in the coating machine. Therefore the appropriate jig is designed and installed with a magnet substrate backside of the jig to magnetically hold parts. The other challenge was designing for masking in the jig. At least 0.7 mm height of non-coating region must be secured

concerning heat damage on coating by laser welding process. Thus the parts should be mounted on the masking jig with high precision. The tolerance of the jig had to be as small as possible to block the inflow of coating material into the gap between spherical part and jig. Moreover the jig should be as thin and narrow as possible to maximize the production amount.

The coating is composed of three layers, Cr as bonding layer, WC or CrN as buffer layer and SiO-DLC as functional top layer. Bonding and buffer layers are coated with reactive or non-reactive sputtering method and top SiO-DLC layer is coated by reactive sputtering with HMDSO (Hexamethyldisiloxane). The minimum properties of hardness was 20 GPa, of coating thickness 1.5-2.5 um and of roughness lower than Ra 0.05 um. With only PACVD, coating hardness of part's equator zone could not be satisfied due to the limitation of complex shape. In conclusion, SiO-DLC coating technique by reactive sputtering with high precise jigging and masking technique resulted best properties for modern powertrain fuel system, detailed described in this paper.

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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[8] K. Eriguchi, J. Phys. D **50** (2017) 333001.

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 multi-

million 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 °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.

Surface Engineering - Applied Research and Industrial Applications
Room Grand Hall - Session GP-ThP
Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-ThP-1 Effect of Plasma Nitriding and Modulation Structure on the Adhesion and Corrosion Resistance of CrN/Cr_2O_3 Coating, *C Huang, F Yang, Y Tsai,* ***Chi-Lung Chang,*** Ming Chi University of Technology, Taiwan

The increasing demand for high performance coatings has led to the production of coatings which are becoming more sophisticated in terms of their engineered microstructure and properties. An extensive interest of high power impulse magnetron sputtering (HiPIMS) as a novel PVD technology in academia and industry owing to their dense and smooth coatings properties when compared to traditional PVD technologies. However, the adhesion strength still not insufficient, therefore a plasma nitriding process is introduced before the HiPIMS process. On the other hand, the carbon steel has a very poor corrosion resistance in an atmospheric environment, which one is needed to solve by various surface treatment technologies in environmentally friendly.

In this study, a continuous process combines both vacuum plasma nitriding and HiPIMS CrN/Cr_2O_3 multilayered coating technology is used. Before CrN/Cr_2O_3 multilayer coating, the vacuum plasma nitriding is carried out at different nitrogen flow rate for 1~5 h with a bias output of HiPIMS power between 0.5 and 2.5 kW, which is at a fixed temperature of 400℃. After that CrN/Cr_2O_3 multilayer films with different bi-layer thickness were deposited onto carbon steel and silicon p-type (100) wafer substrates at 400℃ using Cr targets with a nitrogen (or oxygen)/argon flow ratio of 0.2, by high power impulse magnetron sputtering technique. The bi-layer thickness was varied by time-controlled with a switch in between the nitrogen and oxygen to obtain different nanoscale multilayered period thickness. The modulation structure characteristics of the CrN/Cr_2O_3 multilayer films between 100 nm to 5 nm were systematically investigated. The results have demonstrated that both the nitriding effect and the modulation period (Λ) was strongly to affect adhesion strength between carbon steel and the coating. In addition, the corrosion resistance of carbon steel is strongly improved by the CrN/Cr_2O_3 multilayer film.

GP-ThP-2 Study on SiN and SiCN Film Production using PE-ALD Process with High-density Multi-ICP Source at Low Temperature, ***Hohyun Song,*** *H Chang,* Korea Advanced Institute of Science and Technology, Republic of Korea

SiN and SiCN film production using plasma-enhanced atomic layer deposition (PE-ALD) is investigated in this study. A developed high-power and high-density multiple inductively coupled plasma (multi-ICP) source is used for a low temperature PE-ALD process. High plasma density and good uniformity are obtained by high power N2 plasma discharge. Silicon nitride films are deposited on a 300-mm wafer using the PE-ALD method at low temperature. To analyze the quality of the SiN and SiCN films, the wet etch rate, refractive index, and growth rate of the thin films are measured. Experiments are performed by changing the applied power and the process temperature (300–500 °C).

GP-ThP-3 PEO Coatings for Adhesive Bonded Aluminium Structures, ***Dominic Shore,*** *A Rogov, A Matthews, A Yerokhin,* The University of Manchester, UK

Plasma Electrolytic Oxidation (PEO) has received much attention in research for the production of oxide coatings with excellent tribological performance and corrosion resistance. This study looks into a further application of PEO as an alternative to conventional anodizing techniques for the preparation of aluminium for adhesive bonding. Conventional anodizing processes have been applied to adhesive bonded aluminium components to promote increased bond durability tracing back to the first half of the 20th century. However, Conventional anodizing procedures generally use strongly acidic electrolytes which have a substantial environmental impact. Anodizing procedures are generally multi-stage processes which can be resource intensive and time consuming. PEO offers an alternative route for the production of well adhered oxide coatings where weak alkaline electrolytes can be utilised in place of the highly acidic electrolytes associated with conventional anodizing processes. PEO has the further potential to reduce the number of additional treatments prior to and after the anodizing stage offering scope for resource and time saving. To provide bond durability comparable to that offered by the conventional anodizing techniques currently used, PEO coatings must promote sufficient mechanical interlocking and physical/chemical affinity between the surface and adhesive in addition to good corrosion resistance.

Work has been carried out on the optimisation of PEO coatings on aluminium alloys with regards to the application of adhesion bonding. Through the use of varying processing parameters and different electrolyte compositions, coatings with properties designed to promote enhanced bond strength are being developed. Topological features of the developed PEO coatings, including surface porosity which is important for the promotion of mechanical interlocking in the adhesive bond have been analysed. Chemical analysis of the surface composition of the oxide and the adsorption groups formed at the oxide/adhesive interface has been carried out to deduce the chemical nature of the adhesive bonding occurring on PEO coatings formed under different conditions. As a result, a scientific description as to how the surface features of PEO coatings contribute to adhesive bond durability is being summated, which will lead to further optimisation of PEO coatings for this application.

GP-ThP-5 Hydrogen Barrier Coatings Deposited by Magnetron Sputtering: A Study of Different Oxide Materials and Their Microstructure on the Hydrogen Permeability Properties, ***Sofia Gimeno,*** Fersa Bearings, Spain; *J Garcia,* Universidad Publica de Navarra, Spain; *I Quintana, L Mendizabal, C Zubizarreta,* Physic of Surfaces and Materials Unit, IK4 – TEKNIKER, Spain

White Etching Cracks (WEC) is the main cause of premature failure on bearings used in wind turbine sector. This premature failure mode is still under debate due to the lack of a clear theory about how it is produced and which are the factors involved in the WEC damage. One of the most important theories is based on Hydrogen embrittlement, due to hydrogen diffusion in steel under rolling contact fatigue (RCF) [1].

The development of novel surfaces which -are able to avoid or delay the diffusion of Hydrogen would be considered as a key point to solve the WEC problem. In this study, films based on WO_3, SiO_2 & Al_2O_3 oxides grown by pulsed dc magnetron sputtering have been designed to act as barrier to Hydrogen permeation, delaying or avoiding the diffusion of this in 100Cr6 steel. The objective of this study is to analyze the behaviour of the different oxide materials, as well as the influence of the morphology of coatings on the permeation of Hydrogen.

WO_3, SiO_2 & Al2O3 thin films were deposited on 100Cr6, Niquel and silicon substrates. The adhesion, microstructure and crystal structure of oxide films were investigated and correlated with barrier properties against hydrogen permeation.

Hydrogen permeability of different films was studied using differential pressure method described in ISO 15105-1:2007. Nickel was used as substrate due to the known and high permeability of this material to hydrogen.

GP-ThP-6 Process for Obtaining TiO_2/SiO_2 Systems using Magnetron Sputtering RF from Ceramic Targets: Studies on their Anti-Reflective Response, ***Dario Zambrano,*** *R Villarroel, R Espinoza,* Universidad de Chile, Chile

Nanostructured systems of SiO_2 and TiO_2 produced by magnetron sputtering technique have allowed the development of optical filters that maximize the conversion of light in different devices and applications [1–4]. The anti-reflective coatings (ARCs) of SiO_2 / TiO_2 systems allow obtaining a greater contrast and better image quality in applications such as TV screens, cell phones, projectors, among others. In addition, they improve the quantum efficiency in photovoltaic panels, increasing the power generation capacity [5].

In this research nanostructured films composed by multilayer stacking of SiO_2 and TiO_2 were studied, considering the working pressure and the partial pressure of O_2 as variables for the modification of the microstructure of each monolayer and the influence on the anti-reflective response of the multilayer SiO_2/TiO_2 system.

The nanostructured layers of TiO_2 and SiO_2 were synthesized by magnetron sputtering RF, using ceramic targets of TiO_2 and SiO_2. The modulation of the optical performance of the ARCs were measured using spectrophotometry and ellipsometry. On the other hand, the microstructure of the ARC's was obtained using FE-SEM, AFM, XRD, and FTIR.

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GP-ThP-7 Microstructure Evolution of Overlay Welded Duplex Stainless Steel Joints, ***Paola Andressa Luchtenberg***, *R Torres, P Soares, P Campos,* Pontificia Universidade Católica do Paraná, Brazil

Duplex stainless steels have a good mechanical properties, wear and corrosion resistance and fatigue strength. This material have a higher price compared to austenitic steel, in some cases to lower the cost, companies use low carbon steel or low alloy coated with duplex stainless steel, than t his material can be employed through overlay welded coatings on mild steel components and equipment. In this work, the aim was to evaluate the overlay properties obtained through deposition of ER 2209 duplex stainless steel alloy on a mild steel ASTM A 516 Gr 60. The deposition was performed through GMAW welding process. The coatings were deposited using four heat input levels, which showed influence in phase balance in weld metal austenite/ferrite morphology. Microstructural characterization by optical microscopy and quantification of ferrite by ferritscope, showed that heat input, cooling rate and grain size influences on the formation of secondary phases, because this type of phase precipitate from ferrite or primary austenite. The reheating change the microstructure influencing positively or negatively in corrosion behavior of DSSs . The secondary austenite that precipitates due to the welding process in DSSs are grain boundary austenite (GBA), Widmanstätten austenite (WA), partially transformed austenite (PTA) and intragranular austenite (IGA) and each of them has their characteristic precipitation, like temperature, grain size, cooling rate. However, the corrosion resistance can be avoided by means of appropriate welding procedures and the phase control such as ferrite/austenite balance.

GP-ThP-11 Ion Beam Assisted Deposition of DLC for Sheet Metal Forming Tools, ***Lars Pleth Nielsen***, *K Almtoft, C Jeppesen, C Mathiasen, P Pedersen,* Danish Technological Institute, Denmark

A deposition process combining high-energy ion implantation of chromium ions into a condensing Fomblin-oil has been developed and charaterized. The composition of the IBAD-DLC film was measured by RBS and contain a mixture of elements (C, H, O, F and Si) from the condensing oil (Penta Phenyl Trimethyl Trisiloxane) besides the impinging high-energy Cr ions. The friction properties have been evaluated by pin-on-disk to be below 0.05. The hardness of the IBAD-DLC was measured to 10.7 GPa. Hardness, scratch tests and friction properties will be compared with PVD-based DLCs. Examples of different industrial applications of the IBAD-DLC coating in connection with sheet metal forming in the food sector will be presented.

GP-ThP-13 Effect of Interaction between Microbial Fluid and Electrode on Performance, ***Yu-Chen Liu***, *Y Yang,* National Taipei University of Technology, Taiwan

For the electrode reaction controlled by electron transfer, the electrode material has a great influence on the reaction rate. In terms of the material's conductivity, the reaction rate of the MFC will be improved by the high electron conductivity of the anode and the cathode. About the electrode area, as the electrode reaction is carried out at the electrode-solution interface, the reaction rate will be proportional to the electrode area, so a high surface area of the electrode development is extremely important. In addition, the metal surface modification, in order to develop a corrosion-resistant and highly collectible metal electrode modification is also an important research topic.

Electrodes of the Microbial fuel cell whether used in sewage treatment plants or marine rivers or lakes, the purpose of the production of electricity will be associated with the behavior of the fluid. Fluid behavior for the system efficiency and electrode usefulness would have a great impact. In this study, we focused on the interaction of microfluidic fluids with multi-morphological metal electrodes in the system. Through the observation of fluid mechanics and numerical simulation, we hope to understand the interaction between fluid and electrode, understand the interaction between bacteria and electrodes.

GP-ThP-15 Design of Low-Pressure Chemical Vapor Deposition Reactors Using Vertical Cavity Surface Emitting Lasers, ***Seungho Park***, *Y Noh, Y Kim,* Hongik University, Seoul, Republic of Korea; *B Kim, H Kim,* Viatron Technologies, Republic of Korea

VCSEL modules were investigated to design a LPCVD reactor for promising industrial applications due to advantages of excellent irradiation uniformity, rapid power controllability, and especially extended spatial scalability. Each VCSEL cell radiates perpendicularly from the wafer surface, differently from the conventional EEL.

A laser beam emitted from the VCSEL diffuses slightly as its power load increases, which is critical to irradiation uniformity and spatial scalability. The divergence angles best-fitting the radiative fluxes that were measured experimentally increased monotonically with a very small slope.

Through the experimental investigation on the temperature distribution on the silicon wafer irradiated by the high-power VCSEL beams, the optimal structure for the VCSEL heating system that ensured the uniform irradiation was obtained for wafers of 300 mm in diameter.

Based on the single-step chemical reaction mechanism for the deposition of polycrystalline silicon with silane gas species, the factors for the Arrhenius equation depicting the deposition process were obtained by the comparisons of numerical simulations and the available experimental results.

A simple reactor structure was used to investigate the variation in deposition rates on the wafer during the VCSEL LPCVD process. On the wafer surface the boundary condition of the energy conservation equation for the numerical simulation was given by the heat flux distribution calculated from the radiative irradiation from the VCSEL arrays, rather than the temperature distribution that has been widely used in simulations.

Comparisons of the deposition thicknesses calculated from the simulations under static and practical rotative conditions indicated that the wafer exclusion region increased considerably in the rotative condition due to the decrease in deposition rates in the edge region of the wafer. In order to minimize the wafer exclusion region, the VCSEL emitters which exerted influence on the wafer edge region were controlled to increase the emissive power slightly. As a result, the wafer exclusion zone was reduced considerably, without the help of additional structures to stabilize the gas flow and to reduce the energy loss in the wafer edge region commonly applied in practice.

GP-ThP-16 Optical, Mechanical and Anti-corrosive Property Investigation of Tantalum Oxynitride Thin Films for Hard Coating Applications, ***Jignesh Hirpara***, *R Chandra,* Indian Institute of Technology Roorkee, India

Mechanically hard coating with anti-corrosive behaviour is high in demand for the coating of metal surface in the medicine and industries. Tantalum oxynitride film deposited through reactive magnetron sputtering was investigated for its mechanical and anti-corrosive behaviour. XRD study revealed monoclinic phase with average crystalline size 270Å. Surface topographic was studied through AFM. Micrographs showed high uniformity with low roughness (<100 nm). Highly magnified FE-SEM imaging cleared the formation of nanoscale granules. Optical spectroscopic results demonstrated good transparency of the film (around 85%). Potentiodynamic polarization test and electrochemical impedance spectroscopy were performed with 0.1 M NaCl electrolyte, which demonstrated the high anticorrosive behaviour of the film. The measurement of mechanical hardness of the film was done using the Nanoindentation technique, which has presented the high value of reduced modulus (E_r) 132.98 GPa and hardness (H) 7.30 GPa. Hence, this material with high mechanical strength, transparency and anti-corrosive behaviour is quite suitable for the protective coating of the metal surface.

GP-ThP-17 Synthesis and Properties of Two-dimensional Zirconium Phosphate/Polyimide Nanocomposites as Anticorrosion Coatings, *G Lai,* National Chin-Yi University of Technology, Taiwan; *I Tseng,* Feng Chia University, Taiwan; *T Huang, P Tsai,* ***Mei-Hui Tsai***, National Chin-Yi University of Technology, Taiwan

In this study, novel zirconium phosphate/polyimide (ZrP/PI) nanocomposite was developed as an anti-corrosion coating material. The two-dimensional ZrP was prepared by the thermal reflux method and modified by the surfactant Jeffamine M1000. Various contents (0.5 ~ 5 wt.%) of ZrP were then homogeneously blended within PI matrix to obtain ZrP/PI coatings

with enhanced anticorrosion effect on cold-rolled steel electrodes. The characteristics of two-dimensional ZrP and nanocomposites were confirmed by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM) analyses. A series of electrochemical measurements such as corrosion potential (E_{corr}), polarization resistance (R_p), corrosion current (I_{corr}) and electrochemical impedance spectroscopy (EIS) were performed to evaluate the performance of the anticorrosion coatings.

GP-ThP-18 Improvement of the Corrosion Resistance in the ASTM F75 Alloy by Ball Burnishing, ***Eric Noe Hernandez-Rodrigues***, *D SilviaAlvarez, A Marquez Herrera, A Saldana Rovles, J Moreno Palmerin,* University of Guanajuato, Mexico

The ball burnishing is a process in which the surface of a material is compressed causing plastic deformation, and therefore changing the mechanical and chemical surficial properties. ASTM F75 alloy is used in the field of health for fabrication of orthopedic implants. In this application, the alloy is exposed to physiological fluids which are corrosive media. Therefore, improving the corrosion resistance is desirable in order to extend the lifetime of the implants. In this work, we propose the ball burnishing for improving the corrosion resistance of the ASTM F75 alloy. We implemented a design of experiments (DoE) methodology to minimize the corrosion. Two factors were analyzed in the DoE: burnishing force(F_B) and number of tool passes (N_P). The response variable was the corrosion current (I_{corr}). Tests were conducted in cylindrical ASTM F75 alloy samples (ø 25.4 mm x L 12 mm). The ball burnishing process was carried out in a conventional lathe and was only applied to one flat face of the samples. Burnishing force was varied from 150 N to 450 N, while tool passes was varied from 2 to 6. After burnishing, corrosion tests were performed by means of electrochemical polarization. Hank´s balanced salt solution was employed as the corrosive media. Tafel plots were used for determining I_{corr}. Under studied experimental conditions, $F_B$wasthe more significative factor in determining $I_{corr.}$ It was found that as N_P is set constant (at 2, 4 or 6 passes) and F_B is varied from 150 to 450 N, I_{corr} decreases (and therefore corrosion) when ball burnishing is performed with lower F_B values. On the other hand, when F_B is set constant (at 150, 300 and 450 N) little influence was found when N_P changes. A minimum I_{corr} value was found for 150 N and 4 tool passes. Under this condition I_{corr} was 4.9 nA in contrast to I_{corr} in unburnished samples which was 65.2 nA. These values showed a reduction of I_{corr} up to 92.5% in burnished samples, and therefore, a great improving in corrosion resistance.

GP-ThP-19 Surface Modification of Sputter Deposited γ-WO3 Thin Film for Scaled Electrochromic Behaviour, *R Chandra,* ***Gaurav Malik***, *S Mourya, J Jaiswal,* IIC, IIT Roorkee, India*; J Hirpara,* Indian Institute of Technology Roorkee, India

Here, we have reported the electrochromic properties of the highly ordered γ-WO3 nanoporous thin film grown directly on the indium tin oxide glass (ITO) coated glass substrate using DC magnetron sputtering in a reactive environment (Ar:O_2) at room temperature. To achieve the nanoporous-nanocrystalline behaviour of the active material, a thermal treatment (250°) was given to the active material, which modified the compact film surface into nanospheres. This surface modification is responsible to alter the physical, optical and electrochromic properties of the active material. The physical properties of the active material were characterized in detail using X-ray diffraction, scanning electron microscopy, atomic force microscopy, and energy-dispersive X-ray analysis. The optical and electrochromic behaviour of the active electrode material was analyzed using UV-Vis spectroscopy and cyclic voltammetry. The proposed device revealed large optical modulation, high reversible redox behaviour and good cyclic stability at least up to 1000 cycles. This electrochemically active architecture allows one to fabricate the device for energy harvesting applications at an elevated temperature. Our work indorses human comfort with financial benefits and plays a crucial role in "green nanotechnology".

GP-ThP-21 Nanotexturization and Passivation of Single Crystalline Silicon Surface for Passivated Emitter and Rear Contact Solar Cells, *C Hsu,* Xiamen University of Technology, China*; S Liu,* Da-Yeh University, Taiwan , Taiwan*;* ***Wan-Yu Wu***, Da-Yeh University, Taiwan*; S Lien,* Xiamen University of Technology, China

Passivated emitter and rear contact (PERC) solar cells are currently the most promising product in solar cell market. One way to improve the cell efficiency is to reduce the reflectance at incident surface while maintaining high passivation quality. In this study, nanostructured black silicon has been prepared by using metal catalysed chemical etching with a solution mixture of silver nitrate ($AgNO_3$) and hydrogen fluoride. The $AgNO_3$ concentration is varied from 0.015 to 0.075 M. An aluminum oxide and silicon nitride stack is deposited for passivation and antireflection. The experimental results show that the $AgNO_3$ concentration of 0.06 M produces the most prominent nanostructures, but the silicon nitride cannot well-deposited on the surface. The silicon wafer etched at the $AgNO_3$ concentration of 0.03 M exhibits the lowest average reflectance of 1.6% while not compromising on passivation quality. Solar cell simulation reveals that PERC cells with the optimal black silicon nanostructure can have short-circuit current two percent higher than that of traditional PERC cells, and reach a conversion efficiency of 22.04%.

Keywords: Nanostructure, Black silicon, Single crystalline, PERC, Passivation

GP-ThP-24 Optical Performances of Antireflective Moth-Eye Structures under Thermal and Humid Stress – Application to Outdoor Lighting LEDs., *C Ducros,* ***Agathe Brodu***, *G Lorin, F Emieux, A Pereira,* Univ. Grenoble Alpes, CEA, France

Antireflective moth-eye structures were studied in order to increase optical properties of protection windows for outdoor LED lighting. This antireflective structure was compared to "standard" antireflective coatings elaborated by electron-beam evaporation: MgF_2 single layer and broadband SiO_2/ZrO_2 multilayers. Two types of substrates, glass and polycarbonate (PC) have been treated in order to determine the influence of substrates on failure mechanisms generated during ageing tests.

In a first time, effective refractive index and surface morphology were respectively determined by ellipsometry and scanning electron microscopy (SEM). Reactive ion etching process was then optimised on both substrates materials for maximising transmission in normal and angular incidence in the wavelength range of white LEDs (400-750nm). Best results with moth-eye structure were achieved on glass substrate treated on both sides: we measured an increase of 7% of white LED light transmission comparatively to untreated substrate.

In a second time, three standard ageing tests, normative for outdoor applications, were then enforced in climatic chamber on different antireflective treatments in order to estimate their optical properties degradation. First one is an extreme heat test at 130°C with 50% of relative humidity (RH) during 1 hours. Humid heat test consists in testing coated samples during 4 days at 70°C and 95% RH. Third test is a high humidity heat test at 40°C, 98% RH with condensation during 2 days. Surface energy measurement, ellipsometry and SEM were performed on aged surfaces in order to highlight the main degradation mechanisms. The influence of environmental stress on optical properties were then described for all antireflective surfaces. Three main observations can be pointed out from this study: First, degradation of MgF_2 coating under high humidity conditions was mainly due to its high hydrophilic property: a lowering of 3% of light transmission is measured on PC after high humidity heat test. The second main observation is surface cracking of SiO_2/ZrO_2 multilayer antireflective coating on PC leading to losses of 2% in light transmission under extreme heat test. Finally, only moth-eye structures gives high environmental stability as they maintain their white LED light transmission after ageing tests.

Surface Engineering - Applied Research and Industrial Applications

Room Pacific Salon 1 - Session G2-FrM

Component Coatings for Automotive, Aerospace, Medical, and Manufacturing Applications

Moderators: Tetsuya Takahashi, Kobe Steel, Ltd., **Etienne Bousser**, Ecole Polytechnique, Canada, **Satish Dixit**, Plasma Technology Inc., USA

8:40am **G2-FrM-3 YKK's Sustainable Development: Reduction of Mold Cleaning Load by Diecast Mold Coating and Release Agent**, ***Mai Mizubayashi***, *T Sakuragi, N Watanabe, M Ishida,* YKK Corporation, Japan*; K Matsuda,* University of Toyama, Japan*; M Nose,* Hokuriku Polytechnic College, Japan **INVITED**

In recent years, as a common philosophy in the preservation of the global environment, there is a sustainable development as a concept that is internationally widely recognized.This time, we will introduce the development of die coating and mold release agents, which are working on the continuous development of YKK and die casting technology. In the past technological development, the point of view of material strength and efficiency has been emphasized. We are working on a comprehensive development from the viewpoint of improving the total efficiency of the equipment by reducing the mold cleaning load and reducing operator safety, health care and environmental impact. The result was very good this time. The combination of the developed an amorphous carbon film (a-C film) and the release agent, from the time of combination with the nitriding type and conventional release agent, it was confirmed that the workability is an item that was improved about 15%. The joy of the developers is that the people on the scene are satisfied with the results of the development. We want to make the most of the feature and the charm of the coating, and challenge the next generation manufacturing. I am deeply grateful to all the people who have helped me with this study.

9:20am **G2-FrM-5 Effect of Plasma Electrolytic Oxidation Process on Surface Characteristics and Tribological Behavior**, ***Ran Cai***, *C Zhao, X Nie,* University of Windsor, Canada

Alumina coatings prepared by PEO (plasma electrolytic oxidation) process have been proposed and in a validation process to replace heavy cast iron liners for internal combustion engines. The bipolar current mode in the PEO process is known as an excellent coating preparation condition. However, the industrial production would require an optimized as well as cost-efficient process. The unipolar current mode can si gnificantly reduce the investment on coating facilities. Thus, this research was to use the unipolar mode to prepare oxide ceramic coatings on Al-Si alloy samples with different durations, i.e., 20%, 30% and 40% durations of 1000Hz. One of the samples was used with a normal bipolar mode for comparison. The influence of duty ratios on the coating's deposition rate, porosity and wear resistance was investigated. At a similar coulomb charge input (I × t), the change of duty ratios from 0.8 to 0.2 had an insignificant effect on the coating deposition rates, but the coating's porosities decreased and wear resistance increased after the coated samples were polished to Ra around 25 microns and 20 microns. Dry and lubricated pin-on-disc tests indicated that the coatings produced by unipolar current mode at the lower duty ratio had comparable properties of the one prepared with the bipolar current mode. The tribological behavior of the polished surfaces was analyzed based on their surface morphology characteristics (Ra, Rpk, Vo, skewness and kurtosis). The work provides a new perspective for the optimization of PEO process for automotive application.

9:40am **G2-FrM-6 Effectiveness of Electromagnetic Interference Shielding of Sputtered Nitrogen-Doped Carbon Thin Films**, ***Dian-Hao Liu***, *Y Lai,* National United University Miaoli, Taiwan

In this work, nitrogen-doped carbon thin films are deposited on aluminum foils by RF magnetron sputtering with different N2 flow rates. Film properties are characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy. The electrical properties are conducted by Hall measurements, and the shielding efficiency is extracted from network analyzer in the frequency range of 8.2-12.4 GHz. The Raman spectra confirms that adding small amounts of N in carbon films increases full width at half maximum of G-band and the intensity ratio (ID/IG). A red shift of the G-band is also observed. The Hall measurement reveals that the N doping acts as electron donor, leading to the increase of conductivity and carrier concentrations. Due to the improvement of electrical properties, the electromagnetic interference shielding efficiency, in terms of reflection and transmission loss, increases as well.

10:00am **G2-FrM-7 Challenges for Surface Solutions for Automotive Applications**, ***Jörg Vetter***, *J Becker,* Oerlikon Balzers Coating Germany GmbH, Germany*; P Ernst,* Oerlikon Metco AG, Switzerland*; J Crummenauer,* Oerlikon Balzers Coating Germany GmbH, Germany*; A Müller,* Oerlikon Surface Solutions AG, BTS, Balzers, Liechtenstein

Automobile manufacturers have to consider in addition to the expectations and satisfaction of customers regarding the reliability, functionality, comfort and safety, additional aspects such as: production, consumption and environmental issues. Regional environmental legislation and shorter product life cycles require higher quality and more stringent materials requirements. Higher specific loads (thermal, mechanical etc.),weight and friction reduction (CO2; NOx emission reduction), longer components lifetime, improved corrosion resistance are demanding for modern automotive systems, and multifunctional surfaces like sensory functions. In addition new surface solutions are required for green car development (e.g. HEV, BEV with range extenders). Within the last decades, high performance surface solutions and new or improved surface treatments, especially in the group of plasma assisted processes, both for diffusion and deposition processes (IONITOX, PVD, PACVD, Thermal Spraying) were developed to provide economic applications for automotive parts. It will be shown that these new treatments are becoming more common in engine applications and powertrain. Generating optimized surfaces for different types of substrate materials (e.g. Al-alloys, case hardened steels, plastics etc.) and geometries (e.g. bores) also impacts the running costs. Due to the new developments within these competing surface treatments, it becomes more and more common to substitute traditional treatment-substrate-systems with advanced treatments. Both the application potential and selected examples of different surface treatments will be shown. Besides the wear and friction reduction of various components also decorative applications even for multifunctional purposes are successful implemented in daily production. The potential of optimized functional surface generation by proper coating selection is demonstrated.

10:20am **G2-FrM-8 Hard Turning with PVD Coated p-cBN**, *C Charlton,* Kennametal Inc., USA*;* ***Joern Kohlscheen***, Kennametal GmbH, Germany*; D Banerjee,* Kennametal Inc., USA*; C Bareiss,* Kennametal GmbH, Germany

We will give an overview of uncoated and PVD coated polycrystalline or p-cBN cutting tools that are used in finish turning on hardened steel. Examples include turning of automotive braking disks and precision shafts. Interestingly, PVD coatings can improve wear behavior in many applications. As the hardness of such thin films is comparable to the substrate values the improvement is explained by thermal and chemical protection. As many of the different p-cBN substrate materials show reduced electrical conductivity the deposition process has to be adapted. To improve adhesion and overall performance different interlayers and plasma etching cycles were applied in deposition of AlTiN arc ion plated coatings. Difference in adhesion were determined by indentation and scratch testing. Tool life was compared in turning tests of hardened steel (60 HRc) without coolant. The resulting wear patterns will be discussed.

10:40am **G2-FrM-9 Arc PVD (Cr,Al,Mo)N and (Cr,Al,Cu)N Coatings for Mobility Applications**, *K Bobzin, T Brögelmann,* ***Christian Kalscheuer***, RWTH Aachen University, Germany

Efficiency during operation is besides reliability and cost effective production one of the most important demands on machines and components. Especially within the automotive sector, components need to fulfill these requirements. Since the demands for high efficiency and reliability cannot be met solely by typical base materials such as case hardened steels, physical vapor deposition (PVD) coatings for the application on highly loaded components gain increasing importance. A possible approach to reduce friction and wear in tribological systems are triboactive and tribocatalytic coatings which contain triboactive elements such as Mo and Cu which can interact with lubricants and lead to the formation of friction and wear reducing tribochemical reaction layers. Besides coating development, also the design of lubricants is in the focus of research activities to reach friction reductions. Therefore increasing interest gains towards low viscosity lubricants e.g. for e-mobility applications.

Within the current work, triboactive (Cr,Al,Mo)N and (Cr,Al,Cu)N coatings were deposited by means of cathodic arc evaporation (Arc PVD) in an industrial scale coating unit. The contents of Mo and Cu were varied. As substrate material the case hardened gear steel AISI 5115 (16MnCr5E) was

used. The effects of Mo and Cu on the phase formation were investigated by means of X-ray diffraction (XRD). Analysis of the mechanical properties was conducted by nanoindentation (NI) measurements. Tribological behavior of the coatings was analyzed under continuous sliding conditions in pin on disc (PoD) tribometer under minimum quantity lubrication with lubricant amounts of V = 0.05 ml at a temperature T = 80 °C. As lubricants a low viscosity lubrication oil and a conventional mineral oil were used. Both lubricants contained Sulphur and Phosphorous (S-P) additives. Initial Hertzian contact pressure was set to $p_H \approx 1{,}600$ MPa. In order to investigate the influence of the counter body material on the tribological behavior, inert Si_3N_4 balls and 100Cr6 steel balls were used. Wear was analyzed by confocal laserscanning microscopy (CLSM) and scanning electron microscopy (SEM). Tribochemical interactions between the coatings and lubricants were studied by Raman spectroscopy. It was found that tribo chemical interactions between Mo of the coating and S of the lubricant can lead to the in situ formation of MoS_2 in tribological contact. Triboactive (Cr,Al,Mo)N and (Cr,Al,Cu)N coatings are a promising approach to achieve reduced friction and wear in tribological systems.

11:20am **G2-FrM-11 Ion Beam Stripping Process for Cutting Tools Reconditioning*, Alexey Remnev,*** ITAC Ltd., Group of ShinMaywa Industries, Japan

Presently, various kinds of hard film coatings are used in combination with cemented carbide (WC-Co) and high speed steel (HSS) cutting tools for increased longevity. For further improvement of the coated tools' life-span, their regrinding and recoating are commonly implemented. Successful recoating requires stripping off of a previous coating in order to provide sufficient adhesion. Wet electro-chemical etching (ECE) process is commonly applied for the stripping purpose. Although well established, the ECE method has some known issues such as cobalt binder leaching from the WC-Co tools, HSS corrosion, large amount of chemical waste produced. Moreover, the ECE stripping method cannot be applied to the carbon-based thin films, such as diamond and diamond like carbon (DLC), due to their chemical inertness. In this context new competitive stripping approaches are of high applicational importance.

In the present work we introduce a vacuum stripping process based on ion beam etching (IBE) of the hard films. The IBE method utilizes low energy (~1keV) high current (~0.1A) broad (~10cm) ion beams in order to create sufficient ion and radical fluxes on the tools' surface. In order to etch the metal based films, such as TiN, TiAlCrN, TiCN argon gas was introduced, while carbon based DLC and diamond films were IBE processed utilizing pure oxygen as a working gas for improved erosion rate and selectivity against the carbide material.

IBE erosion rates of commercial PVD and CVD hard coatings on various WC-Co cutting tools were experimentally measured and plasma-chemical aspects of diamond decomposition were discussed. Effect of tool geometry on the IBE uniformity was experimentally studied by measuring the local erosion rate over the tools' surface. Moreover, mathematical model of the IBE process, describing the erosion rate distribution was suggested. Surface condition of the WC-Co substrates treated by IBE were evaluated and no significant deterioration was found. Overall, it was shown that IBE provides sufficient erosion rate and uniformity without significant damage to the tool material for virtually any kind of hard coating used in today's cutting tools industry.

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