Surface Engineering - Applied Research and Industrial Applications

Room Town & Country C - Session G1-WeM

Advances in Application Driven Research: New Methods, Materials, and Equipment for PVD, CVD, and PECVD Processes

Moderators: Ladislav Bardos, Uppsala University, Sweden, **Vikram Bedekar**, The Timken Company, USA

8:00am **G1-WeM-1 Improve Cutting Performance of Carbide Cutting Tools with Multilayer TiAlxN-Based Arc-Cathodic PVD Coating for Industrial Applications***, **Fernando Santiago**,* SADOSA, Mexico*; D. Melo,* ITESM, Mexico

Multilayer TiN/TiAlxN coating deposited by arc-cathodic PVD method evaluated in this work. The adhesion of the single or multiplayer coating was studied and stress formation as the function of bias voltage during the deposition process in solid carbide. Industrial Arc-cathodic PVD with a balanced magnetron was used to coat end-mills carbide. The samples coated were tried in slotting operation in the CNC machine center using extreme cutting parameters.

8:20am **G1-WeM-2 Correlation between Deposition Conditions, Properties and Cutting Performance of Al-Rich AlCrN Wear Protective Coatings Produced by Reactive Arc Evaporation***, **Alexandre Michau**, D. Kurapov, I. Iovkov, S. Fabbro,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; L. Zauner, H. Riedl,* CDL-SEC at TU Wien, Austria*; D. Cahill,* University of Illinois at Urbana-Champaign, USA

Due to its outstanding wear protective properties, the AlCrN system is used in a broad range of cutting and forming tools. For many wear protective applications, AlCrN layers with higher Al content are of particular interest. This might be attributed to a combination of excellent mechanical properties, oxidation resistance, phase stability at high temperatures as well as low thermal conductivity. Having a tool coated with a low thermal conductivity layer during a cutting operation is crucial, as it provides thermal barrier properties. More heat can be dissipated into the chips, preventing the substrate from overheating, improving significantly tool performance.

The reactivity of the arc-deposited AlCrN system is mainly governed by the Al/Cr ratio. If a fcc lattice can be obtained for lower ratios, <70/30 at.%, incorporating more Al triggers gradually the appearance of a hcp-AlN phase. This crystalline transition is accompanied by several other transitions. If the hcp phase exceeds a critical amount, the morphology shifts from columnar to fine-grained and mechanical properties start to decline, with lower values of Young's modulus (E), hardness and residual stress, degrading the wear resistance. Typically, for wear protective applications, AlCrN coatings with fcc crystal structure and E above 400 GPa are preferred.

In this work, AlCrN was deposited by cathodic arc with targets having an Al/Cr ratio from 70/30 to 90/10. Magnetic field configuration as well as bias voltage were varied to adjust the energy influx into the growing film. Influence of the Al/Cr ratio on the morphology, crystal structure, composition and mechanical properties of deposited coatings was investigated at room temperature and after a series of vacuum annealing up to 1200°C, by scanning electron microscope, x-ray diffraction and nanoindentations. Thermal conductivity of the coatings was evaluated by time-domain thermoreflectance as a function of the Al content. It was found that the AlCrN system reactivity towards the bias voltage is independent of the magnetic field configuration, an increasing bias voltage leading to less Al in the films. However, a proper adjustment of the magnetic field configuration allows the deposition of AlCrN films, containing up to 80 at% Al, maintaining fcc crystal structure with columnar morphology and E above 400 GPa. The magnetic field on the cathode surface significantly influences the plasma conditions near the substrate. The coating analysis shows strong dependence of the plasma characteristic on the coating structure and properties. The correlation between the growth conditions of the coatings and their cutting performance is discussed.

8:40am **G1-WeM-3 Designed for Impact: Successful Forming of 3rd Generation Advanced High Strength Steels in Electric Vehicles' Body-in-White***, **Tobias Brögelmann**, T. Hurkmans,* IHI Ionbond Netherlands B.V., Netherlands*; J. Owens-Mawson, G. Savva,* IHI Ionbond LLC, USA

The main goals of the mobility driven global energy system transformation are to increase the efficiency and environmental compatibility of conventional and renewable energy to reduce the global CO_2 footprint. More than 60% of all product innovations are based on the development of new and improved high-performance materials, which requires continuous optimization of associated production technologies and manufacturing processes. Here, the right coating solution produced by physical vapor deposition (PVD), chemical vapor deposition (CVD) and plasma-assisted CVD (PACVD) can increase productivity and ensure excellent product quality while minimizing production downtime and scrap rate in forming and molding tool applications.

Within the automotive sector, there is a prime example of continuous development of new materials in the use of press hardened steels (PHS), martensitic and multi-phase ultra-high strength steels (UHSS), dual phase advanced high strength steels (AHSS) and aluminum alloys in the automotive body-in-white. The associated forming applications cover a broad stress profile that results in complex demands on the forming tools, e.g. a high resistance to impact fatigue and crack formation under cyclic loading and a high resistance to abrasive and adhesive wear. One encouraging way of forming these materials is to reduce the frictional forces between the die and the workpiece to obtain an optimum material flow, and to reduce stresses on the die by extending the work-hardening of the workpiece material. The optimum friction state while minimizing costly and environmentally harmful lubricant usage can be set by incorporating the lubrication properties into the coating.

This paper deals with the investigation of hard coatings with self-lubricating properties for industrial forming applications. Three different lubricant concepts in the as-deposited state are discussed, i.e., solid lubricants with layer-lattice structure such as sulfides (MoS_2) and diamond-like carbon (DLC) as well as oxides. Current R&D needs and the preferred coating solutions are introduced based on the performance during industrial field tests. The gap between basic analysis of the coating solutions and time- and cost-intensive field tests is closed by application-oriented model tests. In collaboration with industrial associations and academia, these cover a strip-pull test and an impact fatigue test. Results from the impact fatigue test demonstrate the importance of plasma nitriding to improve the load-carrying capacity for the PVD coating. The improved impact fatigue behavior of such duplex coatings is also reflected in improved performance in the forming application.

9:00am **G1-WeM-4 In-Situ Incorporation of Nanocontainers During Plasma Electrolytic Oxidation***, S. Al Abri, A. Rogov, A. Matthews, B. Mingo, **Aleksey Yerokhin**,* The University of Manchester, UK

Plasma electrolytic oxidation (PEO) is a surface treatment technique employed to light metals to enhance their properties such as heat, wear, and corrosion resistance. The coating comprises of inner thin layer and a porous outer layer. The inner layer provides passive protection separating the substrate from the surrounding environment. However, the presence of the porous outer layer allows the propagation of aggressive ions toward the substrate initiating localized corrosion.

This study aims to functionalise PEO coating by incorporating corrosion inhibitors encapsulated into nanocontainers in a single-step process. The inhibitors will be released when detecting electrochemical activity associated with corrosion initiation, providing corrosion protection on demand. The incorporation of nanocontainers in a single step allows the homogenous distribution of the nanocontainers through the coating matrix, but the integrity of the nanocontainers might be compromised due to the high temperatures developed at microdischarge sites. To prevent this, the thermodynamic conditions of the plasma process will be optimised by establishing the soft spark regime at the earliest stage of the PEO process, which allows the non-reactive incorporation of nanocontainers.

The presence of nanocontainers in PEO coating was confirmed by scanning electron microscopy and the corrosion behaviour of PEO coating was assessed by electrochemical impedance spectroscopy.

9:20am **G1-WeM-5 High-Resolution Investigation of the Microstructural Features and Crystal Forms of Industrial Ti(C,N) CVD Thin Hard Coating**, ***Idriss El Azhari,*** Saarland University, Germany*; J. García,* Sandvik Coromant R&D Materials and Processes, Sweden*; C. Pauly, J. Barrirero, M. Engstler, F. Soldera,* Saarland University, Germany*; L. Llanes,* Universitat Politècnica de Catalunya, Spain*; F. Mücklich,* Saarland University, Germany

In metal cutting industry, Ti(C,N) is one of the most used thin hard coating during the last two decades. Recently, the authors carried out a multi-scale testing and characterization campaign in which industrial cutting tools coated with Ti(C,N) is contrasted to Zr(C,N). The objective was to reveal the microstructural features that influence their mechanical behavior for milling applications. The more compatible coefficient of thermal expansion of Zr(C,N) with the substrate, better cohesive strength at the grain boundaries and plastic deformation were found to assign to the Zr(C,N) better structural integrity and fracture toughness during intermittent cutting in comparison to the inserts coated with Ti(C,N). In the present work, light is shed on unexplored other characteristics related to the grain boundary complexions and crystal shapes of Ti(C,N). State of the art characterization techniques were used such as atom probe tomography (APT), high-resolution secondary ion mass spectrometry imaging (nano-SIMS) and 3D electron backscatter diffraction (EBSD). Approaches to tailor the microstructure of these compounds to enhance the ductility and maintain the strength are suggested.

Surface Engineering - Applied Research and Industrial Applications
Room Pacific F-G - Session G2-1-WeM

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications I

Moderator: Jan-Ole Achenbach, KCS Europe GmbH, Germany

11:00am **G2-1-WeM-10 Enhanced Tool Surface Properties Against Adhesion in Aluminum Forging**, ***Hanno Paschke****, T. Brueckner,* Fraunhofer IST am DOC, Germany*; A. Thewes,* Institute for Surface Technology, TU Braunschweig, Germany*; J. Peddinghaus,* Institute of Forming Technology and Machines, Leibniz University Hanover, Germany

The occurring wear during aluminum processing in warm bulk forming limits the economic potential of this highly productive process. Mainly due to the occurring adhesive mechanisms during contact between aluminum and hot working steel, a reconditioning of the forging dies is necessary. A tribological optimization of the system is necessary. Compared to steel forging the investigations in aluminum forging are still limited to a simplified level so far. The presented work aims at filling this gap introducing a holistic analytic approach. Different prospective surface modifications are tribologically characterized in a tribometer with ball-on-disc test. Processing level is approximated with ring compression tests and serial forging tests as well. This investigation route allows the identification of influencing factors during material processing such as lubrication effects and the role of anti-adhesive surface chemistry. Thus, it is possible to evaluate the suitability of different tool coatings based on CrXN (X representing dopant), Ti-B-X multiphase systems (X representing additional elements like Si, C and N) and DLC coatings. Diffusion treatments including a boriding treatment were investigated as well.

The general findings reveal adhesive effects caused by the material flow during processing. When the material flow is deflected at obstacles or by high friction, the passive layer breaks and uncovers pure aluminum. Thus, an enlargement of the active surface of the aluminum occurs. An additional superposition of the contact pressure increases this effect. The presented work tries to focus on the industrial application in order to reveal the potential of coated tools to achieve a significant reduction of aluminum adhesion. Thus, an economic processing is possible by extended service life time and reduced downtime.

11:20am **G2-1-WeM-11 Evaluation of Permanent Thin-Film Coatings Applied to Die Surfaces to Reduce Lubricant Use during Aluminum Forging Operations**, *J. Vazquez Gonzalez,* ***Stephen Midson****, A. Korenyi-Both, K. Clarke,* Colorado School of Mines, USA

During the forging process, conventional lubricants such as oils and graphite are applied to the faces of the forging tool, to reduce friction and to minimize transfer of the forged material to the die faces. Although currently required for successful forging operations, there are a number of disadvantages associated with the use of such lubricants, including reduction in part quality, decreased die life, higher costs, increased cycle time, and environmental issues associated with the cleanliness of the workspace. The objective of the research described in this presentation is to reduce or eliminate the need for conventional lubricants during forging through the use of permanent thin-film lubricious coatings applied to the faces of the forging die. Rather than using conventional pin-on-disk type testing to measure friction, this study utilized a functional ring forging test (RFT), where the deformation characteristics of a ring-shaped sample provide an estimate of the level of friction developed during forging. The samples used for forging were rings of aluminum alloy 6061, 25 mm OD, 12.5 mm ID, and 8.4 mm tall. Forging was performed using an instrumented 100 kip forging press. Various thin-film coatings have been evaluated, and testing has been performed at both room and elevated temperatures, and in the lubricated and un-lubricated conditions. The results have shown that two classes of coatings can significantly reduce friction during un-lubricated laboratory ring forging operations, diamond-like carbon (DLC) and a commercial coating containing both graphitic and molybdenum disulfide particles. The results of the testing will be reported, along with analytical testing of the structure and compositions of the coatings.

Surface Engineering - Applied Research and Industrial Applications
Room Town & Country D - Session G3-WeM

Innovative Surface Engineering for Advanced Cutting and Forming Tool Applications

Moderator: Dr. Christoph Schiffers, CemeCon AG, Germany

8:00am **G3-WeM-1 A Novel AlCr-Based PVD Coating Design for Threading Operation of Super Duplex Stainless Steel**, ***Qianxi He****, J. M. DePaiva, T. K. Filho,* McMaster University, Canada*; F. L. Amorim, R. D.Torres,* Pontificia Universidade Católica do Paraná, Brazil*; G. Fox-Rabinovich, S. C. Veldhuis,* McMaster University, Canada

The application of PVD coating is largely employed in industry to improve the tool performance of cutting tools designed to perform cutting in several distinguished materials. As a result, there is a sharp increase in demand for innovative materials with remarkable qualities. Current developments in unconventional cutting materials show the potential of different coating combinations. Based on recent finds PVD Hard coatings based on Al, Cr and Ti are recommended for the machining of super duplex stainless steel (SDSS). In this work, three different PVD coatings systems were applied for the threading process of SDSS. Monolayer Al50Cr50N, Al60Cr40N, and multilayer Al50Cr50N/Al50Ti45Si5N were deposited on cemented carbide inserts. The present article highlighted the effect of alloying and coating architecture design on the mechanical properties, and wear performance of the cutting tools. Adhesion and oxidation were observed as predominant wear mechanisms, and the tool life was superior once the system was coated by the novelmultilayer Al50Cr50N/Al50Ti45Si5N. In order to understand these results, the effect of different parameters on the mechanical properties of the coatings was presented and discussed.

8:20am **G3-WeM-2 Property and Deposition Technology for Highly Al-Containing AlCrN Coatings by Arc Ion Plating**, ***Ryosuke Takei****, T. Takahashi, S. Kujime,* Kobe Steel Ltd., Japan

AlCrN coating is one of the most widely used hard coatings in cutting tool applications. The cutting performance of the coating is dependent on its Al content. The mechanical hardness, wear resistance as well as oxidation resistance at high temperature are known to be increased with the Al content, and hence exhibits a good performance even at a severe machining condition. This feature is generally accepted at an Al content, i.e., fraction of metallic element of Al and Cr, of about up to 70 at.% for AlCrN coatings deposited by physical vapor deposition such as sputtering and cathodic arc, also referred to as arc ion plating. This is mainly linked to the crystallographic structure and characteristics thereof, in which the metastable cubic phase with the favorable mechanical and thermal properties can be sustained at Al content up to 70 at.% while the more thermodynamically stable hexagonal phase with the poor properties tends to form at a higher Al content above 70 at.%. A deposition technique of highly Al containing AlCrN keeping the cubic phase is believed to be a key for further improvement of the coating performance and hence the tool life of cutting tools.

There are some practical challenges for highly Al-containing AlCrN coatings. As compared to typical transition metals of Ti and Cr for nitride coatings, Al

has a low melting temperature of 660°C. Therefore, the use of a binary compound target with a high fraction of Al usually results in emission of a large number of macroparticle, which creates internal defects during film growth and adverse effect on the surface quality of the coatings. Another practical point is to ensure the sufficient adhesion of the coating. Coating adhesion of highly Al-containing AlCrN coating appears to be intrinsically poor as compared to those at less Al content.

In this work, we demonstrate the newly developed coating system of arc ion plating equipped with the deposition technology particularly for highly Al-containing AlCrN coatings. With the combination of a newly developed arc source, etching technology and optimization of deposition process parameters, AlCrN coating at Al content above 70 at.% still exhibiting a good surface quality and adhesion were successfully deposited. The coating deposited were characterized in terms of crystallographic structure, surface morphology, chemical composition, and mechanical properties by XRD, SEM-EDX, and nanoindentation, respectively. In order to investigate the performance of the coatings in application, the coatings were also deposited on typical cutting tools such as end-mills and milling inserts and the cutting performance and wear resistance thereof were evaluated.

8:40am **G3-WeM-3 Challenges and Target-Oriented Paths to Maintenance-Free High-Performance Progressive Dies Using HiPIMS-Coatings***, **Martin Hess**,* Robert-Bosch-Str., 5, Germany **INVITED**

Being able to economically manufacture precision contacts in large-scale production of 10 million units or more requires more than just having the correctly designed systems.

In such a challenging environment, it is not only the current trend towards electromobility that is driving up the quantities of electrical components and connectors demanded by the market. The consequence for the stamping tool manufacturers is the demand of continuously increasing tool efficiency with increasing stroke rates of currently up to 3000 strokes per minute. In order to achieve the wear resistance of the progressive dies required for this purpose, low-wear active elements (punches, dies, bending and coining tools, clamps, sliding guides, etc.) are essential for the shortest possible stamping press downtimes. Since wear and tear on a single active part of a complex progressive die can already lead to a, time-consuming and therefore costly, maintenance intervention, wear-resistant coatings of active parts are an even more relevant key factor for the production of electrical contact components with outputs of several millions parts per day, respectively up to several billion (!) parts (e. g. connectors, cellphone parts, etc.) per year and progressive die. In addition to general coating challenges as known from micro tools for machining, topics specifically related to stamping applications such as micro cavities, influence of cutting air, parallel machining of different materials with strongly different strengths in one tool, low artifact coated surfaces etc. will be addressed.

The presentation places a special emphasis on HiPIMS, as the latest HIPIMS coatings used for machining high-strength stainless steel strip (Rm > 1400 N/mm²) achieve for the first time comparable wear resistance or part yield compared to active parts machining high-performance copper alloy strip in parallel in the same progressive die. As a result, the goal of the maintenance-free progressive die – which can contain more than 1000 PVD-coated active parts – is also achieved for tools that produce complex electrical contacts with contact securing high-strength oversprings in one progressive die for production lots in the higher two-digit million range.

9:20am **G3-WeM-5 Oxidation and Wear Behavior of CrAlMoN with Varied Mo-content for Cutting $TiAl_6V_4$***, K. Bobzin, C. Kalscheuer, **Nina Stachowski**,* Surface Engineering Institute - RWTH Aachen University, Germany*; W. Hintze, J. Dege, C. Möller, P. Ploog,* Institute of Production Management and Technology - Hamburg University of Technology, Germany

The cutting of difficult to machine materials such as titanium is still challenging for the machining industry. Materials properties lead to accelerated tool wear and premature failure. In case of the titanium alloy TiAl6V4, the low thermal conductivity of λ = 5.8 W/mK and the low Young's modulus of 110 GPa ≤ E ≤ 140 GPa combined with the high yield strength $R_{p0.2}$ = 870 N / mm² cause high temperatures, mechanical loads as well as self-excited vibrations at the cutting edge. The use of uncoated carbide tools is currently state of the art. However, temperature active, self-lubricating physical vapor deposition (PVD) coatings like CrAlMoN already showed first promising results to reduce friction and wear during turning of TiAl6V4. In order to develop an effective coating, it is important to understand the wear development and oxidation behavior as a function of the chemical composition of the coating. In the present study, self-lubricating CrAlMoN coatings with x_{Mo} = 20 at.-%, x_{Mo} = 30 at.–% and x_{Mo} = 40 at.–% in the metal content were investigated on cemented carbide tools. The coatings were deposited by hybrid process combining dcMS and HPPMS. Coating morphology, thickness, chemical composition, indentation hardness, indentation modulus at ϑ = 20 °C, ϑ = 200 °C ϑ = 400 °C and ϑ = 600 °C as well as the oxidation behavior were analyzed. Moreover, wear development after cutting tests using a computer numerical controlled (CNC) lathe with a cutting velocity of v_c = 80 m/min and a feed rate of 0.12 mm were analyzed, after defined cutting intervals of t_c = 5 s, t_c = 10 s, t_c = 20 s t_c = 40 s, t_c = 80 s, t_c = 120 s. Independent of the amount of Mo, all coating variants possessed a dense morphology and a smooth surface topography, as well as a coating adhesion class of HF1 to the cemented carbide tools in Rockwell indentation tests according to DIN 4856. The tests were conducted in the initial state and after heat treatments up to ϑ = 800 °C. With increasing amount of Mo, heat treatment temperature and time, more self-lubricating molybdenum oxides such as MoO_3 and Mo_4O_{11} were detected by Raman spectroscopy subsequently. Therefore, the coating with x_{Mo} = 40 at.–% in the metal content possess the highest amount of molybdenum oxides. After cutting tests on the tool flank surface, also molybdenum oxides were found by Raman spectroscopy. Additionally, it was observed, that the areas of tribochemical reactions at the rake faces show a growing trend with higher amount of Mo in the coating. The level of flank wear land width decreases with increasing amount of Mo.

11:00am **G3-WeM-10 The Significance and Application Area of CVD $TiCN/Al_2O_3$ based Coatings for Today's Cutting Tools***, **Christoph Czettl**,* CERATIZIT Austria Gesellschaft m.b.H., Austria*; M. Pohler,* CERATIZIT Austria GmbH, Austria*; N. Schalk, M. Tkadletz,* Montanuniversität Leoben, Austria*; F. Konstantiniuk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leobon, Austria **INVITED**

Chemical vapor deposited (CVD) coatings are frequently used for metal cutting applications, especially on indexable inserts. Beside coating systems like TiAlN, TiB_2 or other innovative CVD systems, the $TiCN/Al_2O_3$ based coatings still play an important role. For turning and milling of cast materials, low carbon steels and martensitic steels these architectures are still the first choice. Thus, recent progress in the development of microstructures and architectures as well as improvements of the deposition techniques are summarized. With their first introduction, in the mid of the 1970's, a huge step in cutting performance could be reached. In the following decades, several optimizations of architecture and deposition techniques were introduced, including the medium temperature process for TiCN, defined growth of α-and κ-Al_2O_3 and highly textured α-Al_2O_3 layers. Modern analytical techniques as well as simulation methods were necessary to create a comprehensive understanding of this coating system and explain why they are still indispensable in industry today. This talk gives an historical overview of the development process of the $TiCN/Al_2O_3$ coating system until reaching the current state of the art.

11:40am **G3-WeM-12 Indentation and Sliding Contact Testing of Three Laser-textured and PVD-coated Cemented Carbide Tools***, **Shiqi Fang**,* Saarland University, Germany*; C. Colominas,* Flubetech, S.L., Spain*; C. Pauly,* Saarland University, Germany*; N. Salán, L. Llanes,* Universitat Politècnica de Catalunya, Spain

In this study, a new concept cemented carbide tool is presented with laser-generated abrasive-like protrusions on their machining surfaces that mimic the surface features of diamond or cubic boron nitride abrasives commonly used on honing tools. The novel tools were first surface textured by a picosecond laser, and then the new surface structure was protected by three different PVD ceramic hard coatings. All three nitride-based coatings, i.e., TiSiN-TiAlN, TiSiN-TiAlN-CrN and AlTiN-CrN, differ in the adhesion layer and coating structure. The coating-substrate systems were assessed by means of indenting and sliding contact testing. Experimental methodology included (1) 'passive' Vickers indentation hardness tests, and (2) 'active' machining tests. In both cases, the resulting surface integrity was inspected by using FIB/SEM/EDS. It is found that both laser texturing and coating deposition significantly increased the hardness of the coated cemented carbide. The tool coated by the two-layer film (TiSiN-TiAlN) achieved the best performance, in terms of both hardness enhancement and damage prevention experienced under both tests. Meanwhile, improvement was much less pronounced by the two-layer (AlTiN-CrN) coated tool. Here, cracks appeared under the Vickers indentations and the film was completely or partially spalled-off at some protrusion tops (cutting fronts), due to the concentrated stress during the machining. Finally, the three-layer coating with the TiSiN on the top (TiSiN-TiAlN-CrN) exhibited an intermediate response, where moderate hardness increase was combined

with some wear – although less severe than for AlTiN-CrN film - taking place at critical points, such as cutting fronts.

Surface Engineering - Applied Research and Industrial Applications

Room Town & Country C - Session G4-WeM

Hybrid Systems, Processes and Coatings

Moderators: Hana Barankova, Uppsala University, Sweden, **Sang-Yul Lee**, Korea Aerospace University, Republic of Korea

11:00am **G4-WeM-10 Water-Repellent and Low Emissivity Coatings on Fabric Prepared by Roll-to-Roll Hollow Cathode PECVD and Magnetron Sputtering**, *J. Jolibois,* AGC Interpane Demonstration Center, Germany*; G. Arnoult,* AGC Plasma Technology Solutions, Belgium*; N. Koyra,* AGC Interpane Demonstration Center, Germany*;* ***John Chambers,*** AGC Plasma Technology Solutions, USA*; H. Weis,* AGC Interpane Demonstration Center, Germany*; H. Wiame,* AGC Plasma Technology Solutions, Belgium

Thin film deposition appears to be a suitable process for textile finishing at a time when environmental protection is a global concern. It enables textile functionalization without the wet processing drawbacks, such as hazardous wastewaters. Moreover, thin film technology limits the use of chemicals, water, etc., and do not require a drying system resulting in low energy consumption. Water and oil repellent finishes by PECVD are among the most studied treatments for fabrics. While recently there is a growing interest in metallizing textiles using the magnetron sputtering method.

In this work, we demonstrate the successful use of the hollow cathode (HC) technology to impart water repellent property on polyolefin fabric with silicone precursor. The effects of parameters such as power, pressure and gas mixture on waterrepellencyare evaluated according to international standards such as the resistance to surface wetting. The water repellent finish has a resistance surface wetting of 4.5 and decreases steadily after several wash cycles.

In addition, we show the deposition of low-emissivity coatings prepared by roll-to-roll on a 1.6-m wide fabric. The low-E property is obtained by magnetron sputtering of metal layer (*e.g.* aluminium) and silicone polymer by HC-PECVD. Here, the silicone polymer is used as a corrosion protection barrier. The low-E layer displays an emissivity of 0.2 and 0.25 after 48h in saline water.

11:20am **G4-WeM-11 Amorphous Carbon Coatings on Glass for High Voltage Protection**, ***Hana Barankova,*** *L. Bardos,* Uppsala University, Sweden

Radio frequency Hollow Cathode based hybrid process integrating both Physical Vapor Deposition and Plasma Enhanced Chemical Vapor Deposition was used for deposition of amorphous carbon directly on glass, without using any interlayer. The films grown at 0.25 – 0.5 % of acetylene in the mixture with argon were subjected to high voltage pulses and the performance was compared with uncoated glass samples to test the protection ability of the films, the ability to prevent the deteriorating effects of corona flashovers/arcs. In contrast to the uncoated glass the well adherent carbon films with thicknesses between 3.5 and 17 µm exhibited an excellent protection of the glass substrate against the flashovers/arc damages in both polarities of the electric field with voltages up to 300 kV.

11:40am **G4-WeM-12 Plasma Pretreatment of Small Parts and Granular Materials in Bulk Vacuum Coating**, ***Heidrun Klostermann,*** *B. Krätzschmar, F. Fietzke,* 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 turns into a drawback during plasma etching due to the competitive processes of sputter cleaning and re-deposition on the parts. However, plasma pretreatment of the surfaces is an indispensable step also in bulk vacuum coating. Otherwise, the permanent mechanical impact during agitation will entail delamination defects due to interface imperfections. Identification of appropriate plasma pretreatment regimes is as important as the coating step itself.

In case of granular materials, the aspect of an effective removal of adsorbents before the coating step is a major issue. It becomes more and more challenging with decreasing grain size, hence increasing outer surface area of an ever bigger number of grains, and even more difficult if the grains consist of porous material, where inner surfaces are loaded with adsorbates as well.

Fraunhofer FEP is developing coating equipment and technology for an efficient coating of small parts and granular materials. Depending on the application, adapted plasma pretreatment steps based on a hollow cathode plasma source are established. In this contribution two applications will be presented: 1. the plasma pretreatment of small metallic parts, 2. The plasma heating of hygroscopic porous granular material. In both cases, the pre-treatment steps are essential for the whole processing and have a big effect on the resulting coating. To establish such processes, many aspects have to be considered: 1. Generation of a sufficiently dense plasma close to the bulk of substrate material to be treated, 2. Identification of parameters for effective material removal, 3. Verification of a sufficient and uniform treatment of the batch, 4. Qualification of etching efficiency, 5. Coating qualification including the indirect approval of the pretreatment step. The presentation will give insight into procedures and results along this sequence.

Surface Engineering - Applied Research and Industrial Applications

Room Pacific D - Session G2-2-WeA

Surface Modification of Components in Automotive, Aerospace and Manufacturing Applications II

Moderator: Dr. Jan-Ole Achenbach, KCS Europe GmbH, Germany

2:20pm **G2-2-WeA-2 Effect of Different Diffusion Treatments on the Surface Properties of Austenitic Stainless Steels*, Phillip Marvin Reinders,*** *P. Kaestner, G. Bräuer,* Technische Universität Braunschweig, Germany

The aim of the present study is to investigate the influence of plasma diffusion treatments with different process gases on the surface properties of austenitic stainless steels. This is necessary to functionalize austenitic stainless steels as a material for hydrogen applications, such as bipolar plates in the proton-exchange membrane fuel cell (PEMFC).

For this purpose, the austenitic stainless steel X2CrNiMo17-12-2 (AISI 316L) was modified by low temperature plasma diffusion treatment. The experimental investigations focus on improving the corrosion behavior and the interfacial contact resistance (ICR) of the modified boundary zone. Nitrogen and carbon as well as the combination of both were used as process gas in a temperature window from 390 to 450 °C.Own preliminary work has shown that temperatures above this could lead to an increase in corrosion current, which can be explained by the formation of chromium nitrides. While lower treatment temperatures can possibly lead to inhomogeneous nitriding zones.

In order to evaluate the properties with respect to corrosion resistance, the samples were exposed to potentiodynamic polarization measurements. The ICR was determined under surface pressure between two copper electrodes coated with gold. The diffusion zone was analyzed by X-ray diffraction (XRD) and Glow Discharge Optical Emission Spectroscopy (GDOES). In addition, standardized surface analytics, like Scanning Electron Microscopy (SEM) combined with Energy Dispersive X-ray spectroscopy (EDX) have been applied.

The results show a clear influence of the treatment temperature and the process gases on the studied properties. Plasma diffusion processes based on nitrogen show a significantly higher influence of the treatment temperature than those based on carbon. The plasma carbonized samples show a corrosion rate up to two orders of magnitude lower than the nitrided samples (between 10^{-4} and 10^{-5} A/cm²) in potentiodynamic measurements. But the IRC is significantly increased after the corrosion measurement from lower than 20 up to more than 100 mΩ*cm². The nitrocarburized samples combine the properties of both individual processes and show a comparatively low corrosion rate at low temperatures in combination with low IRC values at increased temperatures.

2:40pm **G2-2-WeA-3 Fine-Tuning of PVD Conditions for Tools Used in Automotive and Manufacturing Applications*, Miha Cekada,*** *A. Drnovsek, M. Drobnic, M. Panjan, P. Panjan,* Jozef Stefan Institute, Slovenia **INVITED**

Tools used in automotive and manufacturing applications come in different shapes and sizes. The deposition of a protective PVD coating is relatively straight-forward for shank tools (drills, mills, reamers) since a standard planetary mounting enables to set up a more or less uniform batch. Other types of tools (stamps, saw blades, powder compaction tools) have more complex shapes, which complicates mounting and reduces the uniformity of the batch. Thus a standard protocol for a uniform batch of shank tools may have to be adapted depending on the specific collection of tools.

There are several features that influence the coating properties on the surface of tools, despite having been coated in the same batch. The tool shape and size dictate the rotation type (single, double, triple rotation) which in turn strongly influences the microstructure. In high ionization rate processes, such as cathodic arc evaporation, electric field concentration on sharp edges can substantially locally increase the coating thickness; that can be a critical issue in reaming when micrometer-sized tolerances are required. Yet another parameter is the vertical position of tools in the chamber with border areas (top/bottom) where the thickness quickly decreases. A similar effect is observed at shaded areas which are often the working surfaces of some tools, such as dies. In addition to new tools, reground tools can be coated too, which requires more steps to prevent subsequent re-coating.

These features will be addressed based on daily experience in our job coating activities. We will show the dependence of coating thickness, roughness, growth defect density and microstructure. These observations should serve as a guide to reduce unwanted influences and optimize the local coating properties. Our own results will be supported by results published by other authors; nevertheless, these data are relatively scarce since they are often retained as secret know-how within a job coating facility.

3:20pm **G2-2-WeA-5 Development of Al_2O_3-B_2O_3-SiO_2 Glass for Space Shuttle Coating*, Jun-Yan Qiu,*** *Y. Lee, C. You, G. Hung,* Ming Chi University of Technology, Taiwan*; R. Montecillo,* Ming Chi University of Technology, Taiwan, Philippines*; P. Chen, C. Tu, K. Feng,* Ming Chi University of Technology, Taiwan

The development of space technology, which includes information transmission, secure communication, and defense protection, will soon play an important role in every country. At present, the team is mainly engaged in the research and development of outer glass coatings for space shuttles. When space shuttles pass through the atmosphere, high temperatures up to ~1350 ℃ are generated on its surface resulting in thermal cracks, Thermal protection failure. Thus, the glass coating can protect the inner porous ceramic layer and act together as thermal insulation to form a thermal protection system (TPS). Borosilicate glass has a high softening point to achieve a wetting effect fit fiber brick and achieve a self-healing effect. In this study, we developed the Al_2O_3 added in the B_2O_3-SiO_2 glass coating.

The experimental results show that the transition temperature (Tg) of the B_2O_3-SiO_2 glass system (BS system) increases from 650 ℃ to 750 ℃ when the SiO_2 content increases. However, the XRD results show that the devitrification reaction occurs when the B_2O_3-SiO_2 glass with high silicon performance is sintered between 800 ℃ and 1200 ℃. Furthermore, when the sample was sintered at 1200 ℃, the crystal peak shifted from (101) to (004) orientation, which was confirmed in TEM. The FESEM microscopic images showed thermal cracks caused by devitrification transformation. Therefore, the proportion is adjusted by the ternary phase diagram of aluminum boron silicon. Adding Al_2O_3 to B_2O_3-SiO_2 glass suppresses devitrification, reduces thermal cracking, and increases glass transition temperature. DSC analysis observed that Tg increased from 750 ℃ to 950 ℃. The XRD results showed unstable α-cristobalite traced to be in the mullite phase, which proved that the addition of Al_2O_3 can suppress the formation of α-cristobalite, inhibit devitrification, and increase Tg. The FESEM microscopic images also showed a smooth morphology without cracks on the surface, indicating that the Al_2O_3-B_2O_3-SiO_2 glass system (BSA system) has stable properties.

In the past, thermal insulation aluminum-silicon fiber bricks were used, so the development of Al_2O_3-B_2O_3-SiO_2 glass is expected to match the thermal expansion coefficient of the substrate to achieve a stable bonding effect. Subsequent analysis of structural changes, microscopic images, thermal properties, and mechanical properties was performed. It is expected that glass coating materials with high glass transition temperature and Thermal shock resistance can be developed and can be applied as a coating for space shuttles.

3:40pm **G2-2-WeA-6 Analysis of the Temperature Variation of Bizarre Thermal Barrier Coatings and Their Impacts on Engine*, Thirunavukkarasu Raja,*** P.S.V College of Engineering and Technology, India*; P. Sivanandi,* Government College of Technology, Coimbatore, India*; S. Dhandabani, V. Murugan,* Sri Ramakrishna Institute of Technology, India

The automotive industry today focuses on reducing the effects of global warming, supposedly caused by engine exhaust emissions. Ansys simulation and experimentation were used to study the TBC effects on engine performance and emissions. The two different novel thermal barrier coating compositions were identified in this study, and the same materials were coated on the engine pistons. According to transient thermal analysis, it is found that the temperature distributions on the coated surface were reduced by 35 % and 18 % for TBC-1 and TBC-2, respectively. Compared to conventional engines, TBC-1 and TBC-2 coated engines increased brake thermal efficiency (BTE) by 8.7% and 7.52% at full load. A decrease in brake-specific fuel consumption of 27.03 % and 18.91 % is identified for TBC-1 and TBC-2 coated engines. Based on the heat balance sheet, the energy conversion rate and useful work are increased by 3.5% and 2%, which ultimately decreases the emission of CO and HC due to complete combustion.

4:00pm **G2-2-WeA-7 Novel High-Entropy Alloy Powders and Their Thermal-Sprayed Coatings for High-Temperature Applications***, **Shih-Hsun Chen,*** NTUST, Taiwan

With our experience in the research and development of metal materials, we will continue to develop various multi-principal high-entropy alloy powder materials and establish their technical capabilities for additive manufacturing. The alloy powders prepared by gas atomization method can ideally present the characteristics of homogeneous high-entropy alloy through the rapid solidification process, and achieve the most suitable process technology for high-entropy alloy products. Combined with the selected additive manufacturing technologies, such as plasma spraying process, it could implement the application and promotion of high-entropy alloys. The above-mentioned process is common and important technology in the industry. Although material research continues to innovate, there are not many researchers engaged in the development of thermal spray process technology. Therefore, this research will rely the established high-entropy alloy powder manufacturing technology, and the development experience of thermal spraying process, focusing on the development of new high-performance AlCrFeNiSi high-entropy alloy powder products and their applications via additive manufacturing technology. This project integrates high-entropy alloy composition design and powder manufacturing, and practical additive manufacturing of high-entropy alloy workpieces.The goal is to develop industrially applicable products and promote them into the industry.

4:20pm **G2-2-WeA-8 A Facile Fluoride Sealing Treatment to Improve Corrosion Resistance of Magnetism Alloy (AZ31B) Micro-arc Oxidation Layer***, C. Lee,* National Defense University, Republic of China*; J. Lee,* Lung Hwa University of Science and Technology, Taiwan*; S. Jian,* Ming Chi University of Technology, Taiwan*; **Ming-Der Ger,*** National Defense University, Republic of China

In this study, MAO treatment was used to generate a high corrosion resistance MAO layer on AZ31B magnesium aluminum alloy,During the MAO treatment, the coating will be solidified and contracted owing to thermal stress gradient, resulting in structural defects such as microcracks on the surface . Unfortunately, corrosive ions (such as Cl− and H+) will penetrate into the substrate through these structural defects, which deteriorates the protective performance. The porosity, pore size distribution and connectivity with the substrate play an important role in the performance of corrosion resistance.In order to maintain the integrity of the MAO layer, the surface of the MAO layer is sealed with a fluorine (NaF) compound containing, so that the MAO surface covers NaMgF3. The protective NaMgF3 cubic lattice fills the defects to optimize the corrosion resistance of magnesium aluminum alloys.

Scanning electron microscopy (SEM) microscope equipped with Energy Dispersive Spectrometer (EDS) was used to observe the surface of the MAO and fluoride post- sealing treatment coatings,and to detect the corrosion performance of the coating by the polarization curve (PDP), with salt spray test (SST) for a long time observe the occurrence of pitting corrosion in sealing treatment over time, decide the optimization degree of post-treatment. According to the surface morphology, the number of NaMgF3 by low-concentration short-term fluoridation post-treatment is small and only locally distributed, and the surface structure of the micro-arc itself does not change significantly. After high-concentration fluoridation for five mins The NaMgF3 particles are evenly distributed, and more particles go deep into the hole to achieve proper protection.

The relationship between the concentration of the fluorinated post-treatment solution and the soaking time has an extreme value on the corrosion efficiency of the micro-arc layer. The corrosion resistance is the best at a certain concentration. After soaking in 0.5 M fluorinated sealing solution for five mins. According to the polarization curve, icorr 1.08 x10-9, in SST, compared with the MAO layer without sealing treatment, the storage time can extend double, and after sealing, it can be stored for more than 480 hours without surface discoloration and pitting. Based on the above experimental results, can understand about fluoride sealing post-treatment, the appearance of pitting can be delayed, and it is confirmed that the fluoride sealing post-treatment by simple immersion can get crack free MAO coating on AZ31B magnesium alloy, raise up corrosion resistance optimization.

4:40pm **G2-2-WeA-9 Chemical Vapor Infiltration Technology for Coatings of Fibers and 3D Porous Bodies***, **Dennis Zywitzki**, H. Strakov,* IHI Bernex AG, Switzerland

With the increasing demand for fiber reinforced materials, chemical vapor infiltration (CVI) as a means to fabricate protective layers between the reinforcement and the matrix, is of increasing industrial interest. These layers can enhance the thermal stability of composites, for example in heat shields, or can be designed to strengthen or weaken the adhesion of the reinforcement to the matrix and thus tailor the mechanical properties. One main requirement to this technology is high infiltration rates and homogeneity. That’s why batch and continues coating concepts are developed and optimized.

In this context newly developed infiltration processes will be presented and the impact of the equipment design will be discussed. The reactor designs allows for example continuous processing of fiber tows of variable length and stable operation for complete infiltration of 3D porous bodies. Additionally, the modular concept allow a high flexibility in terms of gas feeds and deposited materials, and the extensions for industrial upscaling. CVI processes for the deposition > 1 µm thick BN, PyC and SiC films on SiC fibers were developed and show promising characteristics with regard to the infiltration rate and homogeneity.

Surface Engineering - Applied Research and Industrial Applications

Room Golden State Ballroom - Session GP-ThP

Surface Engineering - Applied Research and Industrial Applications (Symposium G) Poster Session

GP-ThP-1 Enhanced Corrosion Resistance, Wear and Antibacterial Properties of TiO_2-Incorporated Micro-Arc Oxidation on AZ31 Magnesium Alloy, ***Wei-Hao Chen***, *Y. Lee, S. Huang, Y. Chu,* National Taiwan University, Taiwan

As one of the green materials, magnesium alloys are known for their high specific strength and good workability, and thus widely used in various industrial fields, especially in automobiles and aircraft. However, magnesium alloys tend to suffer severe corrosion due to their high chemical activity, which calls for proper surface modification. Among varied surface modification processes, micro-arc oxidation (MAO) can form a ceramic oxide layer on magnesium alloys to improve their corrosion resistance and wear resistance. Nonetheless, even with the elevated corrosion resistance, the porous structure of MAO coating still leaves a diffusion path for corrosive species to penetrate through the coating and react with the substrate. Therefore, in order to modify the microstructural defects in the MAO coatings, this study investigates the effect of TiO_2 nanoparticle addition on the MAO process operated in a fluoride-containing silicate electrolyte system, including corrosion resistance, microstructure, chemical composition, and photocatalytic effect of the coatings.

The preliminary experimental results showed that the increase in the concentration of TiO_2 nanoparticles increased the number of Rutile-TiO_2 in the MAO coating, which results in both an elevated hardness and a change in color from white to gray-black. As observed in electrochemical impedance spectroscopy (EIS), the addition of 2.5g/L TiO_2 of nanoparticle exhibits no significant influence on the corrosion resistance and the total impedance is around 107 $k\Omega cm^2$.However, the coating formed with a high concentration 7.5g/L of TiO_2 nanoparticles performs better corrosion resistance which elevates the total impedance to over 600 $k\Omega cm^2$ and the defects within are effectively reduced. In addition, we also noticed that the different power modes and pause time ratio used in MAO process significantly affect the amount of TiO_2 incorporated, which resulted in tunable corrosion, wear and antibacterial performance of MAO coating.

Keywords: Magnesium alloy, micro-arc oxidation, TiO_2 nanoparticles, EIS

GP-ThP-2 The Influence of the Pause Time on Microstructure and Corrosion Resistance of AZ31 Magnesium Alloy Micro-Arc Oxidation Coating, ***Shih-Yen Huang***, *Y. Lee, Y. Chu,* National Taiwan University, Taiwan

Magnesium is the lightest structural metal in the world. As known for high specific strength, formability and recyclability, magnesium alloys have received much attention in various fields. However, poor corrosion resistance of magnesium alloys resulting from the high chemical activity still blocks their way into application. To enhance the corrosion resistance of magnesium alloys, various means of surface engineering optimizing the surface properties bring worldwide notice, and micro-arc oxidation (MAO) process is one that has been studied for decades. With high electric potential generated on the surface, MAO process improves the corrosion resistance of magnesium alloys by fabricating hard ceramic oxide coatings thereon. Nonetheless, both the thickness of MAO coatings and microstructural defects within are affected by many factors in MAO process, among which the electrical parameters are found to be of much importance and directly influence the properties of the coating. In former studies, some of the electrical parameters have been widely discussed, including current density, frequency, and duty ratio, while the waveform of the voltage employed is yet seldom discussed separately.

In this study, the effect of the pause time after anodic and cathodic polarization in MAO process is investigated. The preliminary experimental results showed that in a bipolar MAO process with fixed total input current, the pause time has apparent influence on the corrosion resistance of MAO coating. In addition, we found that the pause time after anodic polarization played a significant role in controlling corrosion resistance of MAO coating under the same duty ratio condition. As revealed by EIS analysis, the total impedance of the MAO coated specimen with anodic pause period only is about 6 times greater than that of the specimen with cathodic pause period only, while the coating thickness is almost the same.

GP-ThP-3 Microstructure and Properties of HVOF Sprayed Coatings Remelted by Laser, *E. Jonda,* ***Marek Sroka***, *W. Pakieła,* Silesian University of Technology, Poland; *T. Jung,* Łukasiewicz Research Network - Institute for Ferrous Metallurgy, Poland

High-Velocity Oxy-Fuel is a technology that enables the production of coatingsincluding a broad group of materials (metallic, ceramic, cermet, composite, carbides, and polymers) and is most often used to regenerate worn parts of machines or devices or to protect from effect of high temperature, corrosion, and erosion. The undoubted advantage of this method is the slight heating of the substrate during the coating deposition process, thanks to which microstructural changes and substrate deformation are significantly reduced. A characteristic feature of coatings deposited in this way is also the adhesive method of joining the coating with the substrate, as evidenced by the wavy line of these joints resulting from the mechanical jamming of plasticized powder grains during the spraying process.

Laser surface treatment aims to melt the entire thickness of the coating and create a metallurgical bond with the substrate or to melt the coating only to a certain depth. The advantage of this type of surface treatment is the possibility of precise control of remelting process by appropriately selected parameters.

The paper presents microstructure investigations and selected properties of coatings deposited by thermal spraying HVOF (High-Velocity Oxy-Fuel) with the use of WC-CrC-Ni powder and then laser remelted with different values of the laser beam power (YLS-4000). The coatings were heat sprayed with the supersonic method on a substrate made of AZ31 magnesium alloy.

Microscopic investigations and fracture morphology were carried out by scanning electron microscope (Supra 35, Zeiss, Oberkochen, Germany) with secondary electron and backscattered detectors. In addition, chemical composition was analyzed by EDS (Energy Dispersive X-ray Spectroscopy). The experiment was designed to investigate the effects of laser beam power 2 - 3 kW) on microstructure and properties of the remelted coating. Studies were supported by microstructural analysis of remelted zone (RZ), heat-affected zone (HAZ), undissolved carbide particles, substrate material, and precipitates formed during rapid solidification. The study also investigated mechanical features like hardness and instrumented indentation.

GP-ThP-4 Fabrication Feasibility Study on Cu and Cu Alloy Coating for Spent Fuel Canister of Deep Geological Disposal, ***Young-Ho Lee***, *Y. Jung, D. Kim, S. Yoon, H. Kim,* Korea Atomic Energy Research Institute, Republic of Korea

The high-level nuclear waste containers should be designed as a multi-barrier system, which is consists of carbon steel vessel and copper canister including bentonite as the backfill material. Due to the manufacturability and economical concerns of copper canister, the container design is considering the applicability of copper or copper alloy coatings on a carbon steel vessel by using additive manufacturing or traditional welding methods including wire arc additive manufacturing (WAAM), arc plasma spray (APS) and direct energy deposition (DED). This copper coating layer serves as a corrosion barrier and its microstructural characteristics is a key factor for determining corrosion resistance of the high-level nuclear waste container at site-specific geological and groundwater properties. In this study, the microstructural characteristics of copper and copper alloys coatings were examined using SEM and electron backscattering diffraction (EBSD), which fabricated by WAAM, APS and DED methods. The coating layers shows completely different microstructures and porosity distribution, which depends on the applied coating methods. However, no significant difference of uniform corrosion resistance can be found due to fine-grained structures of each coating layer when compared to reference wrought copper

GP-ThP-5 Etching of B-doped Diamond Films Using RF Plasma, ***Ryuhei UEDA***, Chiba Institute of Technology, Japan

Diamond has not only the highest hardness and but also its excellent wear resistance and shape stability, it has been applied as a tool. However, machining of diamond is difficult due to its high hardness.In this study, the effects of RF power and pressure on surface properties on the etching of BDD (boron-doped diamond)by inward RF plasma were investigated.

BDD films were used as the sample. A mixture of Ar and O_2 was used as the etchant with H_2O in the bubbling tank. Pressure was varied from 50 to

200Pa, and RF power was from 50 to 200W. Mo was used as a mask. Surface of the sample was observed by scanning electron microscope (SEM). The surface profile was evaluated by Confocal Laser Scanning Microscopy, and the etching amount was calculated from the depth profiles. Structural analysis was performed using Raman spectroscopy, and surface electrical resistance was measured using the four-probe method. Plasma diagnosis was performed using an optical emission spectrometer during etching.

Clear crystal habit was observed in all SEM images, but the shape was changed like a sphere after etching. The amount of etching was increased with increasing RF power and pressure. In Raman spectra, a peak due to B-B at 500 cm^{-1} and B-C at 1230 cm^{-1}, and a shift to the low wavenumber due to high boron doping near 1300 cm^{-1} were recognized. The B-B and B-C peak heights relative to the diamond peak height increased in the treated area compared with the untreated area only at RF power of 200 W and pressure of 200 Pa. The surface

electrical resistance of the treated area was same or higher than that of the untreated area. From the emission spectra, Ar (389,696 to 810 nm), O (777 nm), OH (282, 308, 357 nm), Hα (656 nm) were observed under all conditions. CO (283 to 629 nm), CHO (330 nm), and BH (433 nm) emitted from the etching of the sample were observed. The intensity ratio of CHO, BH and BO to Hα were increased with RF power. However, the intensity of CHO to Hα decreased with etching time, and the intensity of OH was increased. This is because of the carbon substance is etched as CHO from the BDD at the start of the treatment, but as time elapsed, boron oxide forms on the surface, inhibiting the progress of the etching.

From the above results, it can be concluded that during etching of BDD, due to irradiation damage caused by physical etching by Ar in the plasma, the crystalline diamond becomes amorphous, and the carbon substance is formed as CO and CHO by O and OH dissociated from H_2O, the boron substance is removed as BH by atomic hydrogen.

GP-ThP-6 Fabrication of Si/C/SiNW Arrays Sandwich Structure at Different Annealing Parameters for Solar Cell Application, ***Ai-Huei Chiou***, *J. Wei,* National Formosa University, Taiwan

A Si/C/SiNW arrays ssandwich structure has been fabricated by RF magnetron sputter. The effect of the RTA parameters on the structure, element, hydrophilic-hydrophobic and electrical property of the Si/C/SiNW arrays were studied. The XRD patterns of Si/C/SiNW arrays annealing at different time that clearly show that all structures have an amorphous phase. In this study, a PIN solar cells using titanium dioxide and Si/C/SiNW arrayssandwich structure hybrid. A Si/C/SiNW arrays with un-annealing was relatively hydrophile with a contact angle of 8.42.±4.42°. Heat treatment of the Si/C/SiNW arrays resulted in a substantial and statistically significant increase in surface hydrophobic, which was manifested by a dramatic enhancement of the contact angle to 124.83±2.18°. Raman scattering study of Si/C/SiNW arrays exhibited a development of the relative intensity of the D and G band with increasing of the annealing temperature. The conductivity of Si/C/SiNW arrayssandwich structure t is greatly affected by the annealing time. The present results indicated that the power conversion efficiency (PCE) of the sandwich structure without annealing treatment is superior to that of the annealed solar cells.The PIN solar cells used Si/C/SiNW arrayssandwich structure before annealing, in which the Voc is of 0.046mVand efficiency is of 1.13×10^{-3}%.

GP-ThP-7 Barrier Properties Enhancement of Bio-Based Polymers by Means of Multilayer Coatings Applied by Pulsed DC PACVD, *C. Nicoletti, C. Forsich,* University of Applied Sciences Upper Austria*;* ***Francisco A. Delfin,*** University of Applied Sciences Upper Austria, Austria, National University of Technology, Concepción del Uruguay, Argentina*; S. Augl, S. Danninger,* University of Applied Sciences Upper Austria*; M. Schachinger,* (University of Applied Sciences Upper Austria*; C. Burgstaller, D. Heim, J. Weghuber,* University of Applied Sciences Upper Austria

Biopolymers are very promising materials that find use in several industrial applications, ranging from packaging and food industry to the pharmaceutical and biomedical fields. The main advantages of biopolymers include biocompatibility, biodegradability, non-toxicity and renewability. Despite all their great benefits, biopolymer foils also exhibit a few drawbacks that limit their application, such as poor barrier properties. To overcome these restraints, thin-layer coatings can be applied. One method used for the deposition of coatings is the RF PACVD process, which is difficult and expensive to scale up. In this work, the possibility of coating biopolymer foils using a commercially available bipolar DC pulsed system was studied. This technique turns out to be cheaper and easier to scale up compared to the RF plasma. Polylactic acid and cellulose-based foils were used as substrates. Silicon-based films with a silicon oxide top layer as well as carbon- and silicon-based multilayers were deposited. The coatings were produced according to two-step processes: for the Si/SiOx coatings, the first step consisted of the deposition of the Si-layer followed by a post-oxidation treatment step, while the multilayer coatings comprised two deposition steps, with the first layer being carbon or silicon and the top layer silicon or carbon, respectively. HMDSO and acetylene were used as silicon and carbon precursors. For the Si/SiOx-films, the effect of the coating thickness (up to 15 min deposition time) and the post-oxidation step on the barrier properties of the bio-foils was examined. For the Si- and C-multilayer coatings, a deposition time of 15 min for each layer was used. The generated films were characterized by ATR-FTIR Spectroscopy, WVTR, OTR, SFE and SEM. The ATR-FTIR spectra did not show a clear distinction between coated and uncoated foils, in contrast to the same coatings on PE or PP. The barrier properties were substantially improved for cellulose foils, with a reduction of WVTR up to 66% for the regenerated cellulose-films coated with SiOx and up to 73% for the CA-based foils coated with carbon followed by silicon as top layer. No significant improvements were observed for PLA. SFE was in the range 30-52 mN/m for the Si/SiOx-, 16-25 mN/m for C/Si- and 45-48 mN/m for the Si/C-coatings. SEM observations of the cross-sections permitted to estimate the thickness of the coatings, which was around 100 nm. This study highlights the opportunity to use the bipolar pulsed DC PACVD technique as an alternative for coating polymeric materials, with the appropriate adjustments.

GP-ThP-8 Effect of Fluoride on Adhesion of Electroless Nickel–Phosphorus Coating on MAO-Coated AZ31B Magnesium Alloy, *J. Lee, C. Lee,* National Defense University, Republic of China*; J. Lee,* Lung Hwa University of Science and Technology, Taiwan*; S. Jian,* Ming Chi University of Technology, Taiwan, Republic of China*;* ***Ming-Der Ger****, A. Cheng,* National Defense University, Republic of China

The MAO of magnesium alloy is nickel-phosphorus (Ni-P) plated. The Ni-P coating can make the MAO coating conductive, which is convenient for subsequent processing and improves its applicability.Most of references about electroless nickel-phosphorus plating of magnesium alloys mentions that fluoride is added to the electroless plating solution. It is also known from previous study that fluoride has a certain protective effect on magnesium alloys and keep the electroless plating solution in a stable state.

In this study, the MAO of magnesium-aluminum alloy was improved its corrosion resistance. The MAO coating of magnesium-aluminum alloy with high corrosion resistance and uniform pore size was coated with Ni-P plating, Focus on different level fluoride (NH4HF2) in the electroplating solution. fluoride-free, 6 g/L ,12 g/L and 18 g/L , observing the bonding force and corrosion resistance of MAO coating with Ni-P coating.Scanning Electron Microscope (SEM) and Elemental Composition Analysis (EDS) Mapping to observe surface morphology and elements,The adhesion of Ni-P coating test by the Posi-test AT-M pull-off adhesion tester, PDP tests by Versa STAT 4 potentiostat/frequency to analyze the corrosion behavior of the MAO/Ni–P composite coatings, and the salt spray test (SST) is used to judge the characteristics of the Ni-P coating with different level fluoride.

The results show that the nickel plating solution without fluoride ions will corrode the high corrosion resistance MAO coating, and the Ni-P coating will be coated and peeled off. , it will also damage the MAO coating. In fluoride-free situation , the broken MAO coating has poor bonding force with Ni-P coating and very easy to peel off, a complete Ni-P coating can be obtained by adding the appropriate amount of fluoride, and the adhesion of Ni-P coating 6 g/L ,12 g/L and 18 g/L respectively 5.62Mpa, 7.61 Mpa and 2.33 Mpa. Ni-P coating 12 g/L has better adhesion and corrosion resistance on the MAO coating of AZ31B magnesium alloy.

GP-ThP-9 Effect of Mechanical Stress on Electrical Characteristics of Low-Dielectric-Constant Dielectric Materials, ***Yi-Lung Cheng***, National Chi-Nan University, Taiwan

This paper investigated the effects of mechanical stress on the electrical characteristics of SiO_2, dense low-*k*, and porous low-*k* dielectric films. Both tensile and compressive stresses were applied to the metal-insulator-semiconductor (MIS) capacitor by bending the device. Both mechanical stresses increased the capacitance and reduced the breakdown field for SiO_2, dense low-*k*, and porous low-*k* dielectric films while bent. Compressive stress yielded a larger reduction in the breakdown field and the porous low-*k* film had a serious degradation. As the mechanical stress was removed, the electrical properties were recovered. Furthermore, the

breakdown fields of low-*k* films were improved by performing the specified mechanical stress.

GP-ThP-10 Monolithic Integration of Lead Selenide Films via Surface Morphology Engineering, ***Sejeong Park***, *J. Park,* Opto Diode Corporation, USA

The major challenges in lead chalcogenide-based optoelectronic devices processed with chemical bath deposition (CBD) are uncontrollable electronic properties of thin films. The morphologies and the chemical functions of surfaces strongly influence adhesion at interfaces within the deposited layer and surface-modified supporting substrate as well as the physical properties of the synthesized thin film. Surface treatment modifies these properties at the surface and can improve adhesion. However, the outcome depends upon the specific parameters of the processing.

In this work, we employed the surface modification strategy onto silicon-based substrates to explore how surface treatment parameters will affect the growth of lead selenide thin films in CBD growth and their opto-electrical characteristics, applicable for developing low-cost mid-wavelength IR photodetectors. As a model system, we have chosen CBD-grown PbSe thin films on oxide-free and oxidized Si substrates. To control the interfacial stability between PbSe layers and Si substrates, we utilized a surface plasma treatment of Si substrates and systematically investigated the effects of surface conditions onto the physical properties of as-grown PbSe thin films. To understand the underlying growth process of the integrated PbSe thin films, we characterized the optical and electrical properties using a conventional PL, an IR-PL, and I-V measurements. We also investigated the structural and surface morphology of the PbSe films by means of XRD and SEM/EDS.

GP-ThP-12 Degradation Effect of Multilayer Stacking Super-latticeSi/SiGe/Sichannel on FinFET and GAAFET Device, ***Yu-Hsin Chen***, National Tsing Hua University, Taiwan*; D. Ruan,* Fuzhou University, China*; K. Chang-Liao,* National Tsing Hua University, Taiwan

In recent years, silicon-germanium (SiGe) has been widely used as the substrate material for the fin field effect transistor (FinFET) or gate-all-around field effect transistor (GAAFET) to extend Moore's law beyond 3 nm technology node, due to its superior processing compatibility and higher carrier mobility. In order to further shrink the device scale and increase the drive current, multilayer stacking SiGe, especially the super-lattice (SL) Si/SiGe/Si buried channel, was proposed to replace monolayer SiGe without increasing process complexity. However, the sub-threshold slope and device reliability may be sacrificed, due to the Ge out-diffusion and the defects generated from lattice gap over critical SL thickness. In this work, both the FinFET and GAAFET devices with different periods of SL Si/SiGe/Si were fabricated for investigating the degradation effect. Notably, the mobility of device with one period SL Si/SiGe/Si is higher than that of sample with two periods. It means that the carrier mobility might be serious degraded by those defectsunexpectedly, even exceeding the enhanced mobility effect caused by a higher Ge concentration.

GP-ThP-13 Industrialization of Precious Metal-Free Bipolar Plates for Use in Pem Fuel Cells, ***Julian Kapp***, *V. Lukassek, V. Mackert,* ZBT GmbH, Germany*; M. Welters,* KCS Europe GmbH, Germany*; H. Hoster,* ZBT GmbH, Germany*; R. Cremer, P. Jaschinski,* KCS Europe GmbH, Germany

Limiting climate change by reducing global CO2 emissions is one of the key challenges of the 21st century. Achieving the climate targets requires a transformation of our energy systems and a complete switch to zero-emission technologies in all energy consumption sectors. Hydrogen and fuel cells will play a central role in this in the future and will become one of the key technologies.

In order to make fuel cells accessible to a wider range of applications, cost reduction is required. An important component of the fuel cell with great cost reduction potential is the bipolar plate. At the same time, the quality of the bipolar plate is of crucial importance for the function of a fuel cell and its lifetime.

Metallic bipolar plates have high thermal and electrical conductivity, good mechanical properties and low permeability to the gases hydrogen and oxygen. Furthermore, metallic BPP can be easily transferred to mass production at low cost. Stamping processes, such as traditional stamping and hydroforming, are established manufacturing processes for mass production of metallic BPP.

Due to the possibility of producing metallic BPP very thin and thus very light, they are of great interest especially for mass production and mobile applications. A disadvantage of metallic BPP is their tendency to corrode and form passive layers in fuel cell environments, which increases the contact resistance to the adjacent GDL. The metallic BPPs therefore require a corrosion-resistant and electrically conductive coating.

One aim of this work is the further improvement of developed protective coatings with excellent electrical conductivity on metallic bipolar plates for PEM fuel cells. The coatings were optimized with respect to their corrosion protection properties. The PVD (physical vapor deposition) arc and sputtering processes are used to apply these coatings. When selecting the material for the bipolar plate, attention is paid to cost-effective steel and aluminum alloys. Precious metals are completely avoided in the coating material for cost reasons. At the same time, the coatings were optimized for a series production process to meet the productivity requirements for the large number of bipolar plates.

GP-ThP-15 Corrosion Resistance in Synthetic Seawater Plus Diluted Sulfuric Acid of DLC/Crc/Cr Multilayers Co-Deposited by HIPIMS and DCMS, ***Martin Flores***, *L. Flores Cova,* Universidad de Guadalajara, Mexico

Diamond-like carbon (DLC) and CrC coatings are utilized in a wide range of applications to reduce the sliding friction and improve wear and corrosion resistance of bearings and other components. AISI 4317 steel is used in bearings of crane grabs for the transport of minerals with sulfur content in port facilities. These steels suffer from wear and corrosion promoted by sulfide and chloride ions at the port. The multilayers were deposited by High Power Impulse Magnetron Sputtering (HIPIMS) and DC magnetron sputtering (DCMS), using HIPIMS for Cr target and DCMS for C target. The ion etching cleans the substrate and the metal ion etching promotes a good adhesion to the substrate. In this work the metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target. This work reports the results of the potentiodynamic polarization and Daimler-Benz Rockwell C test methods used to evaluate corrosion and adhesion respectively. Synthetic seawater and seawater plus dilute sulfuric acid (.01M) were used as electrolytes. Raman and XPS techniques were used to study the sp2 and sp3 content of the DLC layer. SEM was used to observe the cross section and corroded surface of coated and uncoated samples of AISI 4317 steel. The structure of the multilayer was studied by XRD. The results show an improvement in the corrosion resistance of the samples coated with the multilayer.

Author Index

Bold page numbers indicate presenter