Surface Engineering - Applied Research and Industrial Applications

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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.

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