Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D2

Bio-corrosion, Bio-tribology, and Bio-tribocorrosion
Moderator: Anna Igual Munoz, Ecole Polytechnique Federale de Lausanne

10:20am **D2-2 Evaluation of Tribocorrosion Kinetics and Biocompatibility of Electrochemically Induced Tribolayer for Hip Implants**, *M Lyvers, D Bijukumar,* University of Illinois College of Medicine at Rockford, IL, USA*; A Moore,* Winnebago High School, USA*; P Saborio,* Rush University Medical Center, USA*; D Royhman,* Rush University Medical Center and Northwestern University, USA*; M Wimmer,* Rush University Medical Center, USA*; K Shull,* Northweswtern University, USA*;* ***Mathew T. Mathew,*** University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

As the number of annual Total Hip Replacement (THR) surgeries continues to increase, the longevity of metal based hip implants is a major concern. Tribochemical Reactions cause the Cobalt-Chromium-Molybdenum (CoCrMo) hip implant to release wear debris that interacts with decomposed proteins to form a tribolayer. We conducted an electrochemical investigation in order to understand the role of molybdenum in the stability of the tribolayer under mechanical wear and electrochemical corrosion. Tribolayers made of a bovine calf serum (BCS) and bovine calf serum with sodium molybdates (BCS-Mo) were electrochemically deposited on high carbon CoCrMo discs and subjected to corrosion and tribocorrosion experiments under potentiodynamic conditions in a hip-simulator . Cyclic-polarization, Electrochemical Impedance Spectroscopy (EIS) tests and surface characterization techniques were carried out. The results indicate an increased resistance to corrosion under mechanical wear by BCS-Mo coated surface which is more distinct when Mo is added into the electrolyte. In addition, biocompatibility evaluation using MG63 osteosarcoma cells on BCS and BCS-Mo coated samples did not show any statistically significant difference in cell growth compared to uncoated CoCrMo discs. These findings suggest a pre-formed electrochemical tribolayer with sodium molybdates may be a promising pre-implantation treatment of THRs to extend the longevity of implants *in vivo*.

10:40am **D2-3 Tribocorrosion from Nano to Macroscale – the Effect of Proteins on Friction of CoCrMo Biomedical Alloy**, ***Nuria Espallargas,*** NTNU, Norway **INVITED**

The tribocorrosion performance of CoCrMo biomedical alloy has been widely studied in many different electrolytes (mainly simulated body fluids) and in the presence of proteins (mainly bovine serum albumin). In a recent review it was pointed out that the main outcome of the tribocorrosion of CoCrMo biomedical alloys exposed to simulated body fluids is the increase in wear as the electrode potential increases from cathodic to anodic. This is a very important conclusion that highlights the importance of the combination of electrochemistry with the mechanical action in biomedical bearing implants. However, it is still unclear what is the role played by proteins in this scenario. Indeed, it is very well stablished that proteins significantly affect the electrochemical performance of CoCrMo biomedical alloys, specially altering the cathodic kinetics and enhancing passive dissolution. However, the role played in friction and ultimately wear is still an open and interesting discussion. Therefore, in an attempt to investigate this phenomenon from a different perspective, I will present a nano-scale tribocorrosion set-up. These results will be compared with the classical macro-/micro-tribocorrosion results.

11:20am **D2-5 Fretting Corrosion of Biomaterials Dedicated to Dental Implants: Quantitative and Qualitative Insights**, *P Corne, A Vaillant-Corroy, P De March, F Cleymand,* Institut Jean Lamour, France*;* ***Jean Geringer,*** Mines Saint Etienne, France

600,000 dental implants are implanted in France every year; it is a question of more than 1 million all over the world. The total implants lifetime is about 10 years nowadays. Unfortunately during these 10 years 15-20% of implants did not succeed. Some combinations of biomaterials are available in order to mimic the anchorage process of teeth. A study based on fretting corrosion investigations has been performed. In order to be so close as possible to the actual conditions, some biomaterials used for manufacturing dental implants have been tested in human saliva. The targeted combination is around the dental implant and the abutment. Ti-6Al-4V, pure Ti, zirconia stabilized with Yttria, PEEK (PolyEtherEtherketone) are the studied materials.

The device is a Fretting corrosion machine that has been developed by Mines Saint-Etienne and Bose Company. The sliding conditions were: a sinusoidal displacement of 80µm during 16 and 4 hours. The contact stress has been estimated from the actual junction between implant and abutment (Astra™ TX4.5, Dentsply™/Atlantis™ titanium abutment) from modeling investigations (Finite elements). The average contact stress was considered of 130 MPa.

After tests, the total average wear volume of titanium was the highest against zirconia material. At the opposite the lowest titanium wear volume has been reached thanks to PEEK counter material. Thus the Open Circuit Potential (OCP) evolution has been precisely checked. The lowest decrease at the beginning of the fretting test has been highlighted by Ti-6Al-4V against PEEK material. Additionally some investigations with SEM high resolution have been performed in order to show different wear mechanisms.

11:40am **D2-6 Mechanical and Anti-Corrosive Properties of Various Titania/Silica Hybrid Composite Film as the Interlayer of a Diamond-Like Carbon Deposited Ti6Al4V Substrate by Sol-Gel Technique**, *N Wu,* ***Wen-Hsien Wu,*** *C Chou,* National Taiwan Ocean University, Taiwan*; R Wu,* National Institute for Materials Science, Japan*; J Lee,* Ming Chi University of Technology, Taiwan

Ti6Al4V alloy is one of the most popular implant material in the bio-medical application. In order to enhance the implant's wear resistance and anti-corrosion capability under the physiological environment, a diamond-like carbon (DLC) film with an amorphous silicon (a-Si) interlayer is the most popular coating system implemented on the Ti6Al4V substrate. However, many clinic failures of the implants caused by the crevice corrosion and delamination of the a-Si interlayer were reported after years of operation. In this study, titania/silica hybrid composite ($TiSi_xO_y$) films were built on Ti6Al4V alloy by sol-gel dip coating technique. The compositions of the films were changed by adjusting the Ti/Si ratios of the precursor solutions, and then, sintered at 650 °C under an argon atmosphere. A DLC outmost layer was deposited on these samples by radio frequency plasma enhanced chemical vapor deposition. An a-Si coated sample was also prepared as a benchmark. The surface and mechanical properties of $TiSi_xO_y$ films were evaluated by using scanning electron microscopy, atomic force microscopy, micro-scratch test, and nano-indentation. The composition and structure of $TiSi_xO_y$ films were investigated by using thermogravimetric analysis, X-ray diffraction spectroscopy, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. The phase and structure of the DLC film was identified by a Raman spectroscopy. Corrosion resistance of Ti6Al4V substrates coated with only an interlayer or the whole DLC system was evaluated by electrochemical impedance spectroscopy. The results showed that an appropriate Ti/Si ratio of the $TiSi_xO_y$ interlayer can increase the hardness and, in the meantime, significantly promote the adhesion and anti-corrosion capability of the DLC-coated Ti medical alloy compared with the traditional a-Si coated one.

Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D1

Surface Coatings and Surface Modifications in Biological Environments

Moderators: Kerstin Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, Argelia Almaguer-Flores, Universidad Nacional Autonoma de Mexico, Mexico

1:30pm **D1-1 Reactively Sputtered Iridium Oxide Films for Biomedical Electrode Coatings: Microstructural Dependence of the In-Vitro Electrochemical Performance**, *N Page, J Lucchi, J Buchan, T Scabarozi,* Rowan University, USA; *S Amini,* Johnson Matthey Inc., USA; ***Jeffrey Hettinger,*** Rowan University, USA

Iridium oxide films have been synthesized by reactive magnetron sputtering in an oxygen rich environment. The films have been deposited onto various substrate materials at temperatures of 20, 200, and 400°C. The partial pressure of oxygen required to synthesize iridium oxide is approximately 20% at an overall pressure of 10mTorr and is reduced as the substrate temperature is increased.

The synthesized films have been characterized using x-ray diffraction, electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The microstructure of the coatings depends on temperature, oxygen partial pressure and the substrate material. For room temperature depositions, the grains are generally less than 100nm in size. As the temperature is increased, the grain size increases. An interesting surface microstructure is observed at elevated oxygen partial pressures and are most notable in coatings deposited with a substrate temperature of 200°C. Images of cross-sections indicate that the microstructure is a surface microstructure and does not extend to the coating-substrate interface.

The electrochemical measurements were performed in phosphate buffered saline solution between 0.80V and -0.60V. The measured results indicate that the most complex microstructures improve the coating charge storage capacity by an order of magnitude. Similar features to those that grow at 200°C grow at room temperature with elevated oxygen partial pressures. These features lead to more modest increases in charge storage capacity. The additional microstructure increases the coating surface area and is associated with the emergence of the (011) diffraction peak.

1:50pm **D1-2 Nanostructured Surfaces based on Tantalum Oxide for Osseointegrated Metallic Implants**, ***CristianaFilipa Almeida Alves,*** *J Oliveira, S Pires, L Marques,* University of Minho, Portugal; *D Schneider,* Fraunhofer Instituit für Werkstoffphysik und Schichttecnhologie, Germany; *A Cavaleiro,* University of Coimbra, Portugal; *S Carvalho,* University of Minho, Portugal

Tantalum (Ta) and tantalum oxide coatings have been proven as bioactive materials, so there are promising materials for promoting osseointegration and the performance of medical devices such as dental implants. A new approach has been used on this work. We propose the development of antibacterial and osseointegrated bioactive surfaces based on the synergetic effect of nanostructured and oxide surfaces of Ta-based materials.

In this work Ta-based coatings were deposited by DC magnetron sputtering onto Ti CP substrates in an $Ar+O_2$ atmosphere. Nanostructured anodic tantalum oxide was successfully prepared by electrochemical deposition.

Structural results show that the small increase of O content leads to a change of Ta phase from stable phase (α-Ta: bcc) to mixture with metastable phase (β-Ta: tetragonal) achieving the oxide phases with a large amount of O. Combined structural and mechanical results with DFT calculations shows that the increased addition of oxygen to the Ta phase, a decrease in the density of the crystal structures and increase in the elastic properties is observed, explained by the smaller atomic substitution of Ta and formation of stable TaO_x amorphous phases at grain boundaries.

Also, Ta surface were anodized and results show that the electrolyte, composed by H_2SO_4 and HF, in a 15-25V potential range allow us to control the Ta interconversion from nanopores to nanotubes array. Despite the capacity needed of HF to dissolve and create anodic oxide nanostructures (dissolution assisted by electric field), there is a clear dependence on H_2SO_4 concentration to obtain highly ordered nanostructures.

2:10pm **D1-3 Development of a Biocompatible Titanium Niobium Alloy Coating as a Buffer for Rigid Coatings on Polyetheretherketon**, ***Markus König,*** *K Bergner, H Scheerer, G Andersohn, M Oechsner,* TU Darmstadt, Germany

For the treatment of spinal disk diseases more and more polyetheretherketon (PEEK) implants are used instead of titanium implants. This is due to the excellent cytotoxicity, radiological transparency and low elastic modulus (E_{PEEK} = 3,5 GPa). Nevertheless using PEEK is going along with some disadvantages like the low tendency for a fast and reliable osseointegration. To overcome this drawback a thin osteoconductive coating is needed. Therefore Physical Vapour Deposition (PDV) offers a frequently applied technique to create good adhering coatings on polymers. Most of these coatings are based on ceramics or metals like *hydroxyapatite* or titanium. These materials have a much higher modulus of elasticity (approx. 100 GPa) and a lower elongation. This is the reason why such composites fail through the "eggshell effect".

To overcome this problem a more elastic and biocompatible layer in between is needed. As a casted alloy titanium and niobium (60 wt% Ti - 40 wt% Nb) has an elastic modulus of 60 GPa and excellent biocompatible properties. Till this day it has been unknown if this characteristics could be produced with thin film techniques. It was possible to generate such coatings by physical PVD magnetron sputtering. This was realized by the investigation of target configuration, power and gas settings. The generated coatings were investigated by nanoindentation, micro-scratch tests as well as modified scratch tests to characterise their mechanical abilities. X-ray diffraction, glow discharge optical emission spectroscopy and energy dispersive X-ray spectroscopy were used to characterise the chemical composition and to prove that an alloy is achieved. The realized alloy coating has a composition of 60 wt% titanium and 40 wt% niobium with an elastic modulus of 63 ± 5,7 GPa. Hence, the mechanical strength of biocompatible coatings on PEEK could be enhanced.

2:30pm **D1-4 Development of Novel Long-Lasting S-Phase based Anti-Bacterial Coatings**, *D Formosa,* ***Xiaoying Li,*** *H Dong,* The University of Birmingham, UK

It is well-known that biologically active Ag/Cu ions are strong bactericides and silver or copper nanoparticles have been used in polymer-based antibacterial coatings. However, their poor durability has limited their use in tribological applications. This problem has been largely addressed recently by developing novel plasma co-alloying of austenitic stainless steel surfaces with both nitrogen and Ag/Cu to form Ag/Cu doped hard and wear resistant S-phase. However, this technology is only applicable to austenitic stainless steel as the S-phase cannot be formed in other materials.

In this study, S-phase based anti-bacterial coatings have been, for the first time, developed using magnetron sputtering through co-deposition of austenitic stainless steel with Ag/Cu to form hard S-phase doped with Ag, Cu or both in monolayer and multilayer structures. These coatings where tested and optimised using multiple techniques such as – transmission electron microscopy, X-Ray diffraction, corrosion and wear testing, scratch and fretting techniques and anti-bacterial tests amongst others.

It has been found that it is possible to produce dense corrosion resistant S-phase microstructure with high adhesion to different substrates. Co-depositing S-phase with Ag and Cu dopants brings about significant anti-bacterial efficacy to the traditionally inactive S-phase surface. This was achieved while preserving the advantageous properties of the S-phase microstructure. As opposed to the popular diffusion based S-phase production such as plasma nitriding, this technology can also be applied on all kinds of surfaces, including low-cost steel surfaces, polymers and ceramics.

2:50pm **D1-5 Single-step, Environmentally-Friendly, Biological Functionalisation through Radicals generated by Plasma Surface Modification of Biomedical Devices**, ***Marcela Bilek,*** *E Kosobrodova, A Kondyurin, B Akhavan, M Santos, E Wakelin, G Yeo, C Tran, D McKenzie, A Weiss,* University of Sydney, Australia; *M Ng, S Wise,* Heart Research Institute, Australia **INVITED**

Plasma Immersion Ion Implantation (PIII) is a process in which a bias voltage is applied to an object immersed in plasma, accelerating ions towards it. These ions are implanted into the surface creating highly reactive radicals in the sub surface region. For polymeric materials, the radicals are mobile within the subsurface so that they may be utilized to covalently immobilize bioactive molecules on the surface upon contact [1]. Where the surface to be functionalized is non-polymeric a carbon containing precursor gas is added so that a plasma polymer is deposited

under ion bombardment. Both of these approaches as well as a new variation of these processes that enables the energetic ion implantation of complex interconnected 3D polymeric networks, such as tissue engineering scaffolds.

Short-lived radicals (with lifetimes of less than a day) as well as long-lived radicals with lifetimes of over a year are created [2]. Their diffusion is temperature activated [3] and kinetic theory shows that the depth of the treatment determines the lifetime of the long-lived radicals [1]. Covalent immobilization of functional (including biologically functional) molecules is then achieved by simple immersion or incubation of the surface in a solution containing the functional molecules to be immobilized. This eliminates the need for multiple stage linker chemistry and the associated solvent disposal and variable yield problems. The use of this approach to surface immobilize bioactive peptides, antibodies, enzymes, single stranded DNA and extra-cellular matrix proteins [4] onto the external surfaces of materials, including three-dimensional structures of biomedical devices, such as cardiovascular stents, scaffolds for tissue restoration and implantable prostheses, will be described. The benefits for and recent progress towards commercial applications in implantable biomedical and diagnostic devices will be reviewed.

References:

[1] Bilek MMM, et al, *PNAS* (2011) **108**:14405-14410

[2] Kosobrodova EA, et al, *NIMB* (2012) **280**:26-35

[3] Wakelin EA, et al, *ACS Appl. Mater & Interfaces* (2015) **7**:26340-26345

[4] M.M. Bilek, *Applied Surface Science* (2014) **310**:3-10

Key words: plasma immersion ion implantation (PIII), plasma immersion ion implantation and deposition (PIII&D), biological surface functionalisation, radicals, biomedical diagnostics, implantable biomedical devices, cardiovascular stents, tissue engineering scaffolds.

3:30pm **D1-7 Deposition and Characterisation of Silver Nanocomposite Coatings on Orthopaedic Grade Cobalt Chromium Alloys and the Related Antimicrobial Effects***, **Liuquan Yang**,* Wallwork Cambridge Ltd, UK*; L Richards,* MatOrtho Limited, UK*; A Misha, J Shelton,* Queen Mary University of London, UK*; S Collins,* MatOrtho Limited, UK*; S Banfield, L Espitalier,* Wallwork Cambridge Ltd, UK*; H Hothi, A Hart,* Royal National Orthopaedic Hospital, UK*; J Housden,* Wallwork Cambridge Ltd, UK

Silver containing materials have shown novel antimicrobial properties in various applications historically. Hard wearing PVD silver nanocomposite coatings have the ability to self-lubricate at high temperature and benefit from antimicrobial effect. This study focuses on the deposition of three different contents of silver nanocomposite coatings deposited on cobalt chromium (CoCr) alloy by electron beam physical vapour deposition (EBPVD) and the related characterisations. The coating structures are studied in terms of scratch test, nano-indentation, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS) and optical surface profilometry (OSP). The specific surface area, surface roughness and morphology of the silver particles are analysed and the coatings tested in vitro for antimicrobial effectiveness and wear characteristics against ultra-high molecular weight polyethylene (UHMWPE). The results have shown the silver nanocomposite hard wearing coatings are promising candidates in orthopaedic applications and may lower the risk of infection. Further investigations will optimise the silver coatings and will be subject to simulator tests and clinical trials.

3:50pm **D1-8 Oral Bacteria Adhesion on Saliva Coated and Uncoated Stainless Steel Surfaces: Experimental Characterisation and Modelling***, **Jinju Chen**, S Chinnaraj, Y Ammar, J Pahala Gedara, N Jakubovics,* Newcastle University, UK

Biofilms refer to bacteria growing within a matrix of extracellular polymeric substances attached to surfaces, which have significant impact to a wide range of industries and environment. The initial bacteria attachment is important for biofilm formation, which can be affected by various materials surface characteristics such as surface roughness, surface hydrophobicity, and surface chemistry. The total interaction energy required for bacteria to adhere to surfaces can be determined by extended DLVO theory (XDLVO) which considers Lifshitz van der Waals interactions, electrostatic interactions and acid-base interactions. The extended DLVO model can further be improved by considering the surface roughness of the materials. However, there is lack of experimental work and modelling of bacteria adhesion on patterned surfaces which are relevant to many medical implants.

In this study, streptococcus gordonii DL-1, a typical cocci shaped bacteria found in oral cavity, was cultured on the patterned stainless steel. The surface coverage of attached cells was calculated using MATLAB code. An in-house C++ code was developed to compute the bacteria deposition by implementing the surface roughness enhanced XDLVO. The simulated results qualitatively agree with the experimental measurement and both have shown that patterned surfaces would promote bacteria adhesion. In addition, it has demonstrated that the saliva coating does not have much effect on the initial attachment of streptococcus gordonii.

4:10pm **D1-9 Towards Antibacterial yet Biocompatible and Bioactive Surfaces***, **Dmitry Shtansky**, I Sukhorukova, A Sheveyko, E Levashov,* National University of Science and Technology "MISiS", Russian Federation

The fabrication of antibacterial yet biocompatible and bioactive surfaces is a challenge that biological and biomedical community has faced for many years, while no "dream material" has been developed so far. Various strategies for development of bioactive and bactericidal films with various antibacterial components (Ag, B, antibiotic, bacteriophages) providing long-lasting antibacterial effect are considered [1-4]. The substrates with different topography were produced via selective laser sintering, pulsed electro-erosion treatment, chemical etching, sandblasting, and laser treatment. Multicomponent biocompatable nanostructured films with different content of antibacterial components were deposited on substrates with different topography and roughness using PVD methods (magnetron and ion sputtering, ion implantation). Different functional treatments to provide antibacterial functionality including saturation with antibiotics or bacteriophages were fulfilled. In addition, thick (up to 30 μm) multicomponent biocompatible yet antibacterial coatings with high surface roughness (R_a > 6 μm) were obtained by pulsed electrospark deposition [5,6]. The obtained results show that under optimal surface chemistry and topography conditions the material can be biocompatible, bioactive and bactericidal.

[1] I.V. Sukhorukova, et al., J. Biomed. Mater. Res. B 2016, DOI: 10.1002/jbm.b.33534

[2] I.V. Sukhorukova, et al., Colloid Surface B 135 (2015) 158-165.

[3] I.V. Sukhorukova, et al., Applied Surface Science 330 (2015) 339-350.

[4] D.V. Shtansky, et al., Surf. Coat. Technol. 208 (2012) 14-23.

[6] A.N. Sheveyko, et al., Surf. Coat. Technol. 302 (2016) 327-335.

[5] N.V. Litovchenko, et al., Surf. Coat. Technol. (in press).

4:30pm **D1-10 Characteristics of Plasma Polymerization Films using HMDSO Precursor on 316L Stainless Steel***, **Si-Bu Wang**, J Lee, Y Lee,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

This study focused on the characterization of the organic film deposited on 316L stainless steel substrate using a plasma polymerization process with hexamethyldisiloxane (HMDSO) precursor. The organic films were fabricated under different HMDSO-O_2 gas ratios and the heating temperature of the monomer. The plasma characteristics during the plasma polymerization process were studied by an optical emission spectrometer. The structure and bonding of the deposited films were analyzed by a Fourier Transform Infrared Spectroscopy (FTIR). The scratch test was employed to evaluate the adhesion properties of coatings. Preliminary biocompatibility studies were carried out using MG-63 cell line (human osteosarcoma) to investigate cell-material interaction. The results of cell viability and toxicity are presented.

It can be found that the plasma polymerization grown films were free of pinholes and showed an excellent adhesion quality to the substrate. Good biocompatibility was also observed for the organic coating. Effects of HMDSO-O_2 gas ratio and the heating temperature of the monomer on the plasma status, structure, film thickness, mechanical property and biocompatibility of the films deposited on 316L stainless steel substrate were further discussed in this work.

4:50pm **D1-11 Structure and Biocompatibility of Fluorine-containing TaCN Thin Films***, **JangHsing Hsieh**, H Lin,* Ming Chi University of Technology, Taiwan*; S Liu,* National Taipei University of Technology, Taiwan

TaN thin film coatings are known to have good mechanical properties, impact toughness, as well as good biocompactibility. However, the friction coefficient of these films is sometimes too high, or the hemocompatibility is poor. The purpose of this study is to reduce the friction coefficient and lower the surface energy of TaN coating by introducing CFx into/onto the nitride coatings. CFx–doped TaN films, with and without CFx top layer, were deposited on silicon and tool steel substrates by magnetron

sputtering. During the deposition process, C2F6 gas with various flow rates was added. During the deposition of 30 nm CFx top layer on some samples, the power to Ta target was shut off. After deposition, these films were then characterized using XRD, XPS, FTIR, FESEM, as well as a tribometer. The tribo-tests were carried out with and without argon flow. Surface energies of the films were also analyzed with contact angle measurement system. According to structural analysis, TaN phase would transform to Ta(FCN) with the increase of the fluoride gas flow rate, which would cause the decrease of friction coefficient and surface energy. According to the results obtained from tribotesting, it is found the increase of CFx would reduce the effects of moisture and oxygen on friction coefficient. The prepared films may have good hemocompatibility and wear-resistance.

Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D3

Medical Devices, Biosensors, and Biodegradation

Moderators: Jessica Jennings, University of Memphis, USA, Robin Pourzal, Rush University Medical Center, USA

8:00am **D3-1 Challenges for Polymeric Orthopedic Implants - Enhanced Surface Functionalities using coatings deposited by HiPIMS**, ***Kerstin Thorwarth,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; G Thorwarth,* IMT AG Greifensee, Switzerland*; J Patscheider,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

For treatment of the human spine and its degenerative diseases, a large variety of materials and treatment techniques are available, to which a short overview is given. One task frequently encountered for new solutions is the need for strongly adherent metallization of polymeric surfaces. Such materials are favored due to their low stiffness, comparable to cortical bone material and radiolucency, but generally they present surface properties unfavorable for successful tissue integration. This is especially true for an unmodified PEEK surface designated for bone integration. To address this issue, the common approach is a metallic coating by plasma spray (APS or VPS). The disadvantages inferred by this process comprise remelting of the surface and incomplete coverage of non-line-of-sight features.

As an alternative, a highly adherent HiPIMS based coating process was developed and is discussed in this presentation. Along with characterization of the general process, it is shown that a proper selection of pre-treatment and coating parameters like surface activation and micro-pulsed HiPIMS operation can improve the adhesion strength to >30 MPa, whilst delivering a surgical grade (ISO 5832-2) conformal titanium coating. Based on FEM simulations, the problem of adhesion measurement on deforming substrates is addressed, and subsequent treatments to further enhance the osseointegration and biocompatibility are elucidated.

8:20am **D3-2 Alginate Coatings on Silver-decorated Calcium Phosphate nanospheres as an Antimicrobial coating component**, ***Jessica Jennings,*** *C Nelson, S Mishra, M Ghimire, J Bumgardner,* University of Memphis, USA

Silver-decorated calcium phosphate nanospheres have been previously studied and shown to inhibit bacterial growth and adhesion when incorporated into chitosan coatings on metal. While effective against bacterial strains common in oral and orthopaedic infections, preliminary cell culture and elution evaluations have demonstrated that substantial and potentially toxic amounts of ionic silver are released during the acidic fabrication process of the chitosan coating. We hypothesized that creating a degradable shell coating around these nanoparticles will prevent initial leaching of silver into the coatings so that a biocompatible antimicrobial surface is maintained over an extended period.

Coatings of alginate were applied to non-loaded and silver-decorated calcium phosphate nanospheres by immersion in sodium alginate at weight% ranges of 1 to 8%. Particles were sonicated for one hour and then centrifuged and rinsed to remove residual alginate. SEM images were acquired of coated and non-coated nanospheres.

Zeta potential of particles decreased from -4.62 to -17.19 after alginate coatings, indicating that alginate shells were formed around calcium phosphtate nanospheres. When incorporated into chitosan coatings, these alginate shells may prevent leaching of silver into coatings for slow release and/or containment within the coatings for surface antimicrobial activity. Ongoing and future studies will determine silver release, incorporation into chitosan coatings, antimicrobial activity, and cytocompatibility.

8:40am **D3-3 Manufacturing, Testing, and Regulatory Aspects of Implant Coatings**, ***Dirk Scholvin,*** *J Moseley,* Wright Medical, USA **INVITED**

Medical implants must meet a number of criteria to serve their intended purpose safely. They must possess basic properties such as an adquate minimum tensile or fatigue strength, wear and corrosion resistance, or elastic modulus. Depending on their use, they may also require an enhanced ability to integrate with the biologic environment. For example, allowing bone ingrowth to achieve improved fixation for an orthopedic implant. They may need to be resistant to bacteria or cell attachment in order to improve sterility of a surgical implant or to prevent biofouling of a sensor surface. It is not uncommon to find applications requiring surface properties that cannot be met by a bulk implant material.

In this presentation, an overview of different types of implant coatings is given, with a focus on the orthopedic implant industry. The history of coatings in the orthopedics industry is used as a case study to show opportunities for device coatings while highlighting testing, manufacturing and regulatory challenges.

9:20am **D3-5 Implant Alloy Microstructure can Enable Cell Induced Corrosion in Total Hip Replacements**, ***Robin Pourzal,*** *D Hall, R Urban, S McCarthy,* Rush University Medical Center, USA*; J Ehrich, A Fischer,* University of Duisburg-Essen, Germany*; J Jacobs,* Rush University Medical Center, USA

Corrosion within modular taper junctions is a major concern for the longevity of total hip replacements (THR). It has been shown that cells within the joint environment can alter the local chemical composition of the joint fluid [1]. We have shown that the presence of cells on the surface of the taper surface of femoral heads is associated with a column-like damage pattern of proximal to distal running troughs [2]. It was the purpose of this study to determine corrosion pathways leading to column damage in THRs.

Thus, a retrieval study was conducted on 165 retrieved femoral heads that had either moderate corrosion (n=57) or severe corrosion (n=108). Samples were screened for the occurrence of column damage. Replicas of the head taper surfaces were made and measured with a non-contact 3D profiler (Ortholux, Redlux).

In selected cases, heads were sectioned to visualize damage patterns in a SEM.The implant alloy microstructure was evaluated by metallographic methods.

Colum damage was observed in 28% of the retrieved heads. The troughs of the column damage pattern exhibited no material pile-up on the sides, had an etched surface appearance, and exhibited a depth of 20-40µm. On 3 of the 15 head tapers analyzed by SEM, there was clear evidence of preserved cells adherent to areas with column damage, but there was no evidence of cells adhering to corresponding stem tapers. Based on morphology and size, the cells appeared similar to macrophages or osteoblasts. It was evident that cells generated an etching trail which exposed crystallographic features. The metallographic analysis revealed that implants with column damage exhibited longitudinal segregations within the implant alloy.

In conclusion, column damage is a common occurrence in femoral heads with corrosion damage. It appears to be the result of a chemical process such as etching. Interestingly, the width an orientation of the troughs appeared similar to segregations within the implant alloy. Such segregations must have been already present in the CoCrMo bar stock material that heads were made form. The result is an alloy microstructure with longitudinal stripes with varying corrosion properties thus enabling local galvanic interactions. It appears that once cells are able to enter the taper interface, they generate a more corrosive environment by the release of reactive oxygen species as earlier suggested [1]. The combination between the segregated alloy and a corrosive environment enabled by cells provides conditions that lead to column damage, increasing material loss and higher risk of implant failure.

[1] Gilbert JL et al Semin Arthoplasty 24(4):246, 2015, [2] Hall DJ Trans ORS 41:400, 2016

9:40am **D3-6 Characterization of Solid-supported Thin Films and Molecular Interactions using Multi-Parametric Surface Plasmon Resonance**, ***Annika Jokinen,*** *N Granqvist, J Kuncova-Kallio, J Sadowski,* BioNavis Ltd., Finland

Surface Plasmon Resonance (SPR) is commonly used method to measure molecular binding kinetics and affinities, however, the physical phenomenon is also applicable to characterization of thin films [1]. Multi-parametric surface plasmon resonance (MP-SPR) utilizes full SPR angular spectral measurement at multiple wavelengths characterizing thin films in terms of thickness and optical properties.

The method effectiveness has been extensively demonstrated using different ultrathin films systems [2-4]. Chemical-vapour-deposition (CVD)-grown graphene films thickness was determined using MP-SPR and after first initial layer thickness was found to be 0.37nm / monolayer on a solid support [3]. Atomic Layer Deposition (ALD) (PICOSUN™ R-150) was used to deposit Platinum (Pt) and nanolaminate (Al_2O_3 and Pt) layers on a glass substrate. Target thickness of the layers were 11 nm for Pt, and altering 5nm each for nanolaminate. Thickness was found to be in good agreement with the target thicknesses. Stearic acid (SA) Langmuir Blodgett films showed approximately 2.5±0.2 nm thickness, and linear increment with increasing layer number [2]. The SPR curves (angular spectra) were

analyzed using BioNavis LayerSolver software to determine layer thickness and refractive indexes. Additionally to layer properties MP-SPR measures in real-time interactions on a thin films. Protein and cell samples binding on a Plasma Sprayed hydroxyapatite coating was measured label free [4].

The non-invasive MP-SPR is proved to be an effective tool for the nanoscale metal, nanolaminate, oxide, polymer, and ceramic layers characterization in air and in liquid. High sensitivity enables characterization of even subnanometer thick layers and within the same measurement also material interactions can be measured.

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10:00am **D3-7 Effect of Processing on the Structure and Biofuncionalization of AlN Thin Films Produced by r.f. Reactive Magnetron Sputtering**, *A Murillo,* ***Olimpia Salas****, L Melo-Máximo, B García, D Melo-Maximo,* Tecnológico de Monterrey-CEM, Mexico*; K García,* Tecnológico de Monterrey-CCM, Mexico*; J Oseguera,* Tecnológico de Monterrey-CEM, Mexico

Al/AlN/Al thin films were evaluated in terms of their structure and easiness of biofunctionalization as prospective materials for biosensors. First, Al/AlN layers were deposited by r.f. reactive magnetron sputtering at various levels of applied power and Ar/N_2 mixtures on stainless steel substrates. The films were characterized by x-ray diffraction, glancing angle x-ray diffraction, scanning electron microscopy + energy dispersive microanalysis, and transmission electron microscopy. The results indicate that the applied power had a stronger influence than the atmosphere composition on the structure obtained and that the orientation of the films can be controlled through the processing parameters. However further work is needed as some residual non-nitrided Al was found within the layers. The films that showed the most promising structural characteristics for biosensing, were then coated with an additional Al layer on the surface and subjected to biofunctionalization experiments.

10:20am **D3-8 Effect of Zn on the Improvement of Corrosion Performance of MAO Coated Biodegradable Mg-Sr-Zn Alloys**, ***Mehmet Yazici****,* Ondokuz Mayis University, Turkey*; Y Azakli, S Cengiz, Y Gencer, M Tarakci,* Gebze Technical University, Turkey

Recenty, magnesium alloys are commonly studied as biomaterials due to their promising biodegradability in ortohopedic applications. Degradability is an important property of a biomaterial tough high corrosion rate is a handicap for orthopedic applications. One of the solutions can be followed is to keep the corrosion rate of the material under limits by modifying its surface. Coating techniques such as microarc oxidation (MAO), sol-gel, electrophoretic deposition etc. might be used to increase the corrosion resistance. In this study, ternary Mg-Sr-Zn alloys with Zn content ranging with 0.35, 1.5 and 3 weight percent were prepared via stainless steel mold casting following induction melting. The MAO coating was deposited on these samples by pulsed direct current. Corrosion experiments of the coated samples were tested in SBF and degradations rates were compared. The surface roughness, microstructure, phase content and chemical composition of the coatings were characterized by using scanning electron microscopy, profilometry and X-ray diffractometry.

10:40am **D3-9 Antimicrobial Silver Oxide Films with Rapid Bacteria Contact Killing**, *A Ogwu,* ***Nathaniel Tsendzughul****, G Mackay, C Williams,* University of the West of Scotland, UK

We report on the antimicrobial properties of silver oxide thin films prepared by reactive magnetron sputtering. The films were characterised with x-ray diffraction combined with radial distribution function analysis to evaluate nano-crystalline particle sizes formed during deposition. The growth mode of the prepared films was monitored with the scanning electron microscope. The chemical composition and stoichiometry of the films was monitored with Raman spectroscopy, FTIR and X-ray photoelectron spectroscopy (XPS) using the binding energy peaks, all confirming the presence of antimicrobial phases in our deposited films. Spectrophotometry was used to confirm up to 80% optical transmission in the visible range. Atomic absorption spectroscopy was used to monitor ion release in the silver oxide films both in water and saline solution. We were able to confirm 100% microbial cell deaths of E.coli and S. Aureus within 20 minutes on exposure to silver oxide films using killing curve measurements. The mechanism of bacterial attack can be associated with nano-crystalline particles in the deposited films, ion release, the ease of ligand replacement in the silver oxide stoichiometries in the films and their exchange and interference with biological ligands in the microbes. Our current finding opens the door to furthering the development of non-ultraviolet (UV), but visible light activated antimicrobial surfaces.

Coatings for Biomedical and Healthcare Applications
Room Grand Exhibit Hall - Session DP

Symposium D Poster Session

DP-2 Bone-like Nano-hydroxyapatite Coating on Low-modulus Ti-5Nb-5Mo Alloy Using Hydrothermal and Post-heat Treatments, *H Hsu, S Wu, S Hsu,* Central Taiwan University of Science and Technology, Taiwan*; C Hsu,* Da-Yeh University, Taiwan*;* ***Wen-Fu Ho,*** National University of Kaohsiung, Taiwan

Titanium and its alloys have been widely used as biomaterials for orthopedic and dental implants because of their excellent biocompatibility and mechanical properties. However, they are considered to be bioinert, such that when they are inserted into the human body these implants cannot bond directly to the surrounding living bone. This study aimed to improve the bioactivity of a low-modulus Ti-5Nb-5Mo alloy with a hydroxyapatite (HA) surface coating using eggshells as a Ca source through hydrothermal reaction and heat treatment. The results showed that the whole alkali-treated alloy surface was covered with amorphous calcium phosphate nanoparticles after hydrothermal reaction at 200 °C for 48 h. When subsequently heat-treated at various temperatures (400, 500 or 600 °C) for 48 h, the surface coating of Ti-5Nb-5Mo alloy was transformed into crystalline rod-like HA nanoparticles. Also, heat treatment enhanced the adhesion between the HA coating and the Ti alloy substrate. Additionally, FTIR analysis confirmed the production of HA containing mixed AB-type carbonate substitutions. To evaluate bioactivity of the bone-like HA-coated Ti-5Nb-5Mo alloy, the capability of calcium phosphate apatite formation on the alloy surface was assessed by immersion in a simulated body fluid (SBF). Dune-like apatite layer was observed to densely deposit on the surface of HA-coated Ti alloy after 6 h of immersion in the SBF. Notably, the ability of Ti-5Nb-5Mo alloy subjected to sequential process with alkali, hydrothermal, and heat treatments to form bone-like HA nanoparticle coating was obviously greater than that of its counterpart without HA coating.

DP-3 Niobium Oxide Scaffolds on Nb and on TNZT for use in Bone Implants, ***Madelyn Kramer,*** University of North Texas, USA*; E Leveque,* University of Rouen, France*; J Barclay, S Aouadi, M Young,* University of North Texas, USA

In this study, a TNZT alloy composed of Ti-35Nb-7Zr-5Ta in at.% and pure niobium were comparatively tested for their ability to grow nano-scaffolds on the surface for biomedical applications such as implant devices. The TNZT alloy was made by vacuum arc melting; and then rolled into a plate where it was subsequently sectioned and cut. The TNZT and niobium samples were polished flat, ultrasonically cleaned, and underwent hydrothermal treatments to grow nano-scaffolds of oxides on the surface. The TNZT and niobium produced Nb_2O_5 nano-scaffolds from a hydrothermal reaction in varying alkaline solutions: KOH at 170°C and NaOH at 60°C. Oxide scaffolding was also created when samples were annealed in air at 900°C for 2 hours. The TNZT and niobium nano-scaffolds were characterized by scanning electron microscopy (SEM). The nano-scaffolds will be characterized by X-ray diffraction (XRD) and Raman spectroscopy and will be further examined in simulated body fluid to further assess their biocompatibility.

DP-6 Muti-functional Porous TaOxNy Film Deposited on Ta/TaN-Ag Layers Prepared by Co-sputtering and De-alloying Approach, *J Hsieh,* ***ChungChieh Hsu,*** *Y Lin,* Ming Chi University of Technology, Taiwan

The oxynitride of a transition metal is able to form a new grade of functional thin film. In this study, TaOxNy-Cu films were first prepared using reactive co-sputtering, with the variation of O/N flow ratios. After deposition, the films were annealed, and Cu was etched away to form porous oxynitride structures with various O/N ratio. These porous films were then built on Ta/TaN-Ag layers, in order to induce antibacterial behavior and improve biocompatibility. The films were characterized using nano-indentation, XRD, and SEM. The results showed that the porosity of these films could be varied depending on Cu contents and O/N ratios. The samples were then tested for their biocompatibility and viability using MG-63 cells, and for the antibacterial efficiency against E. coli. According to the results obtained from biocompatibility and MTT assay testing, it was found that the pore size (or roughness) played a major role in terms of biocompatibility and cell viability. The antibacterial efficiency depends on the temperature and time of the second rapid thermal annealing.

DP-7 Increased Ag+ Dissolution Rate of TaN-Ag Nanocomposite Thin Films by Air Atmospheric Pressure Plasma Jet, *J Hsieh,* ***Yi-Zheng Yang,*** *C Lin,* Ming Chi University of Technology, Taiwan

The present study was aimed at activating nano-sized Ag particles emerged on TaN-Ag thin films by air atmospheric pressure plasma jet (APPJ). It was proved that the dissolution rate of Ag NPs could be accelerated, and bactericidal efficiency could be enhanced. In the experiment, TaN-Ag thin films were prepared by reactive co-sputtering, followed by rapid thermal annealing. The annealed films were then treated in either dry or wet (immersed in buffer solution) environments by APPJ. It is found, after activation, the dissolution rate of Ag ions could be increased significantly. Hence the antibacterial efficiency was increased tremendously.

DP-8 Tribocorrosion Behaviour of DLC-Coated Ti-6Al-4V Alloy Deposited by PIID and PEMS+PIID Techniques for Biomedical Applications, ***Andre Hatem,*** Pontifícia Universidade Católica do Paraná, Brazil*; J Lin, R Wei,* Southwest Research Institute, USA*; R Torres, C Laurindo, P Soares,* Pontifícia Universidade Católica do Paraná, Brazil

One of the main drawbacks observed from the usage of titanium alloys implants is premature failure due to excessive wear and corrosion. These often lead to a total revision arthroplasty and also may expose human body to noxious elements if they are present in the implant alloy composition. Recently, new deposition techniques and coating compositions have been emerged targeting higher mechanical, microstructural and tribocorrosion properties on the implant surfaces. Diamond-like carbon (DLC) appears as a considerable coating option in this case, since it has an amorphous structure chemically inert composed by two types of carbon hybridizations (sp^2 and sp^3) that provides an extreme hardness, low friction coefficient, biocompatibility and still is a solid lubricant. The tribocorrosion behaviour of DLC films are influenced by the fraction between sp^2 and sp^3 bonds contained in the coating microstructure. Nonetheless, not only the bonds fraction affects this behaviour, but also the adhesion between coating and substrate to avoid its detachment, which in turn is strongly related to the applied deposition technique. Moreover, carbide and nitride interlayers are often deposited over substrate to favoring the DLC coatings adhesion. Among the advanced DLC deposition techniques are the plasma immersion ion deposition (PIID) and the plasma enhanced magnetron sputtering (PEMS). Both are examples of the plasma enhancement during film vapor depositions that results in coatings with higher density and adhesion when compared to other conventional techniques. This work aims to investigate the tribocorrosion behaviour of DLC coatings with distinct carbide and nitride interlayers, obtained by PIID only and PEMS+PIID hybrid techniques, applied on Ti-6Al-4V alloy samples for biomedical applications. The tribocorrosion tests were performed under phosphate-buffered saline (PBS) solution on the DLC-coated samples and compared to a Ti-6Al-4V bare alloy sample. Besides tribocorrosion tests, it were performed X-ray diffraction (XRD) analysis, Raman spectroscopy, scanning electron microscopy (SEM), nanoindentation hardness and scratch tests to evaluate the microstructure, morphology, mechanical properties and adhesion of the DLC-coated samples. The tribocorrosion tests demonstrated that the applied deposition techniques and interlayers compositions affect not only the adhesion but also the main wear mechanism, which implies in significant wear rate disparities between the DLC-coated samples. Nevertheless, the results show that DLC coatings deposited by the plasma enhanced techniques could be promissory to improve tribocorrosion behaviour in Ti-6Al-4V alloy implants.

DP-9 Fluorine-Incorporated Hydrogen-free Amorphous Carbon Thin Film for Artificial Heart (Ventricular Assist Device), ***Shunto Maegawa,*** Keio University, Japan*; T Hasebe,* Tokai university, Japan*; M Nakayama, K Bito, Y Yamato,* Keio University, Japan*; T Mine, T Matsumoto,* Tokai university, Japan*; A Hotta, T Suzuki,* Keio University, Japan

Advanced blood-contacting medical devices has been more intensive for reducing the mortality rate of cardiovascular diseases. Surface coating is one interesting method of improving the mechanical, physical and biocompatible properties of devices in direct contact with blood and tissue. Fluorine-incorporated hydrogenated amorphous carbon (a-C:H:F) has received much attention as a coating material because of outstanding blood compatible properties which suppress fatal failure of the devices. However, mechanical strength of a-C:H:F film is too low to apply for mechanical medical devices such as blood pump of ventricular assist device (VAD). Thus, fluorine-incorporated hydrogen-free amorphous carbon (a-C:F) films were newly synthesized with vacuum arc deposition method focused on both blood compatibility of a-C:H:F and excellent mechanical properties of hydrogen free tetrahedral amorphous carbon (ta-C). In this

study, we evaluated the possible medical applications of new a-C:F films for frictional parts of blood pump in VAD.

The ta-C (control) and a-C:F films were deposited by filtered cathodic vacuum arc (FCVA) method using a graphite target and introducing C_3F_8 gas into the chamber. We synthesized these films by varying the pressure of C_3F_8 gas to control fluorine content in the films. The fluorine content of the film surfaces was measured by X-ray photoelectron spectroscopy. Carbon bonding structure was analyzed with Raman spectroscopy. Blood compatibility was evaluated by human platelets adsorption tests, and ball-on-disc tests were used to measure friction coefficient (f) for evaluating wear resistant properties. Finally, we applied a-C:F film on blood pump of ventricular assist device.

The fluorine content rate increased from 10 to 50 at.% with increase of C_3F_8 gas pressure. The shift of G peak position in the Raman spectra became lower with increase of fluorine content, and no peaks was identified at 50 at.% fluorine content as usual in a polymer-like film. The a-C:F films containing fluorine content reduced platelets adhesion than ta-C films. On the other hands, much fluorine doping in ta-C simultaneously degrade wear resistant ability. However, friction coefficient of a-C:F films with fluorine content of 10 and 30 at.% (f = 0.121, 0.138, respectively) were greater than or equal to ta-C (f = 0.138). We applied 10 at.% a-C:F on frictional parts of VAD, and consequently improved driving of VAD without frictional wear.

In conclusion, the fluorine-incorporated hydrogen-free amorphous carbon (a-C:F), which we newly developed by using FCVA method, is a promising candidate for frictional parts of blood-contacting medical devices.

DP-10 A Sustainability Investigation on the Hemocompatibility of Heparin/Dopamine and Heparin/Collagen Self-Assembled Multilayers Coated on a Titanium Substrate, *W Cherng,* Chang Gung Memorial Hospital, Taiwan; ***Chau-Chang Chou***, *Y Pan,* National Taiwan Ocean University, Taiwan; *C Yeh,* Chang Gung Memorial Hospital, Taiwan; *T Wu, Z Dong, J Ho,* National Taiwan Ocean University, Taiwan

This work used self-assembly technology to build a heparin/collagen and a heparin/dopamine multilayers on a titanium substrate. Both the coatings' hemocompatibility and adhesion were investigated. The substrate was commercial pure grade 2 titanium which was electropolished for 48h. The oxidation condition of the dopamine interlayer was achieved by being treated treating in a 2 mg/ml dopamine solution under an atmospheric environment for 8 h. After the pretreatment, the samples were immersed in a poly-L-lysine solution for 30 minutes. Then they were alternatively dipped in a heparin and a collagen solutions for 30 minutes . On the other hand, in a heparin and a dopamine solutions to for 30 or 60 minutes until the desired number of layers were achieved. The hydrophilicity, chemical composition, and surface topography of the films were investigated by water contact angle measurement, Fourier transform infrared spectroscopy, and scanning electron microscopy. The film thickness was evaluated by the cross-sectional technique of a focused ion beam microscopy. The amount of the heparin that attached to the samples was measured by toluidine blue O test. The hemocompatibility was verified by the hemolysis ratio, platelet coverage area, and activated partial thromboplastin time (APTT) in vitro. The adhesion of the multilayers was studied by conducting micro-scratch tests. To investigate the performance under dynamic fluid contact, an orbital shaker was implemented. At dynamic environment state, the heparin quantity which was derived by the toluidine blue O test and APTT were assessed after dynamic test. Experiment results show that, the blood compatibility of heparin/dopamine sample is not superior than heparin/collagen one. Moreover, heparin/dopamine multilayers have stronger binding between multilayers and the substrate while not be capable of improving blood compatibility of titanium substrate. However, the extend of coating time are not conducive for the improvement of the related performance. After the dynamic tests, basing on the comparison of residual heparin content, dopamine is capable of resisting physiological fluid shearing stress, but the capability of anticoagulation are no more significantly enhanced from the original Ti substrate, which is worthy of more extensive investigation in the future.

DP-11 Wear Characteristics of Total Ankle Joint Prosthesis with Their Surface Roughness, *Y Jeong,* ***Jae-Woong Yang***, *K Park, S Lee, T Jung,* Osong Medical Innovation Foundation, Republic of Korea

The ankle joint consists of the tibia and fibula above, and the talus below. In the disabling conditions, total ankle replacement (TAR) is becoming an alternative to arthrodesis, i.e. fusion of the tibio-talar articulation, which implies long immobilization, loss of function, and a variable rate of success. This short comings of ankle fusion have led to the development of numerous ankle joint replacements. The conventional type of prosthesis is the three component prosthesis, have a free gliding core and give multi-axial motion, which designs the upper articulation allows for gliding and rotation and the lower articulation allows for flexion/extension. In spite of the increasing interest in TAR, the high failure rate associated with wear of the PE component that has related with their material property and surface roughness. The aim of this study was to verify the wear characteristics of total ankle joint prosthesis with their surface roughness.

The wear specimen of total ankle joint prosthesis was prepared with Ti-6Al-4V alloy and UHMWPE (ultra-high molecular weight polyethylene) for tibia-talus and bearing component, respectively. A wear test was carried out using a Force 5 (AMTI, Massachusetts, US) wear simulator which can be allowed to move in three axis to flexion-extension, internal-external axial rotation, as well as sinusoidal compressive load. All tests were performed following standard ISO 14243, wear rate was calculated with weight loss of UHMWPE bearing while the specimen has tested at certain cycles. The surface roughness by wear simulation cycles was measured using a SJ-411 surface roughness tester (Mitutoyo, Yokohama, Japan).

As based on the preliminary results, wear rate of UHMWPE bearing was 7.9 × 10^{-6} mg/cycles. The surface roughness (Ra) of tibia-talus increased (0.05 to 0.1) with accumulation of simulation cycles while that of bearing component decreased (1.0 to 0.65).

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Keywords: Total Ankle Joint Prosthesis, Wear, Simulation, Surface Roughness, Biomaterials

DP-12 2D Materials for Bioelectronic Sensing, *W Lai,* University of Dayton/Sensors Directorate, Air Force Research Laboratory, USA; *A Stroud,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA; *R Berry,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA; *P DeRosa,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA; *R Naik,* Human Effectiveness Directorate, Air Force Research Laboratory, USA; ***Christopher Muratore***, University of Dayton, USA

Detection of compounds in liquids (such as sweat or saliva) and vapors (such as air in a workplace, a packaged food container, or the cockpit of a fighter jet) has broad reaching applications in industry, home, and battlefield. Analytical devices such as mass spectrometers or gas chromatographs can be used in these applications but they lack portability and the ability to operate continuously yet unobtrusively. Flexible sensor materials could be wearable or otherwise easily integrated into any of the environments suggested above. Mono- and few-layer TMDs are known to demonstrate extreme mechanical flexibility, accommodating up to 10% strain prior to rupture. In addition to convenient form factors afforded by their flexible nature, the high surface to volume ratio of ultrathin semiconducting materials allows detection of very low concentrations of adsorbed molecules via a measurable alteration of their electrical response (e.g., their current-voltage (IV) curve) as if they are "doped" by the presence of surface adsorbates. While the effects on adsorbate-surface relationships in graphene could be understood in context of decades of studies of p-based interactions dictating nanomaterial behavior, 2D TMD interactions are based on d-electron interactions and therefore respond much differently than carbon-based low-dimensional structures to adsorption events and other interactions with molecules. Non-covalent bonding on 2D TMD is only understood qualitatively. Measuring the response in materials with controlled densities of defects introducing localized metallic-like regions of exposed Mo plane-edge atoms and changing the 2D MoS_2 electronic band diagram systematically as predicted by simulations.will provide insight on charge transfer or redistribution in analyte-functional molecule-2D semiconductor interactions. We have demonstrated attachment of a binding peptide to a functional MoS_2 transistor, and observe a significant response in the I-V characteristic curve. Sensitivity to adsorbed molecules for semiconducting 2D TMDs such as MoS_2 is approximately two orders of magnitude higher than graphene based on the predicted minimum subthreshold swing (SS), defined as the inverse of the slope of a transistor IV curve in its steepest part (for a field effect transistor (FET), $SS=d(V_{gate\text{-}source})/d(I_{drain})$. Smaller values of SS suggest higher sensitivity as a small change in surface potential gives rise to a significant change in current, thus enhancing sensitivity. For 2D MoS_2, the SS is around 60 mV/decade in contrast to 1000-5000 mV/decade minimum

for graphene, suggesting >100 X higher sensitivity for TMD-based 2D sensors in comparison to graphene.

DP-13 Study of TiO_2-MgO Composites to Improve the Corrosion Resistance of Mg for Development of Biodegradable Orthopedic Implants, ***EricNoé Hernández-Rodríguez**, C Vicencio-Acosta, C Íñiguez-Contreras, A Balvantín-García, J Diosdado-de la Peña,* DICIS, University of Guanajuato, Mexico*; R Mis-Fernández, J Peña-Chapa,* CINVESTAV-IPN Mérida, Mexico*; M Zapata-Torres,* CICATA-IPN Legaria, Mexico*; A Márquez-Herrera,* DICIVA, University of Guanajuato, Mexico

In this work we report the study of TiO_2-MgO composites as anticorrosive coatings on Mg substrates. Mg has been extensively studied in order to develop biodegradable implants, however, the fast degradation in the physiological fluid is its main disadvantage. Here, we propose the use of the biocompatible TiO2-MgO composite as a protective coating in order to modulate the corrosion resistance of Mg pieces. TiO_2-MgO composites were deposited on Mg substrates by the RF-sputtering technique, and the TiO_2/MgO ratio was changed through the sputtering power. XRD analysis showed that coatings with a high content of MgO present a cubic crystalline structure, while a decrease on the crystallinity was found as the TiO2 content is increased; finally, coatings with the highest content of TiO_2 are amorphous. XPS analysis showed the formation of Ti-O, Mg-O and Ti-Mg-O bonds; the rate between this bonds is related to the resistance against corrosion of the samples. Corrosion experiments were conducted by using the Hank´s solution as the corrosive media and Tafel curves were obtained by employing a potentiostat in the three electrode configuration. Values of corrosion current (i_{corr}) demonstrate that it is possible to improve the corrosion resistance of Mg by employing the TiO_2-MgO composite; even more, the TiO_2/MgO rate on the coatings permits to modulate the corrosion resistance, with the lowest resistance when the coating is only composed by MgO, and the highest resistance when only the TiO_2 is present.

This work is supported by PRODEP-SEP under project number UGTO-PTC-540.

DP-15 Fabrication and Characterization of Magnesium Incorporated Hydroxyapatite on the Titanium Substrates via Electrochemical Deposition, *Y Chor,* National Taipei University of Technology, Taiwan*; **Chien-Ming Lei**,* Chinese Culture University, Taiwan*; S Chen, K Huang, P Chen,* National Taipei University of Technology, Taiwan

Titanium and its alloys have been widely used for biomedical implant due to their desirable mechanical properties, corrosion resistance, and excellent biocompatibility. However, titanium and its alloys have an issue of their insufficient bioactivity. Recently, studies have shown that hydroxyapatite coated metal surface can improve both biocompatibility and bioactivity.

Hydroxyapatite is the major composition in tooth and bone. Compared to synthetic hydroxyapatite, natural bones have various trace elements which play important roles for cell growth. Magnesium incorporated hydroxyapatite stimulate the proliferation of osteoblast during the early stage of implantation. It has a significant effect in bone metabolism. In this study, magnesium ion was added into the electrolyte which composed of P and Ca ions, and then MHA coatings on titanium substrate were prepared by electrochemical deposition. We carried out characterizations to identify the phase composition, the changes of surface morphology, surface roughness and corrosion resistance of coatings in the simulating body fluid. Results show that magnesium incorporated hydroxyapatite has higher surface roughness and corrosion current density. Moreover, the magnesium incorporated hydroxyapatite can induce nucleation and growth of the new apatite on the surface where $Ca_3(PO_4)_2$ precipitates can be found after immersion test. As a result, the magnesium incorporated hydroxyapatite shows better biocompatibility and bioactivity.

DP-16 Electrochemical Characteristics of RF-sputtered Zn and Si Coatings on HA Coated Ti-6Al-4V by PEO Treatment, ***InJo Hwang**, H Choe,* Chosun University, Republic of Korea

Commercially pure titanium (cp-Ti) and Ti alloys (typically Ti-6Al-4V) display excellent corrosion resistance and biocompatibility. Ti and its alloys are not bioactive. Therefore, they do not chemically bond to the bone, whereas they physically bond with bone tissue. Their poor surface biocompatibility, the surface of Ti alloys has to be modified to improve the surface osteoinductivity. Among various surface modification methods, the electrochemical deposition process provides an effective surface for biocompatibility because large surface area can be served to cell proliferation. Plasma electrolyte oxidation (PEO) enables control in the chemical composition, porous structure, and thickness of the TiO_2 layer on Ti surface. In addition, previous studies have concluded that the presence of Ca^{+2} and PO_4^{3-} ion coating on porous TiO_2 surface induced adhesion strength between Hap and Ti surface during electrochemical deposition.

Radio frequency(RF) magnetron sputtering in the various PVD methods has high deposition rates, high-purity films, extremely high adhesion of films, and excellent uniform layers for depositing a wide range of materials, including metals, alloys and ceramics like a hydroxyapatite. The aim of this study is to research the Zn and Si ions coatings on the micro-pore formed Ti-6Al-4V alloys by RF-magnetron sputtering for dental applications.

Silicon (Si) in particular has been found to be essential for normal bone and cartilage growth and development. Zinc (Zn) plays very important roles in bone formation and immune system regulation, and is also the most abundant trace element in bone. The objective of this work was to study electrochemical characteristics of RF-sputtered Zn and Si coatings on HA coated Ti-6Al-4V by PEO treatment.

The coating process involves two steps: 1) formation of porous TiO_2 on Ti-6Al-4V at high potential. A pulsed DC power supply was employed. The sparking energy also will affect the size of micro pores and the ions concentrations. 2) Electrochemical tests were carried out using potentiodynamic and AC impedance methoeds. The morphology, the chemical composition, and the micro-structure analysis of the sample were examined using FESEM, EDS, and XRD. The enhancements of the Hap forming ability arise from Si/Zn-TiO_2 surface, which has formed the reduction of the Si/Zn ions. The promising results successfully demonstrate the immense potential of Si/Zn-TiO_2 coatings in dental and biomaterials applications (Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr).

DP-18 Nucleation and Growth of Bone-like Apatite Formation on Ti-6Al-4V in Solution Containing Mn, Mg, and Si Ions after Plasma Electrolytic Oxidation, ***SangGyu Lim**, H Choe,* Chosun University, Republic of Korea

Titanium and its alloys that have a good biocompatibility, corrosion resistance, and mechanical properties such as hardness and wear resistance are widely used in dental and orthopedic implant applications. They can directly connect to bone. However, they do not form a chemical bond with bone tissue . Plasma electrolytic oxidation (PEO) that combines the high voltage spark and electrochemical oxidation is a novel method to form ceramic coatings on light metals such as titanium and its alloys . This is an excellent reproducibility and economical, because the size and shape control of the nano-structure is relatively easy.Silicon (Si), m anganese (Mn), and magnesium (Mg) has a useful to bone. Particularly, Si has been found to be essential for normal bone, cartilage growth and development. Manganese influences regulation of bone remodeling because its low content in body is connected with the rise of the concentration of calcium, phosphates and phosphatase out of cells. Insufficience of Mn in human body is probably contributing cause of osteoporosis. Pre-studies have shown that Mg plays very important roles in essential for normal growth and metabolism of skeletal tissue in vertebrates and can be detected as minor constituents in teeth and bone.

The objective of this work was to study nucleation and growth of bone-like apatite formation on Ti-6Al-4V in solution containing Mn, Mg, and Si ions after plasma electrolytic oxidation. Anodized alloys was prepared at 270V~300V voltages. And bone-like apatite formation was carried out in SBF solution for 1, 3, 5, and 7 days. The morphologies of PEO-treated Ti-6Al-4V alloy in containing Mn, Mg, and Si ions were examined by FE-SEM, EDS, and XRD (Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr).

DP-19 Ion Release of Zn, Si, Mn-doped Hydroxyapatite Films Formed on the Ti-6Al-4V Alloy by Plasma Electrolytic Oxidation, ***MinGyu Park**, H Choe,* Chosun University, Republic of Korea

Titanium and its alloys have been used in the fields of orthopedics and dentistry due to their abilities to exhibit high specific strength, high corrosion resistance, and chemical inertness particularly in biological circumstances. Despite these attractive properties, their passive films were somewhat bioinert in nature so that sufficient adhesion of bone cells to implant surface was delayed after surgical treatment. Recently, the Plasma electrolyte oxidation (PEO) of titanium metal has attracted a great deal of attention.

Silicon (Si) in particular has been found to be essential for normal bone and cartilage growth and development. Zinc (Zn) plays very important roles in bone formation and immune system regulation, and is also the most abundant trace element in bone. Manganese(Mn) is important in terms of

protein synthesis, the manganese is insufficient, the generation of cartilage synthesis of the organic matrix is low is delayed, thickness and length decreased abnormal bone generation is performed. Si, Zn, and Mn has a beneficial effect on bone.

The objective of this work was research on i on r elease of Zn, Si, Mn-doped h ydroxyapatite f ilms f ormed on the Ti-6Al-4V a lloy by p lasma e lectrolytic o xidation. Anodized alloys was prepared at 270V~300V voltage in the solution containig Zn, Si, and Mn i ons. Ion release test was carried out using potentidynamic and AC impedance method in 0.9% NaCl solution. The surface characteristics of PEO treated Ti-6Al-4V alloy were investigated using XRD, FE-SEM, AFM and EDS(Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr]).

DP-20 Nanotube Shape Changes on Ti-30Nb-xTa Alloys with Continuously Changed Potentials, ***Han-Cheol Choe,*** Chosun University, Republic of Korea

CP-Ti and its alloys have over the past few decades become the premier choice as biocompatible dental and hip replacement implant materials. Although the Ti-6Al-4V alloy is an acceptable prosthetic biomaterial, recent studies indicated that the release and accumulation of Al and V ions could have harmful effects on the human body. In order to overcome these disadvantages of Ti-6Al-4V alloy, new β type Ti alloy made of non-toxic alloying elements such as Nb, Ta and Zr have been developed. Surface modification is generally essential to improve the chemical bonding between Ti implant and bone tissues. Thus, it has been shown that nano-scale porous as well as tubular oxide layers on titanium alloys can increase the bioactivity of an implant material. Also, it should be possible to control the nanotube size and morphology for biomedical implant use by controlling the applied voltage, alloying element, current density, anodization time and electrolyte. The aim of this study was surface modification of nanotube formed Ti-30Nb-xTa alloys with changes in anodization factors. The Ti-30Nb-xTa alloys with Ta contents of 0, 15 wt. % were melted by using a vacuum arc-melting furnace and, homogenized for 12h at 1000℃. The anodization was performed by changing of applied voltage from high to low (30 V to 10 V) and, from low to high (10 V to 30 V) for 1h. The electrolyte was composed of 1 M H_3PO_4 + 0.8 wt.% NaF. This study was evaluated the phase of Ti-30Nb-xTa alloys using an x-ray diffractometer (XRD), and the microstructure of the samples was investigated with field emission scanning electron microscopy (FE-SEM) and optical microscope (OM). For biocompatibility, fibroblast cell was cultured and contact angle was measured. (NRF: No.2008-0062283; hcchoe@chosun.ac.kr).

DP-21 Shapes of Bone-like Apatite Formation on Sr and Si-doped Hydroxyapatite Surface of Ti-6Al-4V Alloy after Plasma Electrolytic Oxidation, ***Ji-Min Yu,*** *H Choe,* Chosun University, Republic of Korea

Metallic biomaterials have been mainly used for the fabrication of medical devices for the replacement of hard tissue such as artificial hip joints, bone plates, and dental implants. Because they are very reliable on the viewpoint of mechanical performance. This trend is expected to continue. Especially, Ti and Ti alloys are bio- inert. So, they do not chemically bond to the bone, whereas they physically bond with bone tissue. For t heir poor surface biocompatibility, the surface of Ti alloys has to be modified to improve the surface osteoinductivity. Recently, ceramic-like coatings on titanium, produced by plasma electrolytic oxidation (PEO), have been developed with calcium- and phosphorus-enriched surfaces. A lso included the influences of coatings, which can accelerate healing and cell integration, as well as improve tribological properties. However, the adhesions of these coatings to the Ti surface need to be improved for clinical use.

Particularly Silicon (Si) has been found to be essential for normal bone, cartilage growth and development. This hydroxyapatite, modified with the inclusion of small concentrations of silicon has been demonstrating to improve the osteoblast proliferation and the bone extracellular matrix production. Strontium-containing hydroxyapatite (Sr-HA) was designed as a filling material to improve the biocompatibility of bone cement. In vitro, the presence of strontium in the coating enhances osteoblast activity and differentiation, whereas it inhibits osteoclast production and proliferation.

The objective of this work was to study shapes of bone-like apatite formation on Sr and Si-doped hydroxyapatite surface of Ti-6Al-4V alloy after plasma electrolytic oxidation. Anodized alloys was prepared at 270V~300V voltages with various concentrations of Si and Sr ions. Bone-like apatite formation was carried out in SBF solution. The morphology of PEO, phase and composition of oxide surface of Ti-6Al-4V alloys were examined by FE-SEM, EDS, and XRD(Supported by NRF: 2015H1C1A1035241 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr [mailto:hcchoe@chosun.ac.kr]).

[1] A. K. Mishra, J. A. Davidson, R. A. Poggie, P. Kovacs, T. J. FitzGerald, Mechanical and tribological properties and biocompatibility of diffusion hardened Ti-13Nb-13Zr a new titanium alloy for surgical Implants, ASTM Spec Tech Publication 1272 (1996) 96-112.

DP-22 Chemical Bonding Characteristics of Biocompatible TiO2 Oxide Multilayer by the XPS Depth Analysis, ***Jae-Myung Jang,*** GwangJu Nambu University, Republic of Korea*; T Park,* Eco-Tech Korea, Republic of Korea*; H Choe,* Chosun University, Republic of Korea

Most recently, to improve the biocompatibility, various processes that aim at coating an implant material with a bioactive nanoparticles such as synthetic hydroxyapatite have been proposed[1]. For this purpose, barrier and porous/tubular type of anodic oxide films could be formed by electrochemical anodization using a set of specific conditions including optimized potential, electrolyte composition, and temperature. Also, the chemical component of the electrolyte is essential in determining the type of morphology that is eventually formed, and the geometric morphology of TiO_2 oxide film is mutually important in direct contact with biological tissue in dental or surgical implants. In addition, the specific ions in the contact surface with the bone site plays a critical role in terms of adhesion and stability for long periods in the living body.

Thus, in this work, the manufacture of the TiO_2 barrier-type multilayerwas accurately performed in a mixed electrolyte containing HAp, Pd, and Ag nanoparticles. The temperature of the solution was kept at approximatively 32℃and was regularly rotated by a magnetic stirring rod in order to increase the ionic diffusion rate. The manufactured specimens were carefully analyzed by XPS depth profile to investigate the result ofchemical bonding behaviors. From the analysis of chemical states of the TiO_2 oxide multilayer using XPS, the peaks are showed with the typical signal of Ti oxide at 459.1 eV and 464.8 eV, due to Ti 2p(3/2) and Ti 2p(1/2), respectively. The Pd-3d peak was split into Pd-3d(5/2) and Pd-3d(3/2)peaks, and shows two bands at 334.7 and 339.9 eV for Pd-3d3 and Pd-3d5, respectively. Also, the peaks of Ag-3d have been investigated. The chemical states consisted of the O-*1s*, P-*2p,* and Ti-*2p* were identified in the forms of PO_4^{2-} andPO_4^{3-}. Based on the results of the chemical states, the chemical elements into the TiO_2 oxide multilayer were also inferred to be penetrated from the electrolyte during anodic process. The structure characterization of the modified surface were performed by using FE-SEM, and from the result of biological evaluation in simulated body fluid(SBF), the biocompatibility of TiO_2 oxide multilayer was effective for bioactive property(Supported by NRF: 2016R1D1A1B01016542 & NRF: No.2008-0062283 ; hcchoe@chosun.ac.kr)

DP-25 Corrosion and Antibacterial Properties of Micro-Arc Oxidized Biodegradable Mg-Sr Alloys for Biomedical Applications, ***Mehmet Yazici,*** Ondokuz Mayis University, Turkey*; E Gulec,* Gebze Technical University, Turkey*; M Gurbuz,* Ondokuz Mayis University, Turkey*; Y Gencer, M Tarakci,* Gebze Technical University, Turkey

Despite magnesium has some advantages over the present biomaterials it has some handicaps for orthopedic applications, such as high corrosion rate, mechanical properties [1, 2]. To improve the corrosion resistance of magnesium a ceramic layer was produced on the Mg alloys by micro-arc oxidation (MAO) method. To provide a better corrosion resistance Ag ions added antibacterial HA nano particles were added to the electrolyte in the range of 1-15 g/lt. The coated alloys were characterized by using scanning electron microscopy and X-ray diffractometer. Also immersion tests, corrosion tests and anti-bacterial tests were done to compare the coatings.

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