

## Coatings for Biomedical and Healthcare Applications Room Pacific Salon 2 - Session D1-1-MoM

### Surface Coating and Modification for Use in Biological Environments I

**Moderator: Mathew T. Mathew**, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

10:20am **D1-1-MoM-2 Very Thin Gold Films Deposited on Collagen Fabric for Skin Cell Recover**, *Sheng-Yang Huang*, Taichung Veterans General Hospital, Feng Chia University, Taiwan; *Y Chang*, Feng Chia University, Taiwan; *P Hsieh*, Institute of Plasma, Feng Chia University, Taiwan; *C Chou*, Taichung Veterans General Hospital, National Yang-Ming University, Taiwan; *C Chung*, Central Taiwan University of Science and Technology, Taiwan; *J He*, Feng Chia University, Taiwan

The goal of this study is to develop a novel biomedical material, where gold thin film is deposited on collagen fabrics for skin tissue engineering. Type I Collagen had been used in many products for its biocompatibility and critical role in skin recovery. Gold, in the form of nanoparticles (AuNPs), had been proven to improve biomaterial properties, such as mechanical strength, elasticity, degradation resistance, cell attachment, cell proliferation and wound healing. Unlike chemically prepared AuNPs in most of present literature, very thin gold films deposited by high-power impulse magnetron sputtering (HIPIMS) on collagen fibers reveal the advantage of green synthesis process and free from chemical ligand of gold particles.

Scanning electron microscopy (SEM) and X-ray diffraction (XRD) are used to observe the surface morphology and microscopic characteristics of the composites. Fourier transform infrared spectroscopy (FTIR) and circular dichroism spectroscopy (CD) are used to evaluate functional groups and secondary structure of collagen, respectively. Process of biomedical fabrics with collagen and gold thin film in different thickness is established.

**Keywords:** gold thin films, HIPIMS, collagen fabric, skin cell recovery

10:40am **D1-1-MoM-3 Effect of Calf Serum on Tribological Behavior of DLC Coating in Ti-6Al-4V / Ti-6Al-4V Contact for Application to STEM / NECK Contact of Modular Hip Implant**, *H Ding*, *Vincent Fridrici*, *G Bouvard*, Ecole Centrale de Lyon, LTDS - Université de Lyon, France; *J Géringier*, Ecole des Mines de St-Etienne - Université de Lyon, France; *P Kapsa*, Ecole Centrale de Lyon, LTDS - Université de Lyon, France

Influences of new-born calf serum on the fretting behaviors of Ti-6Al-4V and diamond-like carbon coating were investigated using a fretting-wear test rig with a cylinder-on-flat contact. The results indicated that, for the Ti-6Al-4V / Ti-6Al-4V contact, the friction coefficients were high (0.8-1.2) and the wear volumes presented an increase with the increase in the displacement amplitude under dry laboratory-air conditions. Under serum-liquid conditions, the Ti-6Al-4V / Ti-6Al-4V contact presented significantly larger wear volumes under the displacement of  $\pm 40 \mu\text{m}$ ; however, it presented significantly lower friction coefficients (0.25-0.35) and significantly smaller wear volumes under the displacement of  $\pm 70 \mu\text{m}$ . The opposite effects of lubrication and corrosion are studied and analyzed. For the DLC coating / Ti-6Al-4V contact, the coating response wear maps could be divided into two areas: the coating working area (low normal force conditions) and the coating failure area (high normal force conditions). In the coating working area, the DLC coating could protect the substrate with low friction, low wear volume, and mild damage in the coating. The presence of serum had a positive influence on the tribological performance of the DLC coating. Furthermore, the positive influence was more significant under larger displacement amplitudes condition.

11:00am **D1-1-MoM-4 Accelerated Tests for Lifetime Prediction of Interlayers and Interfaces of Coated Implants in Body Fluid**, *Roland Hauert*, *E Ilic*, *A Pardo-Perez*, *K Thorwarth*, *P Schmutz*, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *S Mischler*, Institut des Matériaux IMX, EPFL, Lausanne, Switzerland

**INVITED**  
Hard coatings such as diamond like carbon (DLC) on articulating joints can result in desired surface properties showing extremely low wear. However, an interlayer material or a single row of contamination atoms at the coating/substrate interface can result in altered corrosion behavior and possible adhesion instability. A method to determine the chemical composition of the few atomic rows of altered material at an interface, buried under several microns of coatings, will be shown by low angle polishing down to less than 0.06 degrees (less than 1/1000 steepness).

Corrosion effects such as crevice corrosion, which can cause coating delamination after some years in vivo, cannot be accelerated in simulator testing since it evolves only as a function of time in media. A new setup for accelerated crevice corrosion testing in body fluid, as well as preliminary results, will be presented. Furthermore, stress corrosion cracking and corrosion-fatigue can damage the few rows of reacted atoms present at an interface. By simulating in vivo conditions, we are developing an accelerated test to assess these deteriorating effects at the interface. First results of coating adhesion lifetime expectations, including the influence of small detrimental contaminations, will be shown.

11:40am **D1-1-MoM-6 Thin Film Metallic Glass Coating as an Effective Antiadhesion Coating for Platelet and Cancer Cells**, *Jinn P. Chu*, National Taiwan University of Science and Technology (NTUST), Taiwan; *C Li*, *Y Chen*, *S Chyntara*, National Taiwan University of Science and Technology, Taiwan; *M Chen*, Mackay Medical College, Taiwan; *S Chang*, Mackay Memorial Hospital Tamsui Campus, Taiwan

The adhesion of platelet cells is viewed as a first step in thrombus formation, and cancer cell attachment can lead to cancer seeding. The amorphous structure of metallic glasses (MGs) is a new group of coating materials exhibiting excellent hydrophobicity and resistance to bacterial colonization, as well as relatively low coefficient of friction. In this presentation, we will report a study which has been published in *Surface and Coatings Technology*, Vol. 344, p. 312-321 (2018), describing the feasibility of utilizing  $\text{Zr}_{53}\text{Cu}_{33}\text{Al}_9\text{Ta}_5$  thin film metallic glass (TFMG) to minimize the adhesion of various human cancer cells (breast cancer cell, colon cancer cell, and esophageal cancer cell), human and animal platelets. TFMG was respectively grown on glass substrates to a thickness of 200 nm using magnetron sputtering. TFMG was shown to reduce surface roughness of glass. The concentrations of all major ions released from the TFMG were well below toxic levels. TFMG surfaces were effective in increasing the contact angle of water, phosphate buffer saline and blood from different animal species. The application of TFMG to bare surfaces was shown to reduce the attachment area of human platelets by 77 % and that of pig platelets by 63%. TFMG also reduced the attachment of cancer cells by up to ~87%. These characteristics can be attributed to a low surface free energy of TFMG-coated surfaces (31.89 mN/m), which is far below that of bare glass (47.80 mN/m). These findings demonstrate the considerable potential of TFMG coatings in the fabrication of medical instruments aimed at preventing the adhesion of platelet and cancer cells.

12:00pm **D1-1-MoM-7 Improvement of Surface Properties of Nitinol Alloy through Deposition of Graphene by Electrophoretic Deposition Technique for Biomedical Applications**, *Madhusmita Mallick*, *N Arunachalam*, Indian Institute of Technology Madras, India

The superelastic nature of biocompatible material nitinol & its alloys is utilized for the application of orthodontic archwires due to its ability to prevent strain localization & plastic deformation. However, they tend to wear over time due to continual contact with body fluids and release toxic metal ions ( $\text{Ni}^{2+}$ ) into the body. In order to overcome this limitation smooth layers of graphene was deposited on Nitinol wires by Electrophoretic Deposition technique to improve its wear resistance and other mechanical properties.

The electrodeposited coatings were characterized by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-Ray diffraction, Raman spectroscopy and Potentiodynamic polarization technique. Raman spectroscopy showed the presence of graphene & 2-D graphitic phase. Finally, a post deposition treatment was done to evaluate in-vitro bioactivity by Simulated Body Fluid (SBF) immersion test. The results showed that graphene coating onto Nitinol substrate improved anti-corrosion rate and anti-bacterial properties while reducing friction as compared to bare Nitinol wires.

Hence, this bioactive coating exhibited better mechanical strength, enhanced wear and corrosion resistance indicating high potential for biomedical applications.

## Coatings for Biomedical and Healthcare Applications Room Pacific Salon 2 - Session D1-2-MoA

### Surface Coating and Modification for Use in Biological Environments II

**Moderator: Mathew T. Mathew**, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

1:40pm **D1-2-MoA-1 Recent Development of Biocompatible Thin Film Metallic Glass Materials**, *Jyh-Wei Lee*, Ming Chi University of Technology, Taiwan; *B Lou*, Chang Gung University, Taiwan; *Y Yang*, National Taipei University of Technology, Taiwan; *C Lin*, National Taiwan University, Taiwan

#### INVITED

The thin film metallic glass (TFMG) materials have been intensively studied due to their promising physical and mechanical properties, such as high strength, flexibility, and excellent corrosion resistance. Recently, the biomedical applications of TFMGs also attracted lots of attentions from researchers. Improved sharpness and non-stick effects of the dermatome and syringe needles have been reported, respectively, by the coating of thin film metallic glass. In this work, several Zr-, Ti- and Fe-based TFMGs were fabricated using magnetron sputtering method. The corrosion resistance and in-vitro biocompatibility tests of TFMGs were studied. The antimicrobial test of some Cu or Ag containing TFMGs was also evaluated. The in-vivo animal test on Zr-Ti-Si and Fe-Zr-Nb TFMGs was further investigated. In addition, fracture resistance evaluation of dental Ni-Ti rotary instruments with TFMG coating was conducted. It is found that excellent anti-corrosion properties were observed for these TFMGs. Remarkable antimicrobial performance was obtained for the Cu or Ag containing TFMGs. In-vitro test showed that the TFMGs had good proliferation and differentiation of cultured cell. The in-vivo animal test also indicated that no allergy, toxicity or carcinogenic reaction was caused by the TFMGs to the rats. The Ti-based TFMG coating can effectively improve the fatigue fracture resistance of dental Ni-Ti rotary files. We can conclude that the biocompatible Zr-, Ti- and Fe-based TFMGs show very promising application on the dental and orthodontic surgical tools.

2:40pm **D1-2-MoA-4 Antibacterial and Biocompatible Properties of Ga-doped TaON Thin Films**, *Jang-Hsing Hsieh*, *Q Liu*, Ming Chi University of Technology, Taiwan; *C Li*, National Yang Ming University, Taiwan

Recently, gallium ions have been studied for its multi-functional bio-activity. While gallium has no known function in human physiology, the chemical properties that it shares with iron allow it to bind to iron-containing proteins (Trojan Horse effect), including the iron transport protein transferrin. Thus, malignant cells and microorganisms may be tricked into incorporating gallium in place of iron for iron-dependent processes essential for bacterial viability and growth. Hence, rather than facilitate iron-dependent cellular function, gallium disrupts it. As a result, the interaction between gallium and iron-proteins can be exploited for therapeutic purposes in cancers and bactericidal treatments. Accordingly, it is of great interest to know how Ga can be doped into surface coatings.

In this study, the deposition processes of tunable TaOxNy-Ga thin film coatings were studied systematically. Following this, the resultant mechanical, structural, and, bio-related properties were examined, in terms of O/N ratio, surface roughness and Ga contents. However, due to low melting point of Ga (~29 °C), it is relatively difficult to sputter Ga into those oxynitride coatings. Therefore, Ga<sub>2</sub>O<sub>3</sub> target was used in this study to provide oxygen and Ga. According to the results, it was learned that small amount of oxygen (2~5%) and gallium (1~3%) in the coatings could be beneficial to the improvement of mechanical and antibacterial properties. The enhanced dissolution of Ga ions was observed with the addition of oxygen. The highest hardness could reach 30 GPa, while an antibacterial efficiency of >90% could be found after 48 hrs of immersion. The films showed good biocompatibility with MG63 cells.

3:00pm **D1-2-MoA-5 TiO<sub>2</sub> Nanotubes Produced in Aqueous Electrolytes with CMC for Biomaterials Application**, *Robinson Aguirre Ocampo*, *M Echeverry-Rendón*, *S Robledo*, *F Echeverría*, Universidad de Antioquia, Colombia

Nanotubular structures were produced on the c.p. Titanium surface by anodization in an aqueous electrolyte that contains carboxymethylcellulose (CMC) and NaF. The internal diameter obtained at voltages of 20, 10 and 2 V was about 100, 48 and 9.5 nm, respectively. Those diameters were measured using Scanning Electron Microscopy (SEM), Transmission

Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Scientific reports about nanotube produced by anodization with internal diameters upper than 30 nm are very common, however, reports about lower nanotube diameters (<20 nm) are scarce. Several heat treatments at 200, 350 and 600 °C were made to produce nanotubes with different TiO<sub>2</sub> polymorphs (Anatase, Rutile), at 200 °C no phase change was observed, at 350 °C the nanotubes change from amorphous phase to Anatase, and at 600 °C the rutile phase was predominant. These phases were corroborated by XRD and Micro-Raman microscopy. All the tested surfaces were superhydrophilic (high surface free energy), and the superhydrophilic behavior is maintained after at least 25 days, regardless of the heat treatment. The aim of produce nanotubes with different diameters and various heat treatments was to correlate the nanotube characteristics (morphology, internal diameter, composition) and the biologic behavior (cell adhesion and proliferation and antibacterial properties). The heat treated samples showed higher antibacterial properties in contrast to the as anodized samples. All nanotube coatings of TiO<sub>2</sub> were non-cytotoxic, nevertheless the anodization parameter or electrolyte composition used. However, some differences in terms of cell adhesion were found. Based on those results, these coatings can be applied as drug carriers, surface modification of biomaterial devices and catalyst, among others.

3:20pm **D1-2-MoA-6 Electrochemical Evaluation of Titanium Oxide Coatings Deposited on Magnesium Alloys**, *B Millan-Ramos*, Universidad Nacional Autonoma de Mexico, México; *J Victoria-Hernandez*, *S Yi*, Magnesium Innovation Centre, Helmholtz-Zentrum, Germany; *D Letzig*, Magnesium Innovation Centre, Helmholtz-Zentrum, Germany, Germany; *Phaedra Silva-Bermudez*, Instituto Nacional de Rehabilitación, Mexico; *S Rodil*, Universidad Nacional Autonoma de Mexico, México

Titanium oxide (TiO<sub>2</sub>) has been recognized as the active layer responsible for the good biocompatibility and osteogenic properties of the Ti-based medical alloys used for dental and orthopedic applications. Meanwhile, magnesium (Mg) and its alloys are currently widely researched for orthopedic applications, since their mechanical properties are more adequate to balance load transfer between bone and implant, but also due to its biodegradability. Extensive mechanical, in-vitro and in-vivo studies have been done to improve the biomedical performance of Mg alloys through alloying, processing conditions and surface modifications, including coating deposition. The main purpose of such modifications is to extent the degradation rate of the alloy in order to match it with bone self-healing time. In this work, we are investigating the use of titanium oxide coatings deposited by reactive magnetron sputtering on high purity Mg alloys.

Here, we present the electrochemical response of TiO<sub>2</sub>-coated Mg-alloys in simulated physiological fluids. The results indicate that independently of the TiO<sub>2</sub> film thickness (60 - 250 nm) and the use of a Ti-buffer layer, the corrosion rate of the Mg alloy is not significantly reduced. Such response is probably associated to specific chemical reactions occurring between Mg and Ti that were not expected.

4:00pm **D1-2-MoA-8 Metallization of Polymers for Medical Applications**, *Aarati Chacko*, *H Hug*, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *S Gauter*, Christian-Albrechts-University Kiel, Germany; *K Thorwarth*, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Metallization of polymers has been of interest for years, as a means to achieve barrier coatings in packaging, biocompatible interfaces for medical implants, or to produce light-weight alternatives to metal parts in the automotive and aerospace industries, to cite a few examples. As the performance requirements of metalized plastics increase, so too must our understanding of plasma-polymer and metal-polymer interactions that occur in coating processes. High Power Impulse Magnetron Sputtering (HIPIMS) is a physical vapor coating method that allows one to span a whole range of energetic regimes; close to direct current sputtering, with low metallic ion discharge, up to almost fully ionized discharges. This versatile technique is our method of choice to study and tailor the substrate-film interphase region responsible for 'good' and long-lived coating adhesion.

In our study we vary the pulse-on/off time, thus controlling the time allowed for surface processes to occur between metal-species fluxes. We evaluate the chemical state of our interface using XPS and gauge the practical adhesion of the resulting films using a modified ASTM D4541 pull-off test. In addition, we study the effect of sample pre-treatment on adhesion, also using the above methods. The test metal-polymer system

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for this study is titanium on PEEK, which has shown exemplary adhesion in the case of orthopedic implants for use in spinal fusion surgery.

4:20pm **D1-2-MoA-9 Characteristics of a Composite Ceramic Coating Fabricated on Mg-1.2Zn-0.5Ca-0.5Mn Alloy Towards Biodegradable Bone Implants**, *Hamdy Ibrahim*, University of Tennessee at Chattanooga, USA; *D Dean*, Ohio State University, USA; *M Elahinia*, University of Toledo, USA

**INTRODUCTION:** Mg and its alloys possess a biodegradable nature that has recently made them attractive for developing biomedical devices that are expected to degrade and bioresorb completely *in-vivo* after the healing of the body tissue. In addition to their biodegradable nature, Mg alloys are biocompatible, and they have low density and modulus of elasticity, close to the bone. We have developed a patent-pending alloy, Mg-1.2Zn-0.5Ca-0.5Mn produced using biocompatible alloying elements, and a heat treatment process that is likely to provide the needed mechanical stability during bone healing and reliably resorb following the healing of a reconstructed skeletal segment. Our goal is to investigate the use of a composite ceramic-based coating to delay device corrosion (weakening) for 4-6 months.

**METHODS:** We heat-treated Mg-1.2Zn-0.5Ca-0.5Mn alloy samples to achieve significant mechanical strength and then coated them using plasma electrolyte oxidation (PEO) and layer-by-layer coating techniques to achieve corrosion resistance. The coated samples were characterized for their morphological and chemical properties using SEM, EDS and XRD methods. Finally, the corrosion characteristics before and after coating were determined using Potentiodynamic polarization test conducted in a simulated body fluid (SBF).

**RESULTS:** PEO-coated samples show pitting and pores, a common observation following PEO coating, and a tight junction with the subsequent layer-by-layer coatings. The composite coated samples showed a major enhancement in the corrosion resistance compared to the only PEO-coated and uncoated samples. The XRD patterns showed the presence of the incorporated compounds on the coating surface in addition to the presence of biocompatible corrosion products on the surface after corrosion such as hydroxyapatite (HA) and magnesium hydroxide (Mg(OH)<sub>2</sub>). The use of heat treatment followed by composite ceramic coating may be beneficial for the fabrication of Mg-1.2Zn-0.5Ca-0.5Mn skeletal fixation devices with predictable resorption rates.

## Coatings for Biomedical and Healthcare Applications

### Room Pacific Salon 3 - Session D3-TuM

#### Surfaces and Coatings to Promote Tailored Biological Responses

**Moderators:** Sandra Rodil, Universidad Nacional Autónoma de México - Instituto de Investigaciones en Materiales, Vincent Fridrici, Ecole Centrale de Lyon - LTDS

8:40am **D3-TuM-3 In Vitro Evaluation of Macrophage Response to Ionic Liquid-Coated Titanium**, Sutton Wheelis, L Guida, D C. Rodrigues, University of Texas at Dallas, USA

**Introduction:** Dicationic Imidazolium-based ionic liquids with amino acid anions (IonL) have been proposed as a multifunctional coating approach for dental implants. IonL are able to form a temporary, stable coating on the surface of titanium (cpTi), providing lubrication and antimicrobial properties to address the multiple causes of early dental implant failures while maintaining bone and soft tissue cell compatibility *in vitro*. However, there is limited information regarding the response of immune cells to this coating, which is significant as they are often determining factors in implant healing. The aim of this study is to evaluate the proliferation and cytokine gene expression of human macrophages in response IonL-coated cpTi *in vitro* to infer the possible effect of the coating on the onset of the acute immune response *in vivo*.

**Methods:** IonLs with the best combination of antimicrobial and host cell compatibility properties (IonL-Phe, IonL-Met) were chosen as the coatings for investigation. CpTi disks (5 X 2 mm) were drop coated in 1  $\mu\text{mol}$  of each IonL on the disk surface. Uncoated cpTi disks and 1  $\mu\text{mol}$  of pure IonL were used as controls. Samples and controls were plated individually in 6 well plates in experimental duplicates ( $n = 36$ ), seeded with primary human macrophages (MO, Cellprogen), then incubated for 1 or 3 days with a 135,000 or 50,000 cells per well. One set of experiments underwent a 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assay to determine cell proliferation in each well. The other experimental replicate were evaluated with a quantitative polymerase chain reaction (qPCR) to determine changes in IL6, TNF $\alpha$ , TGF $\beta$ 1, iNOS, ARG1 and FIZZ1 gene expression to determine MO polarization. Statistical analysis was performed using ANOVA ( $\alpha = 0.05$ )

**Results:** Results from 1 day MTT assays showed a significant difference in viability in IonL-Met coated samples and uncoated cpTi control. Results from 3 days showed a significant difference in viability of the control versus both IonL coatings, as well as between IonL-Met and IonL-Phe coated samples. However, in both 1 and 3 day experiments, viability in all samples did not drop below 70% when scaled to the uncoated cpTi.

**Conclusions:** MTT assays show that although there is a significant drop in viability after 3 days of IonL exposure, the coating is still not considered cytotoxic. Similar viability results were seen when the same assay was performed on bone and soft tissue cells. Therefore, the IonLs retain their cell compatibility and qPCR results will likely corroborate viability results, showing a lack of significant stimulation towards pro- or anti-inflammatory phenotypes.

9:00am **D3-TuM-4 Materials To Control Biological Function**, Karine Anselme, CNRS, France **INVITED**

Surface modifications of materials are used to monitor and evaluate cellular function for several decades. An example of this is the ability to control tissue integration of medical prostheses by changing their composition, surface topography, chemistry, energy, or their mechanical properties. Similarly, control of the surface of materials is also a key element in the effectiveness of diagnostic tools, devices for cell culture, bio-sensors or drug delivery systems (1).

The cells have the ability to discriminate and specifically react to surface characteristics of the materials considered at the micrometer scale as well as the nanometer scale. In this talk, I will present our experience on the response of cells to functionalization of implants with mixed coatings associating inorganic and organic compounds such as hydroxyapatite and biologically active proteins (fibronectin, bone morphogenetic proteins) (2). Also, our last experience on response of living cells to topography at their own scale will be detailed and in particular our recent discovery of a new cellular ability which we term "curvotaxis" (3).

#### References:

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3. L. Pieuchot\*, M. Vassaux, J. Marteau, T. Cloatre, T. Petithory, I. Brigaud, P-F. Chauvy, A.Ponche, J-L. Milan, P. Rougerie, M. Bigerelle, K. Anselme, Curvotaxis directs cell migration through cell-scale curvature landscapes (2018) Nature Communications, 9:3995

9:40am **D3-TuM-6 Comparison of Elution of Antibiotic and Biofilm Inhibitor from Manually Applied and Spray Deposited Phosphatidylcholine Coatings**, Zoe Harrison, R Awais, R Gopalakrishnan, J Jennings, University of Memphis, USA

When implanting medical devices, the resultant wounds are often at high risk of infection. This infection is often caused by the formation of a biofilm, which occurs when microorganisms attach to the surface of the implanted device. Previous work in our lab has shown the effectiveness of cis-2-decenoic acid (C2DA) to disperse and inhibit biofilm, especially when combined with antibiotics. Previous studies have shown that phosphatidylcholine (PtC) can be loaded with C2DA and antibiotics to create a crayon-like solid, which can be used to "draw" a thick layer of coating onto an implant and thus prevent infection. While this application method showed promising results for drug elution and prevention of bacterial growth, this method of application has drawbacks of slow application process and uneven coating, especially for devices with complex shapes. To overcome these clinical issues, a system has been developed to spray phosphatidylcholine directly onto the device via an aerosol sprayer. This study seeks to determine if this aerosol spraying method provides similar drug elution capabilities as the previously manual coating method. PtC crayons loaded with 15% ciprofloxacin and 15% C2DA were dispersed in water and sprayed onto stainless steel coupons. Manually applied coatings were used as controls. Elution over 7 days in PBS was analyzed using high performance liquid chromatography. Results indicate that though mass of coating applied was lower using the spray setup, coating uniformity is improved with this method. Elution study results indicate that while the thicker manual coating showed higher elution of ciprofloxacin per day, the spray coating only eluted concentrations above inhibitory levels of ciprofloxacin through day 3. Current studies are being conducted to test the efficacy of sprays dispersed in polyethylene glycol 400 (PEG 400) and phosal 53 MCT (a 50/50 blend of PtC and medium chain triglycerides), which may increase elution and spray deposition. Furthermore, modifications are being made to the aerosol sprayer to improve the portability of the system, the speed of coating, and the thickness of the sprayed coating.

10:00am **D3-TuM-7 In vitro Osseointegration Analysis of Bio-functionalized Titanium Samples in a Protein-rich Medium**, S Rao, S Hashemiastaneh, J Villanueva, University of Illinois at Chicago, USA; F Silva, University of Minho, Portugal; C Takoudis, University of Illinois at Chicago, USA; D Bijukumar, University of Illinois College of Medicine, USA; J Souza, University of Illinois at Chicago, USA; Mathew T. Mathew, University of Illinois College of Medicine, USA

Titanium (Ti) or Ti-based alloys are commonly used for the biomedical implant applications. The long-term survivability of the implants is strongly influenced by the osteointegration aspects of the metal-bone interface. Several techniques on Ti surface modification have been reported in the literature to improve osteointegration of implants to bone. Here, biological materials such as protein are used to functionalize titanium surfaces to enhance the ability of implants to interact with human tissues for accelerated osseointegration. The main aim of this study is to functionalize titanium surfaces in a medium enriched with fibrinogen.

Commercially pure titanium grade IV discs (8 mm Dia x 3 mm thick) are etched using two different acidic substances (HF/HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>/HCl). Fibrinogen is processed and precipitated by a standard procedure to obtain high molecular weight fibrinogen under repeated centrifugation. Fibrin gel is prepared by adding thrombin to fibrinogen. Surfaces coated with and without fibrin are analyzed by white light microscope, SEM, and WCA to check for the surface properties. Osteoblasts are cultured on the surfaces to assess cell proliferation, adhesion as well as the mineralization process. Osteoblastic proliferation on these surfaces is quantified by Alamar blue

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assay and visualized under confocal microscope and SEM; qPCR is performed to investigate the expression of genes specific to osteogenic cells and mineralization assay is done to check calcium and phosphate deposits.

This study demonstrates a method of increasing roughness and hydrophilicity of the implant surface by etching followed by protein functionalization. Such a method can reduce the time for osseointegration that can decrease risks in early failures of implants. Also, the adsorption of fibrinogen on titanium surfaces is influenced by the method of acid etching.

10:20am **D3-TuM-8 Microstructural and Electrochemical Properties of TiAlN- (Ag,Cu) Nanocomposite Coatings Deposited by DC Magnetron Sputtering for Medical Applications**, *H Mejía, Aida Echavarría, G Bejarano*, Universidad de Antioquia, Colombia

AISI 420 stainless steel is currently used in the manufacture of surgical and dental instrumentation due to its hardenability, acceptable biocompatibility and resistance to corrosion. However its resistance to wear is relatively low, and therefore multiple strategies of surface modification are offered such as plasma nitriding, hard coatings and self-lubricating ceramic coatings deposited by the physical vapor deposition techniques PVD, among others, to reduce the wear rate and to confer this steel other variety of specific properties. In the case of coatings that include metallic solid lubricants, the anticorrosive properties can be affected by the formation of galvanic pairs and the high chemical reactivity of the metallic phase. Therefore, it is absolutely necessary to evaluate the electrochemical behavior and the corrosion resistance of these composite coatings. In this work TiAlN coatings doped with four different contents of Ag and Cu nanoparticles (11 at.% to 20 at.%) were deposited onto 420 steel by means of DC magnetron sputtering equipment using two composited targets of Ti/Al and Ag/Cu (both 50/50 at.% and 99,95 purity), which were facing each other at 180 degrees. The microstructure, chemical and phase composition were analyzed by scanning and transmission electron microscopy (SEM/TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction, while the roughness were determined using atomic force microscopy (AFM), respectively. The corrosion rates were obtained from the polarization curves and the electrochemical behavior was evaluated by electrochemical impedance spectroscopy (EIS) in artificial saliva. The reduction in the corrosion rates of the steel was evident once it was superficially modified with the TiAlN (Ag,Cu) nanocompound, forming a substrate protection barrier when exposed to the selected body fluids. The TiAlN (Ag-Cu) coatings presented an electrochemical activity superior to the TiAlN matrix, and consequently exhibited higher corrosion current densities. This behavior becomes greater with the increase of the Ag-Cu content in the compound and is correlated mainly with the continuous and increasing dissolution of silver and copper in the surrounding medium and to the greater chemical activity of the Ag- particles as compared to the ceramic matrix. However, all coated samples showed an enhanced corrosion resistance compared to the steel substrate, obtaining the best electrochemical behavior by the sample coated with TiAlN (Ag-Cu) with 17at.% Ag-Cu. The development of this nanostructured coating system might be considered for potential application in in surgical and dental instrumentation.

## Coatings for Biomedical and Healthcare Applications Room Pacific Salon 3 - Session D2-TuA

### Bio-corrosion and Bio-tribology

**Moderators:** *Jessica Jennings*, University of Memphis, USA, *Steve Bull*, Newcastle University

**1:40pm D2-TuA-1 Bio-Tribocorrosive Behavior of the Contact M30NW Stainless Steel against HDPE Reinforced with MoS<sub>2</sub> Particles. New Polymer Implant: Promising Material?**, *A Salem, M Guezmil, W Bensalah, S Mezlini*, Université de Monastir, Tunisia; *Jean Géringier*, Mines Saint-Etienne, France

Some new polymer composites are under investigation in order to enhance the biocompatible usage of new biomaterials. This paper deals with the tribological behavior of High Density PolyEthylene/molybdenum disulphide (MoS<sub>2</sub>-HDPE) composites against M30NW stainless steel. As received HDPE pellets were milled and blended with MoS<sub>2</sub> particles using a ball milling machine. The reinforced HDPE specimens with different contents of MoS<sub>2</sub> were elaborated using a compression molding machine. Tribological characterization including wear rate and friction coefficient was investigated using a linear reciprocating pin-on-disc tribometer under dry conditions. Tribocorrosion tests were carried out in the presence of bovine serum solution. It is highlighted that the use of MoS<sub>2</sub> enhances the tribological performances of HDPE composites compared to the unfilled polymer under dry and lubricated conditions. In both cases, an optimal content of MoS<sub>2</sub> was around 4 wt.%. Morphological and chemical investigations using SEM and EDS analyses were carried out on the composite discs after wear tests. Thus the wear scenario was discussed in relation to the MoS<sub>2</sub> content.

**2:00pm D2-TuA-2 Evaluation of the Adhesion of Electrospayed and Solution-Cast Chitosan Coatings on Titanium Surfaces**, *V Suresh, E Chng, J Bumgardner, Ranganathan Gopalakrishnan*, University of Memphis, USA

**INVITED**

Biomedical implant devices for dental/craniofacial and orthopedic applications are a reliable and effective means for repairing/re-storing function of damaged, diseased or missing tissues. Despite the success of these devices, there are still challenges in their use with respect to improving their integration into bony tissues, promoting healing and resisting/preventing infection. Electro spray coating technologies provide an additive manufacturing route to endow implant surfaces with new properties to improve their performance by controlled deposition of desired materials, compounds and/or agents in the form of nano- or micro-particles on the surface of implant devices under relatively mild conditions. This ensures that the biomaterials do not get denatured under high temperature or harsh chemical environments commonly employed in many coating methods. They also provide a means to control the structure of coatings with high precision that allows the functionalization of complex 3D geometries of the implants with a range of physical and bioactive properties. Devices such as dental implants, total joint replacement devices, bone plates and screws that cannot be easily coated by other manufacturing methodologies such as solution casting, sputter coatings, or electrochemical treatments can be robustly handled by the electro spray technique. This project focuses on assessing the adhesion of electrospayed chitosan coatings on model titanium surfaces and screws to explore their potential as an implant treatment technology. Currently, the most widely used technique for implant coating with biomaterials is solution casting. This method limits the coverage of chitosan on complex surfaces of implants, and provides little control on the thickness of the coating and leads to excessive wastage. This research also evaluates the effectiveness of the electro spray as a delivery method of aerosolized chitosan to coat complex implants with precise thickness control, multilayer coatings for controlled drug delivery and to reduce wastage. Adhesion strength values are reported and compared between electrospayed and solution cast chitosan coatings.

**2:40pm D2-TuA-4 Study of the Mechanical and Tribological Properties of the TaN with Ti Inclusion Multilayer Films on Si Substrate**, *Ernesto García*, Cátedras-CONACyT, Universidad de Guadalajara, México; *J Berumen*, ITESO, Universidad Jesuita de Guadalajara, Tlaquepaque, Jalisco, México; *M Flores-Martinez*, Universidad de Guadalajara, México; *E Camps*, Instituto Nacional de Investigaciones Nucleares, México; *S Muhl*, Instituto de Investigaciones en Materiales-UNAM, México

The hip prosthesis surfaces are exposed to high mechanical, chemical and tribological stress conditions. For that binary and ternary transition metallic nitride films have been studied in order to improve the wear and corrosion resistance of the metallic surfaces of the prosthesis. This work shows the first studies of the TaN with Ti inclusion multilayers films. These were produced using DC magnetron cosputtering with a Ta and Ti targets in an N<sub>2</sub>/Ar atmosphere in a multilayer arrangement with similar thickness, incremental layer and decremented layer thickness on a silicon substrate. The films were structural, chemical and topologically characterized, using X-Ray diffraction (in theta-2 theta and in-plane configuration), Raman spectroscopy and Electronic microscopy, respectively. The mechanical properties were studied using nanoindentation (at 10 mN) and scratch test (from 0 to 8N) with a Rockwell C indenter. The tribological characterization was carried out with a linear reciprocating with a Rockwell C indenter, with at 0.5, 1 and 2 N of load and 5 cycles of 5 mm of length. The wear track produced for the scratch and the tribological test were studied with optical and electronic microscopy. The layers had a combined structure of a cubic of TaN and hexagonal and cubic of Ta. The coating presented a lower Hardness than the reported for the TaN films. The coating with the incremental arrangement presented a better tribological performance but with lower hardness.

**3:00pm D2-TuA-5 Enhancement of Tribocorrosion Properties of Ti6Al4V by Formation of a Carbide-Derived Carbon (CDC) Surface Layer**, *Kai-yuan Cheng*, University of Illinois at Chicago, USA; *R Nagaraj, D Bijukumar, M Mathew*, University of Illinois College of Medicine, USA; *M McNallan*, University of Illinois at Chicago, USA

Metal implant materials not only face corrosion or friction individually but the synergism of tribology and corrosion, which has been called "tribocorrosion". Especially, on the bearing of hip implant in the synovial fluid, the usual CoCrMo alloy endures severe tribocorrosion reaction, sometimes resulting in the formation of wear and corrosion products which cause the adverse local tissue reaction. In 2011, a graphitic tribolayer was discovered on retrieved hip implants at Rush Medical Center, which suggested that the tribolayer might offer lubrication and corrosion protection. Therefore, a coating of graphitic material might be beneficial to the performance of orthopedic implants.

Carbide-derived carbon (CDC) is a primarily graphitic material formed on silicon carbide, which improved tribological performance in non-biomedical applications. If CDC can be applied on the metal substrate, its high lubrication and chemical inertness should provide the same improvement as the graphitic tribolayer found on the retrieved hip implant. To produce a CDC layer on a metal, the metal is first carburized to form a surface layer of metal carbide, and subsequently the carbide is decomposed to form CDC. In this study, Ti6Al4V alloy was chosen as our substrate due to its high affinity to form carbides on its surface and its poor tribocorrosion property, by which CDC's protection can be demonstrated. As long as CDC can properly protect Ti6Al4V alloy, it is possible to reproduce the same effect on other metal surfaces.

In this presentation, recent tribocorrosion results obtained in the hip simulator at Rockford Medical Center, CDC treated metal shows a smaller voltage drop during ( $\Delta E_{\text{CDC}} = -0.2 \pm 0.047(\text{V}) < \Delta E_{\text{Ti6Al4V}} = -0.89 \pm 0.13(\text{V})$ ) testing in an open-circuit potential condition, a smaller induced current ( $\Delta I_{\text{CDC}} = -4.8\text{E}-6 \pm 4.4\text{E}-6 (\text{A}) < \Delta I_{\text{Ti6Al4V}} = -3.94\text{E}-4 \pm 8.02\text{E}-5 (\text{A})$ ) when tested under potentiostatic conditions, a smaller wear loss ( $\Delta V_{\text{CDC}} = -0.001 \pm 5.85\text{E}-4(\text{mm}^3) < \Delta V_{\text{Ti6Al4V}} = -0.43 \pm 0.025(\text{mm}^3)$ ) and smaller values of friction coefficient ( $\mu_{\text{CDC}} = 0.0045 \pm 0.0025 < \mu_{\text{Ti6Al4V}} = 0.47 \pm 0.135$ ). The biocompatibility tests have shown CDC is as biocompatible as the Ti6Al4V substrate. In general, the CDC protected Ti6Al4V performs better in tribocorrosion without sacrificing biocompatibility.

**4:00pm D2-TuA-8 Considerations when using Additive Manufacturing to make Medical Devices**, *Alejandro Espinoza Orías*, Rush University Medical Center, USA

**INVITED**

Additive Manufacturing has demonstrated to be and gone beyond being a disruptive technology as many industries have adopted it to mass-produce parts on demand. In the medical arena, however, there are some concepts that part manufacturers need to be familiar with before going to mass

production. A big part of the orthopedic market is that of hip and knee implants that have seen steady growth in the last decade. Corrosion is a natural process and changes the properties of metallic structures. In the case of orthopedic implants, such as total hip replacements, titanium alloys are the most frequently used metal due to their elevated resistance to corrosion, compared to other alloys suitable for implantation in the body. Some of these considerations are as diverse as the patient population meant to benefit from AM: patient privacy, metallurgy, mechanical properties and cleanliness. The aspects of bio-corrosion and bio-tribology have received little attention when new additively manufactured implants hit the market. A big reason for this is the 510(k) process that allows manufacturers to 'grandfather-in' the designs. However, we know little about the differences in metallurgy that are related to the additive manufacturing process that has key contrasts to that of traditional subtractive manufacturing. The most relevant aspect of utility from the additive manufacturing point of view is the direct ability to print highly rough and porous surfaces that are meant for bone ingrowth. While this manufacturing method is capable of producing high-resolution surface finishes with or without built-in designed porosity, not much is known about the surface interaction properties of said finished surfaces. The need for better and more accurate methods to describe bio corrosion and bio tribological aspects of additively manufactured implants makes this type of characterization crucial since the durability of the implant is in play. Current traditionally manufactured designs, last about 15 years not without their own survivability issues. It remains to be seen if the materials and the processes involved in additive manufactured can match the same type of performance benchmarks of the standard manufactured implants.

4:40pm **D2-TuA-10 Nanostructured Surfaces for (Bio)sensors, Vitezslav Stranak**, University of South Bohemia, Czech Republic; *R Bogdanowicz*, Gdansk University of Technology, Poland; *P Sezemsky*, *V Prysiaznyi*, *J Kratochvil*, University of South Bohemia, Czech Republic; *M Smietana*, Warsaw University of Technology, Poland; *O Kylian*, Charles University, Czech Republic; *Z Hubicka*, *M Cada*, Institute of Physics CAS, v. v. i., Czech Republic

The contribution reports our study of nanostructured surfaces preferentially used for bio-sensing applications. Nanostructured surfaces were prepared by low-temperature plasma assisted deposition employing magnetron sputtering of bulk target. The advantages of nanostructures for sensor applications have been demonstrated several times. Here we focus on two approaches: (i) the first one utilizes homogeneous transparent conductive oxide (TCO) films for Lossy Mode Resonance (LMR) sensors while (ii) the second employs Ag nanoparticles for detection and signal calibration of matrix assisted laser desorption/ionization mass spectrometry.

Bio-sensors working on LMR principle represent rather new concept which appeared a few years ago. The LMR sensors, equipped by precisely tailored TCO film (in our case indium doped tin oxide - ITO) are based on the optical fibre and allow optical as well as electrochemical sensing. The optical sensitivity is achieved by spectral shift of transmission spectra of the light passing through the optical fibre, while the electrochemical effects can occur on the sensor surface. Our main aim represents tailoring of the ITO film deposition to achieve relevant optical and electrochemical properties of ITO with adequate LMR and electrochemical response [1]. The detection of substances as, e.g. ketoprofen [2], will be reported, too.

The second part will be devoted to nanostructures for independent mass-to-charge calibration of laser desorption/ionization mass spectrometry (LDI MS). Properly tailored Ag nanostructured surface - formed as homogeneous thin film, isolated nanoislands, and spherical nanoparticles - can effectively substitute protonation agent for low-mass molecules instead of conventionally used matrices. Beside the surface characterization, the impact of LDI MS laser, irradiating the nanostructured surfaces responsible for Ag cluster production, will be discussed [3]. It is the nanoparticle size and the surface coverage that play a key role and have to be optimized.

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[3] V. Prysiaznyi, F. Dycka, J. Kratochvil, V. Stranak, P. Ksirova et al. J. Vac. Sci. Technol. B 37, (2019), 012906.

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

### Coatings for Biomedical and Healthcare Applications (Symposium D) Poster Session

**DP-ThP-4 Development of Multilayer HA-Ag and TiN-HA-Ag Coatings Deposited by RF Magnetron Sputtering with Potential Application in the Biomedical Field,** *Julian Lenis, G Gaitán*, University of Antioquia, Medellín, Colombia; *P Rico, J Ribelles*, Universitat Politècnica de València, Spain; *F Bolívar*, University of Antioquia, Medellín, Colombia

The use of composite coatings emerges as a great alternative to induce superficially the combination of properties widely desired in surgical implants, such as: osteointegration and bactericidal character, which can not be conferred by a single material. In the present investigation, the effect of the incorporation of an intermediate layer of titanium nitride (TiN) on the chemical composition, structure, morphology, phases and adherence of a multi-layer Hydroxyapatite (HA) - silver (Ag) coating deposited on Ti-6Al-4V by magnetron RF sputtering was evaluated. The elemental composition analysis was performed by energy dispersive spectroscopy, while the techniques of micro-Raman spectroscopy, scanning electron microscopy and atomic force microscopy were used to determine the structure and morphology of the obtained coatings. A variation in the Ca/P ratio, the Ag content and the thickness in the HA-Ag coatings deposited on the TiN layer was found compared to the HA-Ag system deposited on the metallic alloy. In the same way, the roughness and structure of this coating was modified according to the surface where it was deposited.

Key words: Magnetron sputtering, Hydroxyapatite, Ca/P ratio, structure, multi-layer coating, intermediate layers, critical load.

**DP-ThP-5 Electrochemical Activated Iridium Oxide Film as a Bio-interface Electrode for Neurostimulation Applications,** *Y Chiu, P Chen*, National Taipei University of Technology, Taiwan; *Chien-Ming Lei*, Chinese Culture University, Taiwan; *P Wu*, National Chiao Tung University, Taiwan

Electrode materials for neural stimulation have been widely investigated for implantable devices. Among them, iridium and iridium oxide are attractive materials for bio-interface applications due to their desirable stability, electrochemical performance, and biocompatibility. In this study, metallic iridium thin film was deposited on a transparent conducting oxide substrate (ITO-coated glass) by radio-frequency (RF) magnetron sputtering, and we carried out an electrochemical activation to produce iridium oxide film through a repetitive biphasic pulsed current. The process parameters for sputtering of iridium film and electrochemical activation of iridium oxide film were optimized. The activated iridium oxide film exhibited superior electrochemical performance, including large charge storage capacity (CSC), high charge injection capability, low electrochemical impedance, and excellent stability. In addition, the biocompatibility of activated iridium oxide was evaluated by cytotoxicity, and the iridium oxide/iridium film showed high cell-viability. These findings suggest that the activated iridium oxide film is a promising candidate as an electrode material for the development of neurostimulating devices.

**DP-ThP-6 HIPIMS Titanium Dioxide on Laser Roughened PEEK Surface for Biomedical Application,** *P Hsieh*, Institute of Plasma, Department of Materials Science and Engineering, Feng Chia University, Taiwan; *Chi-Jen Chung*, Central Taiwan University of Science and Technology, Taiwan; *H Tsou*, Taichung Veterans General Hospital, Taiwan; *H Chen*, China Medical University Hospital, Taiwan; *J He*, Institute of Plasma, Department of Materials Science and Engineering, Feng Chia University, Taiwan

Polyetheretherketone (PEEK), known for its comparable elastic modulus to human cancellous bone characteristics and X-ray radiolucency, is greatly considered for spinal implant material. However, the bio-inertness and hydrophobic surface properties of PEEK results in poor osseointegration when implanted into human bodies. The aim of this study is to develop a combination method, viz., laser roughening process and titanium dioxide (TiO<sub>2</sub>) deposition, for modifying the biological properties of PEEK surface. A femtosecond pulse laser was utilized to avoid the thermal damage on PEEK, while high power impulse magnetron sputtering (HIPIMS) was employed to deposited high crystalline TiO<sub>2</sub> coating at low temperature. The results showed that the hierarchically patterned PEEK surfaces composed of nano- and microstructures can be obtained by adjusting laser parameters. Such structure resulted in varied surface roughness and water wetting ability. On

the other hand, the highest rank (5B) in adhesion tape test proved the superior adhesion of the HIPIMS prepared TiO<sub>2</sub> coating even on roughened PEEK surface. The strong adhesion is believed to arise from the advantage of high ion energy and high-density plasma characteristics of the HIPIMS discharge. Under proper laser roughening condition followed by HIPIMS-TiO<sub>2</sub>, the *in vitro* osteoblast compatibility test performed a much higher level than bare PEEK.

**DP-ThP-7 Corrosion Property and Biocompatibility Evaluation of Fe-Zr-Nb Thin Film Metallic Glasses,** *B Lou*, Chang Gung University, Taiwan; *T Lin, Jyh-Wei Lee*, Ming Chi University of Technology, Taiwan; *J Wang, Y Yang*, National Taipei University of Technology, Taiwan

The amorphous thin film metallic glasses (TFMGs) have drawn lots of attention by researchers due to their unique properties and ease of fabrication. Recently, the biocompatibility of Zr-based TFMG becomes an important issue because of its excellent corrosion resistance and bio safety. In this work, six Zr-Ti-Si TFMGs with different Si concentrations were fabricated on the bio-grade 316L stainless steel plates and Si wafer, respectively, by a hybrid bipolar high power impulse magnetron sputtering and radio frequency sputtering technique. The chemical composition of Si increased gradually from 3.3 to 34.7 at.%, respectively, as the Si target power increased from 25 to 250 W. The crystalline structure was observed for TFMG containing 3.3 at.% Si, whereas the amorphous phase was found for the TFMG containing higher than 9.6 at.% Si. The cross-sectional morphology changed from columnar to fine and featureless microstructure as more silicon contents were added into the thin film. Acceptable adhesion qualities, HF1 to HF 3, were obtained for all Zr-Ti-Si thin films. The maximum hardness, 15.7 GPa, and the highest H/E value around 0.088 were achieved for TFMG containing 34.7 at.% Si. The corrosion resistance of 316L stainless steel disk can be improved effectively by TFMGs. The lowest corrosion current density around 0.02 mA/cm<sup>2</sup>, and the highest polarization resistance around 1042.1 kWcm<sup>2</sup>, were achieved for TFMG containing 31.6 at.%. Six thin films had better biocompatibility than that of 316L stainless steel substrate. The hybrid HIPIMS-RF grown Zr-Ti-Si TFMGs with adequate hardness, good biocompatibility can be used as a promising candidate to improve the surface biocompatibility of biomaterials.

**DP-ThP-9 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; *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-ThP-10 Surface Characteristics and Structure of Porous Ti-Ni Alloy for Biomedical Applications,** *W Ho*, National University of Kaohsiung, Taiwan; *S Wu, S Hsu, W Hsiao, Hsueh-Chuan Hsu*, Central Taiwan University of Science and Technology, Taiwan

Titanium (Ti) and some of its alloys have been used widely as load-bearing implants because of their excellent mechanical properties, superior biocompatibility, and good corrosion resistance. Lately, there has been an increasing interest in studying porous alloy, which could imitate bone structures by altering the porosity of alloy. In this study, a biomedical porous Ti-5Nb-5Mo (wt.%) alloy was fabricated by mechanical alloying

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(MA) process for different ball-milling times. The metal powders of Ti (99.9% pure), Nb (99.9% pure), Mo (99.95% pure) were milled in a planetary ball milling machine for 3 h, 15 h and 30 h. The ball milled Ti-5Nb-5Mo powders were compacted of 7 mm in diameter and 11 mm in height. The sintering process was carried out in two steps. The compacts were initially sintered at 175 °C for 2 h and then increased to 1100 °C for 5, 10 and 15 h respectively. The results found in this study are summarized as follows: The Ti-5Nb-5Mo particle size increased with the ball-milling time increased from 3 h (35 µm) to 15 h (72 µm). The ball milling produced alloy particles gather together, and caused a larger particle size. The ball milled Ti-5Nb-5Mo particles were significantly refined, and the Nb and Mo was integrated and uniformly distributed in the matrix. XRD analysis shown that the porous Ti-5Nb-5Mo was a  $\alpha$  phase and has no obvious diffraction peaks of elemental Nb and Mo remained which confirmed Nb and Mo was integrated and uniformly distributed in the matrix. While the sintering of powder by ball milling enhances the homogeneity. The compressive strength and modulus of all the porous Ti-5Nb-5Mo match the necessary mechanical property of cancellous bones. Especially for the B3S15 specimen (Balling 3 h and sintering 15 h) which shows the highest strength. After soaking in a SBF solution for 7 days, the porous TNM alloy formed a dense apatite layer on the surface. It exhibited a better apatite-forming ability. The study reveals that the use of porous TNM satisfies the need of implants with an adequate mechanical strength and elastic modulus for the patients.

**DP-ThP-11 In vitro Wear Tests of the Dual-layer Grid Blasting-plasma Polymerized Superhydrophobic Coatings on Substrates Made into Dental Stainless Archwires, Cheng-Wei Lin,** Feng Chia University, Central Taiwan University of Science and Technology, Taiwan; *C Chou,* Taichung Veterans General Hospital, National Yang-Ming University, Taiwan; *C Chung,* Central Taiwan University of Science and Technology, Taiwan; *J He,* Feng Chia University, Taiwan

Dental stainless archwires, frequently used in orthodontics and dentofacial orthopedics, may accumulate food debris, promote bacterial overgrowth, and subsequently result in dental caries. A dual-layer grid-blasting plasma-polymerized (GB-PP) superhydrophobic coating was developed in a previous work by changing the micro- and nano-structured surface morphology on AISI 304 stainless substrates. In this study, in vitro wear tests were performed in artificial saliva that mimicked tooth brushing, peanut-chewing, and nougat-chewing modes to determine the durability of the superhydrophobic layer. Experimental results show that peanut-chewing causes more damage to the superhydrophobic surface than nougat-chewing because the carbohydrate, protein and oil ingredients in peanut and nougat might be transferred onto the surface, subsequently masking some of the fluorocarbon layer (also verified by SEM, EDS, and FTIR analyses). In conclusion, the GB-PP coatings deposited on medical-purposed stainless steel substrates exhibit good durability after tooth brushing and nougat-chewing wear tests.

**DP-ThP-19 Obtaining of CVD Nanodiamonds and Evaluation of the Cytotoxicity in B16F10 Cells for Treatment of Melanoma, C Wachesk,** Federal University of São Paulo (UNIFESP), Brasil; *C Hurtado,* Institute of Science and Technology, Federal University of São Paulo (UNIFESP), Brazil; **Rebeca Falcão,** Institute of Science and Technology, Federal University of São Paulo (UNIFESP), Brasil; *D Arruda,* University of Mogi das Cruzes, Brasil; *D Tada,* Institute of Science and Technology, Federal University of São Paulo (UNIFESP), Brasil; *V Airoldi,* National Institute for Space Research (INPE), Brasil

Recent studies have shown the potential use of nanodiamonds (NDs) as drug carriers for the therapy of cancer due to their high stability and small size. With the aim of obtaining a new system to be applied as drug delivery platform for the therapy of metastatic melanoma, a new technique of obtaining NDs from CVD diamond thin film was developed. The synthetic CVD-diamond film has similar physical and chemical properties to natural diamond: extreme hardness, excellent thermal conductivity, biological compatibility and chemical stability at temperatures below 800°C. Herein, CVD NDs were prepared by using laser ablation. The NDs were characterized by X-ray (XRD), (MEV-FEG), (TEM), energy dispersion spectroscopy (EDS), (XPS), Raman spectroscopy and dynamic light scattering. Furthermore, since cytocompatibility is one of the main features required for a drug delivery platform, the cytotoxicity of NDs was evaluated in B16-F10-Nex2 cells by MTT assay. The results showed that the laser ablation process reduced CVD particle size. The mean hydrodynamic diameter in aqueous suspension after the centrifugation changed from 54 nm. The high stability of aqueous suspension of CVD NDs was indicated by the low polydispersity index (0,2) and a small increase in the mean value of

hydrodynamic diameter during the observed period ( $D = 215$  nm). The high stability was provided by the high charge density on NDs surface as suggested by the high value of Zeta-potential (-36.39 and -30.94 mV). EDS analysis showed that NDs were composed of carbon (77.2%) and oxygen (22.2%). By X-ray diffraction analysis, it could be observed the characteristic peak of NDs at 43°. Raman spectrum of CVD NDs showed three peaks at: 1332, 1500 and 1600  $\text{cm}^{-1}$ , corresponding to D and G bands of diamond. Cytotoxicity assay showed 60% and 80% of cell viability after 24h 48h 72h and 96h of incubation with NDs. The high value of cell viability is an indicative of the cytocompatibility of NDs, indicating the potential use of NDs in biomedical applications such as drug delivery platforms.

**DP-ThP-22 Tantalum Oxynitride PVD Coatings a Potential Candidate for Dental Implants Application, O Banakh,** University of Applied Sciences (HES-SO), Switzerland; **Pierre-Albert Steinmann,** Positive Coating SA, Switzerland

Coating technology offers innovative solutions to improve the quality and durability of medical devices. Among new materials, titanium oxynitride coatings (TiOxNy) are considered promising for applications in implantology (cardiovascular stents) due to their high biocompatibility. The purpose of this study is to test tantalum oxynitride coatings (TaOxNy) as a potential candidate in dental implants application. Coatings with different nitrogen and oxygen contents were deposited by conventional reactive magnetron sputtering and by High Power Impulse Magnetron Sputtering (HIPIMS) in mixed Ar-O<sub>2</sub>-N<sub>2</sub> atmosphere. The coatings were deposited onto titanium micro-rough substrates (Ti-SLA) and stainless steel substrates. In some experiments water vapor was used as a reactive gas, instead of oxygen. The Ti-SLA uncoated sample was chosen as control in cellular response biological tests. None of the specimens presented any signs of cytotoxicity. Their biological response was similar to that of Ti-SLA. The coatings produced with water vapor showed an improvement of the corrosion resistance as well as a slight enhancement of cell adhesion. Even though the tantalum oxynitride coatings didn't show a noticeable enhancement of biological response on Ti-SLA surfaces, their application looks promising on other substrates such as stainless steel.

**DP-ThP-25 Influence of Ag-Cu Nanoparticles on the Microstructural and Bactericidal Properties of TiAlN- (Ag,Cu) Coatings Deposited by DC Magnetron Sputtering for Medical Applications, H Mejía, G Bejarano, Aida Echavarría,** Universidad de Antioquia, Colombia

Most of the surgical and odontological instrumentation is manufactured using martensitic stainless steel AISI 420 and 440 due to their acceptable biocompatibility, good hardenability, proper hardness and resistance to corrosion. However, the resistance to wear of this type of steels is relatively low and may be susceptible to contamination with bacteria representing a potential risk to the health of patients. This research work focused on the development of a coating system of titanium-aluminum-nitride doped with silver and copper nanoparticles TiAlN (Ag, Cu) to provide it with an appropriate bactericidal effect for possible biomedical applications.

TiAlN coatings doped with four different contents of Ag and Cu nanoparticles (11 at.% to 20 at.%) were deposited onto 420 steel by means of self-manufactured DC unbalanced magnetron sputtering using two composited targets of Ti/Al and Ag-Cu (both 50/50 at.% and 99.9% purity), which were facing each other at 180 degrees. The diffusion of the Ag-Cu nanoparticles to the sample surface, as well as their quantity, size, shape and distribution was controlled by an appropriate adjustment of the power applied to the Ag/Cu-target, the temperature and time of the deposition process, since the mechanical, tribological and bactericidal properties of the compound depend, among others, on these characteristics of the nanoparticles. The microstructure, surface topography, chemical and phase composition were analyzed by scanning and transmission electron microscopy (SEM/TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction. To evaluate the bactericidal effect of steel and coated samples in vitro inhibition and adhesion test were carried out selected *Staphylococcus aureus* and *Escherichia coli*, two of the major pathogen frequently found in surgery and dentistry rooms and associated with infections. The coating without doping presents a structure of columnar growth, which becomes densified with the increase of the Ag-Cu content and takes a glassy appearance accompanied by an increased size of the Ag-Cu particles and consequently also in the surface roughness. All the coated samples exhibited a higher bactericidal effect in comparison with the uncoated and with TiAlN coated steel, however the greater inhibition (100%) and less adherence to both bacteria was showed by the sample coated with 17% at Ag-Cu. Based on the results obtained, the developed

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nanostructured coating system might be considered for potential application in surgical and dental instrumentation.

**DP-ThP-26 Antibacterial Activity of Conductive Thin Films Deposited on Water Filter Paper**, *D Mihut, A Afshar, S Hill, L Khang, Nicholas Cordista*, Mercer University, USA

There is a high interest to investigate nanomaterials that can work effectively against different types of bacteria and provide alternative substitution for chemical substances and antibiotics. In this research, conductive materials nanoparticles in the form of thin films were deposited on water filter papers by using direct current (DC) high vacuum magnetron sputtering technique. The effectiveness of the nanoparticles to remove bacteria from polluted water was tested during the experiment. The morphology of the coatings and their adherence to the water filter paper was examined using the Scanning Electron Microscopy and their chemical composition was investigated using the X-ray diffraction technique. All thin films showed good adhesion to water filter fibers and ensured a high area of exposure to contaminated water. The antibacterial effect of different conductive thin films was characterized by using the standardized membrane filtering technique for water and wastewater examination. The testing media (i.e. contaminated water) containing bacterial samples were collected from local wastewater basins. Water was tested for the bacterial content before and after the exposure to conductive thin films coated filters.

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Anselme, K: D3-TuM-4, **4**  
Arruda, D: DP-ThP-19, 9  
Arunachalam, N: D1-1-MoM-7, 1  
Awais, R: D3-TuM-6, 4  
— B —  
Banakh, O: DP-ThP-22, 9  
Bejarano, G: D3-TuM-8, 5; DP-ThP-25, 9  
Bensalah, W: D2-TuA-1, 6  
Berumen, J: D2-TuA-4, 6  
Bijukumar, D: D2-TuA-5, 6; D3-TuM-7, 4  
Bogdanowicz, R: D2-TuA-10, 7  
Bolívar, F: DP-ThP-4, 8  
Bouvard, G: D1-1-MoM-3, 1  
Bumgardner, J: D2-TuA-2, 6  
— C —  
C. Rodrigues, D: D3-TuM-3, 4  
Cada, M: D2-TuA-10, 7  
Camps, E: D2-TuA-4, 6  
Chacko, A: D1-2-MoA-8, **2**  
Chang, S: D1-1-MoM-6, 1  
Chang, Y: D1-1-MoM-2, 1  
Chen, H: DP-ThP-6, 8  
Chen, M: D1-1-MoM-6, 1  
Chen, P: DP-ThP-5, 8  
Chen, Y: D1-1-MoM-6, 1  
Cheng, K: D2-TuA-5, **6**  
Chiu, Y: DP-ThP-5, 8  
Chng, E: D2-TuA-2, 6  
Chou, C: D1-1-MoM-2, 1; DP-ThP-11, 9  
Chu, J: D1-1-MoM-6, 1  
Chung, C: D1-1-MoM-2, 1; DP-ThP-11, 9; DP-ThP-6, **8**  
Chyntara, S: D1-1-MoM-6, 1  
Cordista, N: DP-ThP-26, **10**  
— D —  
Dean, D: D1-2-MoA-9, 3  
Ding, H: D1-1-MoM-3, 1  
— E —  
Echavarría, A: D3-TuM-8, **5**; DP-ThP-25, **9**  
Echeverría, F: D1-2-MoA-5, 2  
Echeverry-Rendón, M: D1-2-MoA-5, 2  
Elahinia, M: D1-2-MoA-9, 3  
Espinoza Orías, A: D2-TuA-8, **6**  
— F —  
Falcão, R: DP-ThP-19, **9**  
Flores-Martinez, M: D2-TuA-4, 6  
Fridrici, V: D1-1-MoM-3, **1**  
— G —  
Gaitán, G: DP-ThP-4, 8  
García, E: D2-TuA-4, **6**  
Gauter, S: D1-2-MoA-8, 2  
Géringer, J: D1-1-MoM-3, 1; D2-TuA-1, **6**  
Gopalakrishnan, R: D2-TuA-2, **6**; D3-TuM-6, 4  
Guezmil, M: D2-TuA-1, 6  
Guida, L: D3-TuM-3, 4  
— H —  
Harrison, Z: D3-TuM-6, **4**  
Hashemiastaneh, S: D3-TuM-7, 4  
Hauert, R: D1-1-MoM-4, **1**  
He, J: D1-1-MoM-2, 1; DP-ThP-11, 9; DP-ThP-6, 8  
Hill, S: DP-ThP-26, 10  
Ho, W: DP-ThP-10, 8; DP-ThP-9, **8**  
Hsiao, W: DP-ThP-10, 8  
Hsieh, J: D1-2-MoA-4, **2**  
Hsieh, P: D1-1-MoM-2, 1; DP-ThP-6, 8  
Hsu, H: DP-ThP-10, **8**; DP-ThP-9, 8  
Hsu, S: DP-ThP-10, 8; DP-ThP-9, 8  
Huang, S: D1-1-MoM-2, **1**  
Hubicka, Z: D2-TuA-10, 7  
Hug, H: D1-2-MoA-8, 2  
Hurtado, C: DP-ThP-19, 9  
— I —  
Ibrahim, H: D1-2-MoA-9, **3**  
Ilic, E: D1-1-MoM-4, 1  
— J —  
Jennings, J: D3-TuM-6, 4  
— K —  
Kapsa, P: D1-1-MoM-3, 1  
Khang, L: DP-ThP-26, 10  
Kratochvil, J: D2-TuA-10, 7  
Kylían, O: D2-TuA-10, 7  
— L —  
Lee, J: D1-2-MoA-1, **2**; DP-ThP-7, **8**  
Lei, C: DP-ThP-5, **8**  
Lenis, J: DP-ThP-4, **8**  
Letzig, D: D1-2-MoA-6, 2  
Li, C: D1-1-MoM-6, 1; D1-2-MoA-4, 2  
Lin, C: D1-2-MoA-1, 2; DP-ThP-11, **9**  
Lin, T: DP-ThP-7, 8  
Liu, Q: D1-2-MoA-4, 2  
Lou, B: D1-2-MoA-1, 2; DP-ThP-7, 8  
— M —  
Mallick, M: D1-1-MoM-7, **1**  
Mathew, M: D2-TuA-5, 6; D3-TuM-7, **4**  
McNallan, M: D2-TuA-5, 6  
Mejía, H: D3-TuM-8, 5; DP-ThP-25, 9  
Mezlini, S: D2-TuA-1, 6  
Mihut, D: DP-ThP-26, 10  
Millan-Ramos, B: D1-2-MoA-6, 2  
Mischler, S: D1-1-MoM-4, 1  
Muhl, S: D2-TuA-4, 6  
— N —  
Nagaraj, R: D2-TuA-5, 6  
— P —  
Pardo-Perez, A: D1-1-MoM-4, 1  
Przyiazny, V: D2-TuA-10, 7  
— R —  
Rao, S: D3-TuM-7, 4  
Ribelles, J: DP-ThP-4, 8  
Rico, P: DP-ThP-4, 8  
Robledo, S: D1-2-MoA-5, 2  
Rodil, S: D1-2-MoA-6, 2  
— S —  
Salem, A: D2-TuA-1, 6  
Schmutz, P: D1-1-MoM-4, 1  
Sezemsky, P: D2-TuA-10, 7  
Silva, F: D3-TuM-7, 4  
Silva-Bermudez, P: D1-2-MoA-6, 2  
Smietana, M: D2-TuA-10, 7  
Souza, J: D3-TuM-7, 4  
Steinmann, P: DP-ThP-22, **9**  
Stranak, V: D2-TuA-10, **7**  
Suresh, V: D2-TuA-2, 6  
— T —  
Tada, D: DP-ThP-19, 9  
Takoudis, C: D3-TuM-7, 4  
Thorwarth, K: D1-1-MoM-4, 1; D1-2-MoA-8, 2  
Tsou, H: DP-ThP-6, 8  
— V —  
Victoria-Hernandez, J: D1-2-MoA-6, 2  
Villanueva, J: D3-TuM-7, 4  
— W —  
Wachesk, C: DP-ThP-19, 9  
Wang, J: DP-ThP-7, 8  
Wheelis, S: D3-TuM-3, **4**  
Wu, P: DP-ThP-5, 8  
Wu, S: DP-ThP-10, 8; DP-ThP-9, 8  
— Y —  
Yang, Y: D1-2-MoA-1, 2; DP-ThP-7, 8  
Yi, S: D1-2-MoA-6, 2