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

### Surface Coatings and Surface Modifications in Biological Environments I

**Moderators: Mathew T. Mathew**, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, **Phaedra Silva-Bermudez**, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

10:00am **D1-1-MoM-1 Corrosion Evaluation of $ZrO_2$ Coatings Deposited on Biodegradable MgZnCa Alloy for Orthopedic Applications**, ***Benjamin Millan (bmillan@ciencias.unam.mx)**, S. Rodil,* UNAM, Mexico; *J. Victoria-Hernandez,* Helmholtz-Zentrum Geesthacht, Germany

The development of biodegradable of Mg-based devices for orthopedic applications has been limited due to its high corrosion rate in biological media, which is accompanied by hydrogen (H2) evolution. This could lead to alkalization of the media and H2 accumulation can cause osteolytic lesions. In a previous work, we reported that a ZrO2 coating deposited by RF magnetron sputtering on a MgZnCa alloy enhanced the corrosion resistance and reduced the H2 evolved. However, an optimization of the deposition parameters to enhance the protectiveness offered by the coating was not done. Therefore, we propose an experimental design that involves power, deposition time and oxygen flux fraction as independent variables. The effect of these variables on the corrosion performance of the coated samples was evaluated using electrochemical impedance spectroscopy (EIS) and H2 evolution assessment with gas chromatography. The charge transfer resistance R can be obtained from the impedance modulus at medium frequencies (0.99Hz). In Fig. 1d, R is summarized as function of the thickness including all the deposition conditions. The conditions A and C deposited at 400 W during 30 and 90 min improves substantially the R (refer to Table 1 for labels). According to H2 results, the corrosion process of the coated samples does not change significantly as the deposition power increases, Fig 2a. But, the higher the deposition time the lower the H2 evolved, Fig. 2b. Increasing the O2 flux fraction is detrimental for the corrosion resistance for the coated samples since the H2 evolved raises, Fig. 2c. Thus, the combined effect of deposition time and O2 flux fraction plays an important role in the amount of H2 evolved. However, the tendency observed in H2 evolution measurements in Fig. 2c does not corresponds to the R in Fig. 1d. We think that H2 evolution measurement with gas chromatography can determine more accurately the short-term corrosion resistance of the coated/uncoated samples since electrochemical techniques have some limitations for corrosion rate assessment of Mg alloys. In conclusion, the effect of the deposition parameters of a ZrO2 coating on the corrosion resistance of MgZnCa alloy was studied. The higher R corresponds to the B43, B49, C43 and C49 samples. The results form H2 evolution measurements indicate that the deposition time and O2 flux fraction are determinant parameters. The O2% flux fraction may induce different growth rates which can contribute to change the coating compactness. This is visible in Fig. 2c, where the ZrO2 coating deposited at 20% of O2 flux fraction shows a reduction of 44 % in the amount of H2 evolved.

10:20am **D1-1-MoM-2 Novel Duplex Treatments Prepared by HiPIMS and HVOF/Solgel on Biodegradable Magnesium Alloy for Biomedical Applications**, ***Adrián Claver (adrian.claver@unavarra.es)**,* Universidad Pública de Navarra (UPNA), Spain; *I. Fernandez, J. Santiago,* Nano4Energy SL, Spain; *I. Quintana,* Fundación Tekniker, Spain; *L. Mendizabal,* Fundación Tekniker , Spain; *J. García,* Universidad Pública de Navarra (UPNA), Spain

Magnesium-based biomaterials have become a great candidate to be used in biomedical implants due to their great biocompatibility, biodegradability, and their mechanical properties similar to those of bones. However, Mg-based alloys corrode rapidly in aggressive environments such as human bodily fluids, losing their mechanical properties because of the uncontrolled corrosion and with the risk of infection in the body. In this study, duplex treatments consisting in TaN or TiN doped with Cu and Ag coatings deposited via high power impulse magnetron sputtering HiPIMS with positive pulses followed by a hydroxyapatite (HA) deposited via High Velocity Oxygen Fuel (HVOF) or Solgel top layer, were applied on biodegradable ZK60 magnesium alloy in order to improve the corrosion resistance, antibacterial properties and osteointegration properties of the substrate. Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD) were used to characterize the coatings. Scratch test and nanoindentation were performed to study the adhesion and hardness of the coatings, while contact angle measurements were carried out to compare the wettability of the surface. The samples were immersed in SBF to study the corrosion resistance, mass change and hydrogen evolution. Electrochemical tests were performed to estimate the corrosion behaviour of the samples. Furthermore, antibacterial tests were carried out. The treated surfaces showed better hydrophilicity than the uncoated samples, which improves the ability of cell attachment. The results of in-vitro corrosion tests showed that the duplex treatments improved the corrosion resistance of the uncoated magnesium alloy samples, while antibacterial tests showed an improvement of antibacterial properties of the treated samples. Duplex treatments exhibit suitable properties including high corrosion resistance, osseointegration capability, antibacterial properties, and biocompatibility, so that they can be considered as a promising option to be used in biodegradable magnesium implants.

10:40am **D1-1-MoM-3 Surface Properties Control Immune Response to Implanted Biomaterials**, ***Rene Olivares-Navarrete (ronavarrete@vcu.edu)**,* Virginia Commonwealth University, USA **INVITED**

Implanting a material into the body generates an immune response, both from the surgical procedure and in response to the material surface. Following this initial insult, wound healing begins with the onset of hemostasis. Due to the range of physical and chemical properties of implanted biomaterials, the initial interactions between biological tissues and biomaterials are not fully understood. Following homeostasis, the inflammatory phase, predominated first by neutrophils and then by macrophages, begins. Furthermore, we have recently explored the affect of Ti surface characteristics in neutrophil behavior. Neutrophils are the most abundant immune cell in blood and arrive in scores to the injury site within minutes following trauma or biomaterial implantation. Neutrophils are known for their antimicrobial activity via phagocytosis, degranulation, enzymatic release, and the production of large DNA-based fiber networks called neutrophil extracellular traps (NETs). However, they are understudied in the context of biomaterials. New studies from our lab have demonstrated their key role during the inflammatory phase of biomaterial integration. Macrophages can be activated by biomaterials to release factors that alter the peri-implant microenvironment, directing the activation and recruitment of additional immune cells and/or progenitor cells. Macrophages exist along a broad spectrum with two opposite phenotypes. The pro-inflammatory (M1) phenotype is characterized by the release of factors such as IL1β, IL6, and TNFα that promote inflammation and secretion of chemokines (Ccl2, Ccl4, Ccl7) that recruit additional immune cells such as neutrophils and T cells. On the other end of the spectrum are the alternatively activated macrophages (M2 phenotype), which release immunomodulatory factors to reduce and resolve the inflammatory state and recruit progenitor cells for regenerative process. Biomaterial surface properties can be tailored to improve the healing response following implant placement. In this presentation, I will discuss how material surface properties can be tailored to control neutrophil and macrophage activation following biomaterial implantation and enhance subsequent recruitment of other immune and stem cells to the implant site to aid healing.

11:20am **D1-1-MoM-5 Metal Oxide Thin Films as Osteoinductive Coatings**, ***Phaedra Silva-Bermudez (phaedrasilva@yahoo.com)**, M. Fernández-Lizárraga, D. Morquecho-Marín,* Unidad de Ingeniería de Tejidos, Terapia Celular y Medicina Regenerativa, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico; *B. Millán-Ramos ,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México; *J. García-López ,* Unidad de Ingeniería de Tejidos, Terapia Celular y Medicina Regenerativa, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico; *S. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Biomaterials that exert an appropriate biological response and simultaneously meet biomechanical requirements are essential for orthopedic and dental implants. Mechanical properties of materials are mainly determined by the bulk material while the biological response is mainly directed by the surface properties. Thus, biocompatible coatings with functional properties, such as osteoinduction and osteoconduction, are interesting options to tailor the surface of mechanically- and degradation-wise appropriate bulk materials, to develop novel biomaterials for orthopedic and dental implants. $ZrO_2$, $Nb_2O_5$ and $Ta_2O_5$ are of great interest as coatings for orthopedic and dental implants, since they might promote adequate oseointegration, in a similar way as $TiO_2$.

Nanocrystalline $TiO_2$ and$ZrO_2$, and amorphous $Ta_2O_5$ and $NO_2O_5$ thin films were deposited on Si(100) substrates, from pure metallic targets by magnetron sputtering, under reactive Ar/$O_2$ atmosphere, and using RF-power. The properties of the coatings were characterized by Optical Profilometry, Scanning Electron Microscopy, X-Ray Photoelectron Spectroscopy and Water Contact Angle. To characterize the biological response, human mesenchymal stem cells isolated from bone marrow (BM-MSC) were plated and cultured on uncoated and oxide-coated substrates; $TiO_2$-coated substrates were used as positive controls (osteoinductive and appropriate oseointegration). Cells were cultured at 37°C, changing the culture media every other day. Cell viability and metabolic activity was assessed at different days of culture by the Calcein-AM/Ethidium homodimer fluorescent kit and the Alamar Blue assay. At 7 days of culture, cells were fixed, dehydrated and evaluated by SEM. Potential cell differentiation towards the osteoblastic phenotype was qualitatively assessed by immunofluorescence assays against characteristic markers of the osteoblastic phenotype such as osteopontin, osteocalcin and Runx2, and quantitatively assessed by immuno ELISA assay against Osteocalcin and osteopontin, and colorimetric assays to evaluate phosphatase alkaline specific activity. All metal oxide coatings were biocompatible; however, results suggested that number of cells adhered on the substrate and cell differentiation was dependent on the coatings.

Acknowledgements to financial funding from CONACYT CB-2016-1-288101 and FOINS-FC-1740 Grants, CONACyT postgraduate scholarship for M. F-L and D. M-M

11:40am **D1-1-MoM-6 Synergetic Effect of Porous $Ta_2O_5$ Surface With Zn/ZnO Core-Shell Nanoparticles on Antimicrobial Activity and Corrosion Resistance***, **Luísa Fialho (luisafialho@fisica.uminho.pt)**, C. Rebelo,* University of Minho, Portugal*; C. Alves,* Instituto Pedro Nunes, Coimbra, Portugal*; J. Castro,* University of Coimbra, Portugal*; P. Sampaio,* University of Minho, Portugal*; S. Carvalho,* University of Coimbra, Portugal

As an alternative to the conventional Ti dental implant surfaces, Ta surface biofunctionalization was investigated using different surface treatments to endow it with the microbicidal ability and enhance corrosion resistance. To achieve this innovative design, the adopted strategy was accomplished in two main steps: i) development of a bioactive surface based on the synergetic effect of anodic $Ta_2O_5$ with multilevel porosity (nano to micro) with osteoconductive elements incorporated; ii) development of an antimicrobial delivery system by deposition, by magnetron sputtering, of zinc/zinc oxide (Zn/ZnO) nanoparticles deposited onto the anodic $Ta_2O_5$ structured surface with or without an additional thin carbon layer.

First, a micro/nano-porous calcium phosphate-enriched $Ta_2O_5$ layer was developed by plasma electrolytic oxidation (PEO, also known as micro-arc oxidation - MAO) mimicking the bone morphology and chemical composition. Secondly, Zn/ZnO nanoparticles were deposited onto the porous $Ta_2O_5$ surface by DC magnetron sputtering to promote antimicrobial activity. In addition, the Zn/ZnO nanoparticles were encapsulated by a thin carbon layer to ensure the desired mechanical resistance and provide the antimicrobial agent-controlled release, and consequently improving corrosion resistance.

The antimicrobial effect and the molecular mechanisms involved in the antimicrobial action of Zn/ZnO nanoparticles were evaluated using *Candida albicans*, which is an opportunistic fungal pathogen present in the oral cavity that shows increased resistance to antifungal treatment agents. All the porous surfaces doped with Zn/ZnO nanoparticles showed a strong capability to inhibit cells growth and proliferation, revealing a significant antifungal activity. The surface with more Zn nanoparticles demonstrated a higher influence on cellular growth.

Morphological and chemical composition properties of the samples' surfaces were correlated with the corrosion behavior in artificial saliva. Right after the immersion, theporous $Ta_2O_5$ layer slowed the corrosion rate compared with the untreated Ta surface. The deposition of the Zn/ZnO nanoparticles decreased the corrosion rate and increased the corrosion resistance, indicating an improvement in corrosion behavior throughout the immersion time (14 days). OCP results showed an improvement on these surfaces between the first 2 and 24 hours of immersion, stabilizing afterward, which is related to zinc ions release profile.

Attributing to the excellent *in vitro* performance, this work is progress on the strategy to develop a new generation of dental implants surfaces to prevent implant's infection.

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

### Surface Coatings and Surface Modifications in Biological Environments II

**Moderators: Mathew T. Mathew**, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, **Phaedra Silva-Bermudez**, Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

1:40pm **D1-2-MoA-1 Microstructural and Electrochemical Characterization of 3D Printed Biomedical Implants (Virtual Presentation)**, ***Mozart Neto (mozart_q_neto@rush.edu)***, *R. Pourzal,* Rush University Medical Center, USA **INVITED**

Ti6Al4V is the most used alloy in orthopedic implants such as total hip, knee and shoulder replacements. Implants are conventionally made by cast or wrought alloys, but additively manufactured (AM) implants are increasingly used. Although Ti6Al4V is known for its great corrosion behavior, there are increasing reports of corrosion and fretting-corrosion related implant failures. Currently, it is unknown how alloy microstructure impacts the electrochemical behavior of Ti6Al4V, and its implication on in-vivo corrosion. Therefore, we tested six frequently occurring microstructure types occurring in Ti6Al4V implant components. Our hypothesis was that, despite identical chemical composition, differences in microstructural features can dictate the corrosion behavior of implant alloys. This study included three types of wrought alloys, one cast alloy, and two types of AM alloys: wrought alloys with A) fine equiaxed grains, B) coarse equiaxed grains and C) bimodal grain; D) lamellar dendritic (cast alloys); AM alloys with E) lath-type grains and F) needle-like grains. While A-E exhibited varying degrees of β phase within an α matrix, F exhibited a α' martensitic structure. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were performed within simulated joint fluid (30 g/L protein) at pH 7.6 and 37°C to determine the corrosion behavior. We observed differences in corrosion current (icorr), polarization resistance (Rp) and capacitance (Q), but not in the corrosion potential (Ecorr). The needle-like group had the inferior corrosion behavior attributed to the metastable nature α' and the presence of built defects (local crevice corrosion), followed by equiaxed coarse and lath-type groups attributed to the galvanic coupling between α and β phase, specifically when a difference in Ti and V content of >10%occurred between both phases. Therefore, the microstructure does influence the corrosion behavior of Ti6Al4V implants, however the distribution of alloying elements also played a role.

2:20pm **D1-2-MoA-3 Diamon-like Carbon Coatings with Precise and Localized Silver Doping for High-Performance Biomedical Applications**, ***Abdul Wasy Zia (abdul.zia@northumbria.ac.uk)***, Northumbria University, UK*; M. Panayiotidis,* The Cyprus Institute of Neurology & Genetics, Nicosia, Cyprus*; M. Birkett,* Northumbria University, UK

Diamond-like carbon (DLC) coatings are recognised due to superior mechanical, biomedical, and tribological performance. Therefore, these coatings are actively being used for artificial orthopaedic joints, stents, heart valves, etc applications. Silver is doped in DLC coatings to boost its biocompatibility for superior biological performance. The increasing amount of silver is inferred to deliver better biological performance. However, DLC coatings lose their unique mechanical and tribological characteristics, such as high hardness, low friction coefficient, and low wear rates due to silver-induced-ductility in the coatings. In this work, silver doped DLC coatings are made with magnetron sputtering technique and the deposition process is controlled to dope silver in the form of small isolated nanoparticles at defined depths. The coatings are characterised for microstructure, hardness and Young's modulus, friction and wear, and cytotoxic studies. The preliminary results suggest that the silver nanoparticles are ~17nm in diameter and uniformly distributed in a plane and embedded at control depths. It is observed that ~ 2at.% silver when doped in DLC with the controlled deposition process gives similar cytotoxicity levels as delivered by ~18at.% silver which was doped with conventional co-sputtering methods. Whereas, the baseline DLC has a hardness of ~20GPa which is reduced to ~17GPa and ~10GPa for 2at.% and 18at.% silver doped DLC coatings. The investigations suggest that a relatively small amount of silver will be required to boost biocompatibility without compromising mechanical properties if the coatings are made with the proposed process.

Acknowledgement:

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2:40pm **D1-2-MoA-4 Corrosion Resistance and Biocompatibility Evaluation of TiZrNbTaMo High Entropy Alloy Coatings**, *S. Hou,* Ming Chi University of Technology, China*; B. Lou,* Chang Gung University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been attracted lots of attentions due to their unique properties compared to conventional alloy coatings. In this study, an equimolar TiZrNbTaMo target connected to a high power impulse magnetron sputtering (HiPIMS) power and a pure Ti target connected to a radio frequency (RF) power were used to fabricate five TiZrNbTaMo (TZNTM) HEA thin films with different Ti contents on the surfaces of cp-Ti substrates.In this study, scanning electron microscope (SEM), electron probe X-ray microanalyzer (EPMA), transmission electron microscope (TEM) and X-ray diffractometer (XRD) were used to analyze the cross-sectional morphology, composition and crystal structure of each thin film. The corrosion resistance of TiZrNbTaMo HEA films was studied using a potentiostat in the Ringer solution. Furthermore, the in vitro biocompatibility of MG 63 human osteoblast-like cells on the HEA films were evaluated. This study found that the corrosion resistance and biocompatibility of TiZrNbTaMo high entropy alloy film were improved with increasing titanium contents in the thin films.

3:00pm **D1-2-MoA-5 Corrosion Risk Evaluation of Carbide-Derived Carbon (CDC) Surface Modification for Hip Implants**, ***Yani Sun (ysun98@uic.edu)***, University of Illinois at Chicago, USA*; K. Kinnerk,* City Colleges of Chicago, USA*; K. Cheng, M. Mathew,* UIC College of Medicine at Rockford, USA*; M. McNallan,* University of Illinois at Chicago, USA

Ti6Al4V is a commonly used alloy for biomedical applications as it has excellent corrosion properties, which are mainly attributed to the oxide layer on the surface. Nevertheless, the early failure of total hip replacements has happened on Ti6Al4V alloys due to its poor tribocorrosion behavior. Previously, we have proved that carbide-derived carbon (CDC) can provide superb protection to Ti6Al4V from tribocorrosive damages[1]. However, the basic corrosion behavior of CDC stills remains unknown. In this work, experiments were conducted to investigate CDC's corrosion behaviors in comparison with the substrate alloy (Ti6Al4V).

Two groups of experiments were designed to evaluate CDC's corrosion performances: (1) Ti6Al4V as the control group, and (2) the CDC. Each group was repeated three times (N=3) to confirm the reproducibility. For Group (1), Ti6Al4V discs (11 mm dia x 7 mm) were ground and polished to a mirror finish. In Group (2), CDC was fabricated by the electrolysis method[2]. Furthermore, a three-electrode corrosion chamber was employed, where the tested sample was used as the working electrode, a graphite rod as the counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. With an aim at the application for hip implants, bovine calf serum (BCS) was selected as the electrolyte, with the temperature maintained at 37˚C. Finally, the electrochemical protocol for the Ti6Al4V was set as open-circuit potential 1 (OCP1) for system stabilization – potentiostatic (PS) for surface cleaning – OCP2 (stabilization) – electrochemical impedance spectroscopy (EIS) – Cyclic polarization. Same protocol without PS was followed for Group (2) as the CDC layer was coated on the surface. After the corrosion testing, JEOL JSM-IT500HR SEM with Oxford AZtec EDS and Bruker-Nano Contour GT-K Optical Profilometer were utilized to examine the sample surface.

The geometric sample area exposed to the solution is 0.1256 $cm^2$, which was used to calculate the current density and impedance for Ti6Al4V. However, instead of having a smooth surface like the polished Ti6Al4V, the prepared CDC has a rough and porous structure with a large surface area. Therefore, we estimated our CDC area exposed to the solution based on the Brunauer-Emmett-Teller (BET) surface area of Ti-CDC reported by Huang et al.[3]. Consequently, according to the potential dynamic and EIS results, the CDC shows higher corrosion resistance than Ti6Al4V. However, the actual surface area of our CDC products is still needed, which will be achieved in the upcoming studies.

1. Cheng, K *Surf. Coat. Technol.***2020**
2. Sun, Y *Surf. Coat. Technol.***2021**
3. Huang, P *Science.***2015**

3:20pm **D1-2-MoA-6 Enhancing the Mechanical and Biomedical Properties of Super Hard β-$Ti_3Au$ Intermetallic Thin Films by Doping with Known Antimicrobial and Interstitial Elements**, *C. Cherian Lukose* , ***Martin Birkett (martin.birkett@northumbria.ac.uk)***, Northumbria University, UK; *M. Panagiotidis* , The Cyprus Institute of Neurology & Genetics, Cyprus

Owing to their excellent mechanical hardness and biocompatibility, $Ti_3Au$ intermetallic materials are being extensively researched as thin film coating systems to protect the surface of load bearing implants and thereby extending their lifetime within the human biological environment. However, bacterial biofilm formation around the newly implanted device and wear of implant devices in the load bearing joint are known to be the leading causes of implant failure. The mechanical and biomedical properties of β-$Ti_3Au$ intermetallic thin films doped with low quantities of a known antimicrobial element like silver and known interstitial element like nitrogen is explored. Thin films of $Ti_3Au$ intermetallic were deposited by magnetron sputtering onto glass and $Ti_6Al_4V$ substrates at elevated substrate temperature to promote development of the super hard β phase. Silver doping was introduced in one set of samples using a titanium-silver mosaic target, whereas, reactive nitrogen gas was introduced into the argon environment in a separate set. Elemental analysis using Energy dispersive X-ray spectroscopy confirms that the required 3:1 ratio of Ti and Au is achieved and the doping concentration of ternary element is below 5 at%. X-ray diffraction of the samples explores the development of β phase of $Ti_3Au$ with addition of ternary element and is corelated to microstructure images captured using electron microscopy across sample surface and cross section. Surface features were also probed by Atomic force microscopy to account for change in surface roughness. Mechanical hardness and elastic modulus of the samples were measured by nanoindentation technique using a Berkovich tip in a displacement control mode. Biocompatibility of the films were evaluated by performing cytotoxicity test on L929 mouse fibroblast cells and measured by Alamar blue assay while concentration of leached ions from thin films were analysed using Inductively coupled plasma optical emission mass spectroscopy technique. Antimicrobial performance was tested using *E. coli* and *S. aureus* and by following the reduction in colony formation. Mechanical hardness better than 12 GPa and a low elastic modulus value of 148 GPa, combined with cell viability better than 95% encourages use of β-$Ti_3Au$ as coating material. Nitrogen acts like a interstitial defect raising the energy of the barrier to dislocation movement thereby enhancing the mechanical hardness. Leached ion concentrations lower than 1 ppm sustains the non-cytotoxic nature, whereas, increased release of silver ions with addition of silver in the thin film matrix lends additional antimicrobial functionality to the material system.

## Coatings for Biomedical and Healthcare Applications
## Room Pacific C - Session D2-TuM

### Medical Devices: Bio-Tribo-Corrosion, Diagnostics, 3D Printing

**Moderators: Steve Bull**, Newcastle University, UK, **Hamdy Ibrahim**, University of Tennessee at Chattanooga, USA, **Margaret Stack**, University of Strathclyde, UK

8:00am **D2-TuM-1 Characterization of Hydroxyapatite Coatings Produced by Pulsed-laser Deposition on $Ti_6Al_4V$ Substrates Fabricated by Electron Beam Melting***, **Octavio Andrés González-Estrada (agonzale@uis.edu.co)**, R. Ospina, A. Pertuz,* Universidad Industrial de Santander, Colombia

Additive manufacturing is a disruptive technology that has changed the design of bone implants for clinical applications. In this work, the effect of the deposition energy parameter on the mechanical properties and surface microscopy of Ti6Al4V alloy substrates manufactured by electron beam melting (EBM) and coated with hydroxyapatite (HA) deposited by the pulsed laser technique (PLD) was investigated. The average hardness and microhardness values were obtained under microindentation and indentation tests following the standard practice for instrumented indentation ASTM E384-17, as well as, scratch tests for adhesion behavior. The morphology and chemistry of the substrate coating were evaluated using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), resulting in average values of HA particle formation size of the coating. Variables that reflect the incidence of deposition parameters in relation to the mechanical and micrographic properties of the HA coating were assessed.

8:20am **D2-TuM-2 Preclinical in Vitro and in Vivo Assessment of High-Strength and Corrosion-Controlled Magnesium-Based Bone Implants***, C. Billings,* University of Tennessee Knoxville, USA*; M. Abdalla,* University of Illinois - Chicago, USA*; D. Anderson,* University of Tennessee Knoxville, USA*;* ***Hamdy Ibrahim (HAMDY-IBRAHIM@UTC.EDU)****,* University of Tennessee at Chattanooga, USA

Magnesium is a lightweight metal that is naturally present in the human body with a biodegradable nature in aqueous mediums. These properties make magnesium an attractive material for its use in various biomedical applications when the material is not recommended to stay permanently in the body, such as bone implants. Some of the main challenges that hinder the use of magnesium for bone fracture repair are its limited mechanical strength and fast corrosion rates which results in peer biomechanical performance in the body. To this end, we have developed both a biocompatible magnesium alloy (Mg-Zn-Ca-Mn-based alloy) and a fabrication method (heat treatment and coating) that deliver a high-strength and corrosion-tailored material that can provide the needed stability during the healing period for bone implant applications, and subsequently degrade until vanished completely after the healing of tissues. The created coating consists of two layers; a first ceramic layer (10 µm thick) made by using the micro arc oxidation (MAO) process followed by a thinner layer (1-2 µm thick) of Ca/P-based ceramics created by using the sol-gel technique. The sol-gel coating resulted in a significant reduction in corrosion rate, as low as 1.1 µm/year which is 27 times less than that for the MAO-coated alloy alone. In vitro and in vivo assessments of our magnesium alloy and fabrication method showed high levels of biocompatibility in terms of cytotoxicity, degradation rates, and fracture healing. For instance, our animal studies, using New Zealand white rabbit utilizing a lateral femoral condyle model, showed no negative effects on bone formation, and no evidence of a strong or persistent inflammatory reaction. The results of this study show that it is possible to produce biocompatible magnesium-based implants with stronger and more corrosion-controlled properties.

8:40am **D2-TuM-3 Understanding Tribological Contact in Biomedical Applications; The Role of Surface Film Formation and Its Correlation With Friction and Wear***,* ***Mark Rainforth (m.rainforth@sheffield.ac.uk)****,* The University of Sheffield, UK*; R. Namus, J. Qi, J. Nutter,* University of Sheffield, UK **INVITED**

The impact of tribology (friction and wear) on the economy is a substantial 5-8% of GDP and plays a central role in everyday life, for example, in transport, manufacturing, process engineering and medical devices.The tribological performance of a component is a strong function of the interaction between the component surface and the operating environment, and how the surface changes in response to the contact stresses. In many cases, the tribo environment activates electrochemical reactions, which is particularly true in orthopaedic components. It is these dynamic changes that determine the success or failure of the component. In many cases, distinct surface structures are generated by the sliding contact. Of these, the formation of tribofilms is perhaps the most important. Evidence is mounting that tribofilms play a crucial role in the success of components, particularly in the articulating surfaces in orthopaedic components. The conditions under which tribofilms form is still far from clear. In this work a detailed analysis of the tribocorrosion behaviour of Ti-6Al-4V and CoCrMo alloys was undertaken under a range of electrochemical and load conditions in order to determine the conditions under which a tribofilm forms and the role that the tribofilm plays. The structure of the tribofilm is considered in detail, down to the atomic scale. High resolution transmission(scanning) electron microscopy and electron energy loss spectroscopy have been used to characterise the structure and chemical composition of the tribofilm. A detailed, quantitative, analysis of surface deformation was also undertaken, in particular, the geometrically necessary dislocation (GND) density was quantified using precession electron diffraction (PET). For the first time, graphitic and onion-like carbon structures were found. It has been clearly shown that the presence of carbon nanostructures in the tribocorrosion process and the formation of the tribofilm leads to an improved tribocorrosion behaviour of the system, in particular a reduction in wear and friction. A clear correlation between applied potential and tribofilm formation has been established, with tribofilms forming on a passive surface, but not on a metal surface where an oxide is not present. Interestingly, there appears to be a correlation between the extent of surface deformation with the presence of a tribofilm and the surface potential; anodic conditions result in much greater surface deformation than cathodic conditions. However, there was no correlation between the surface deformation and the wear rate. The implications for these observations on the wear performance of these materials is discussed.

9:20am **D2-TuM-5 Corrosion Resistance of Cerium Oxynitride Thin Films for Use in Implants and Prothesis***, G. Numpaque Rojas,* ***Brian Felipe Mendez Bazurto (bfmendezb@unal.edu.co)****, G. Cubillos Gonzalez,* Universidad Nacional de Colombia

Due to its chemical properties and high corrosion resistance, the cerium oxide has been widely used in aeronautical and naval industry as coating of aluminium alloys [1, 2]. The CeO is deposited mainly by suspended techniques, clean high vacuum techniques deposit of cerium oxide has not been studied since being a pyrophoric solid, and the films obtained are porous and easily delaminated. In this work, we determine the conditions of pressure, temperature and nitrogen flow to deposit homogeneous films on stainless steel AISI 316L surgical grade and corrosion resistance cerium oxynitride was evaluated. CeOxNy/ZrOxNy coatings were obtained from a 4 in. ×1/4 in. Zr-Ce (99.9%) target (Stanford Advanced Materials). RF reactive sputtering technique, in atmosphere of N2/O2, with a flow ratio ΦN2/ΦO2 of 20 was used. The structural analysis carried out through X-ray diffraction (XRD) showed that the CeOxNy/ZrOxNy coatings had a cubic polycrystalline structures preferencial growth for CeOxNy, while ZrOxNy is amorphous. The SEM analysis evidenced that the films grew with homogeneous morphology and exhibited a columnar growth. Corrosion resistance evaluated from the potentiodynamic polarization curves in Hank's solution [3], showed that the coating increases the corrosion resistance of steel by two orders of magnitude. CeOxNy/ZrOxNy coatings deposited on surgical grade stainless steel could be a promising candidate to be used in osteosynthesis processes.

9:40am **D2-TuM-6 Porous Ti Under Tribocorrosion Solicitations: Some Positive Feedback and Some Scientific Benefits***, A. Gomes Costa,* CMEMS-Minho University, Portugal*; F. Viana,* FEUP, Portugal*; L. Rocha,* DTX, Portugal*; F. Toptan,* DMSE, İYTE, Turkey*;* ***Jean Geringer (geringer@emse.fr)****,* Mines Saint-Etienne, France

About biomaterials dedicated to bone substitutes, some candidates are promising like Hydroxyapatites, cell growth boosters, etc. One candidate is titanium foam for two reasons: promoting vascularization thanks to 3D structure and bone cells attachments and growth. Some concerns are on tribocorrosion resistance. This work is dealing with titanium foam (void 50% approx.) under tribocorrosion solicitations in physiological environment, i.e. bovine serum. The consequences of the micro-displacements (+- 40 µm sinusoidal displacement) under normal loads from 22.5N till 200N were analyzed through the materials integrity. Moreover the tribological analysis was investigated and the Master curve, A (dissipated energy over the total dissipated energy) vs. 1st OCP (Open

Circuit Potential) drop was used to manage the influence with normal load and displacement amplitude. The results are in accordance with stick/slip phenomenon. A fretting map was illustrated and the fretting regimes were highlighted. The A-1st OCP curve is in accordance with the type of degradations, i.e. macroscopic wear.

## Coatings for Biomedical and Healthcare Applications
## Room Pacific D - Session D3-TuA

## Biointerfaces: Improving Cell Adhesion and Avoiding Bacteria. What Kinds of Coatings Should be Used?

**Moderator: Danieli B.C. Rodrigues**, University of Texas at Dallas, USA

1:40pm **D3-TuA-1 Enhanced Mechanical Properties and Microbiological Behavior of a Ag-C:H Coating Produced by Reactive pDCMS**, *N. Fukumasu, **Pâmella Esteves (pamellaesteves@usp.br)**, V. Malaquias,* University of São Paulo, Brazil*; E. Prados,* Federal University of ABC, Brazil*; M. Hirata, A. Tschiptschin, I. Machado, R. Souza,* University of São Paulo, Brazil

Surfaces presenting antimicrobial activity became more relevant during the COVID-19 outbreak, in which restricting the spread of virus and bacteria agents become important in crowded places, such as hospitals and public transportation. Literature reports the use of metallic coatings, such as silver and/or copper, promote excellent antimicrobial activity but present lower adhesion and mechanical properties, mainly when compliant substrates are used. Nanocomposite coatings based on silver and carbon may be applied to improve such characteristics, preserving the antimicrobial activity. The deposition of carbon coatings, using physical vapor deposition techniques, may require high substrate temperature (>200ºC) for long periods of deposition time (>1h), which is not suitable for overall polymer substrates. In this work, the pulsed direct current magnetron sputtering (pDCMS) technique was applied to produce Ag-C coatings on PMMA-based substrates. High purity silver and carbon targets were used to produce Ag and Ag-C coatings using Ar as plasma gas. In addition, a mixture of Ar+H allowed the production of Ag-C:H coatings. The mixture of Ar+H was applied only during the carbon deposition phase to enhance the coating growth rate and promote additional features, including a higher degree of $sp_3$ carbon bonds, which improves mechanical properties. All coatings were analyzed using Raman spectroscopy, XPS, instrumented indentation, scratch test, SEM+EDS and microbiological tests (*E. Coli* and Sars-CoV-2). Results indicate that Ag-C coatings presented an increase in hardness and substrate adhesion, but lower antiviral and bactericidal activity when compared with pure Ag coating with similar thickness. Nevertheless, the use of Ar+H mixture, in which $H_2$ acted as a reactive gas during the deposition of the amorphous carbon, resulted in an Ag-C:H coating with higher mechanical properties while presenting improved antiviral and bactericidal effects than pure Ag coating.

2:00pm **D3-TuA-2 Coating of Titanium Surfaces with Silver-Chitosan using Silane Linkers**, ***Emily Coleman (cclman22@memphis.edu)**, E. Abuhussein, M. Edwards, J. Bumgardner, J. Jennings,* University of Memphis, USA

Titanium implants and instruments are widespread in the field of orthopedics due to the material's strength, resistance to corrosion, and bone-like mechanical properties. Silver ions have broad spectrum antimicrobial properties against bacteria and fungi and thus are advantageous as an implant coating in combination with chitosan biopolymer. Previous titanium coating attempts with chitosan-silver solutions gave weak adherence to the substrate and removal of the coating after contact with saline. In the current study, methods were demonstrated for attaching chitosan-silver conjugates to titanium using silane linkers to increase stability and adherence of the coating. Titanium coupons were polished and sonicated in soapy water to remove oil and residue, then in acetone and ethanol. The coupons were covered in sodium hydroxide (5 M) for 24 hours at 60°C to allow the titanium surface to accumulate hydroxide reactive groups. After rinsing with deionized (DI) water, the coupons were immersed in a 95% (v/v) ethanol solution (pH = 4.5). Using a nitrogen environment glove box, the silanization agent was added to create a 2% (v/v) silane solution in ethanol. Non-adhered silane was removed with ethanol, and coupons were dried at 110°C for 10 minutes before addition of chitosan silver (Chitozan Health, LLC). After drying overnight, coupons were immersed in phosphate buffer for 1 hour before rinsing with DI water and drying fully. To evaluate the bonding strength between the titanium coupons and the chitosan coating, Instron mechanical testing with a custom fixture was performed on coupons that were glued to pegs using GorillaWeld Steel Bond Epoxy Two Part Adhesive. Electron dispersive spectroscopy (EDS) was used to evaluate the success of the coating process by determining the presence of silver after 24-hour aqueous exposure. The mechanical testing suggested that the coating process was successful, and coating-adhesive strength exceed the adhesive strength of the glue-peg interface. EDS results indicated that the amount of silver on the surface of silanated coupons (10-15%) was significantly greater than non-silanated coupons (<1%), and the silver was homogenously distributed on the silanated coupon surface (**Figures 1 and 2**). Overall, results suggest that the silanation procedure for coating titanium surfaces promotes retention of silver on the titanium surface. Further studies are planned to assess the antimicrobial efficiency over time and human cell compatibility of the coatings. Coating strategies could be implemented with many application methods including dip coating, solution casting, electrospraying, and electroplating.

## Coatings for Biomedical and Healthcare Applications
## Room Golden State Ballroom - Session DP-ThP

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

**DP-ThP-3 Antimicrobial and Aging Properties of Ag-, Ag/Cu- and Ag Cluster-Doped Amorphous Carbon Coatings Produced by Magnetron Sputtering for Aerospace Application**, *G. Sanzone, J. Yin,* ***Hailin Sun (hailin.sun@teercoatings.co.uk)***, Teer Coatings Ltd, UK

Inside a spacecraft, the suitable temperature and humidity, designed for onboard human crew, also creates an ideal breeding environment for the proliferation of bacteria and fungi, which can present hazard for both the safety running of equipment and human health. To address this issue, it is proposed to coat the key parts and components with wear-resistant antimicrobial thin films prepared by magnetron sputtering. Silver and copper are among the most studied active bactericidal materials for a long history. In this work we investigate the antibacterial properties of silver doped, silver-copper doped, and silver cluster doped amorphous carbon coatings for aerospace applications and their longevity, which is heavily influenced by the metal diffusion rate to the coating surface. Samples have been prepared with different silver and copper volume fractions via co-sputtering, while Ag cluster samples are prepared using a cluster source to better control the metal particle size distribution in the amorphous carbon coating matrix. Antibacterial tests are performed under both terrestrial gravity and microgravity conditions, to simulate the condition in the space. Results show that silver doped coatings are very effective in terms of antimicrobial property but with a faster silver atom diffusion, while those silver-copper doped samples have generally a slightly lower antimicrobial activity, but no obvious metal diffusion observed. For the silver cluster doped samples, they show a high antimicrobial activity despite a much lower silver volume fraction, and a seemingly slow Ag metal diffusion rate.

**DP-ThP-4 Structure and Mechanical Properties of Superelastic TiZrNb and TiSnZrNb Coatings for Biomedical Applications**, *T. Choquet, A. Fillon,* Institut des Sciences Chimiques de Rennes, France*; A. Michel,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; M. Vayssade,* Université de technologie de Compiègne, France*; T. Gloriant,* Institut des Sciences Chimiques de Rennes, France*;* ***Gregory Abadias (gregory.abadias@univ-poitiers.fr)***, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Titanium alloys are propitious materials in biomedical implants for their mechanical properties and biocompatibility. Nitinol (Ni-Ti), especially, has been used because of its superelasticity (up to 12% recoverable strain) due to a reversible martensitic transition. Ni, however, has been proven allergenic and so in the past decade, research has focused on β-type titanium alloys with non-toxic and non-allergenic elements such as Nb, Sn, Ta or Zr with the aim of replacing Ni-Ti. In this study, novel coatings based on ternary and quaternary titanium alloys have been elaborated. Their properties have been studied for bulk materials; however, the structural and mechanical properties for their thin film counterpart remain to be elucidated, which is the aim of the present study.

Ti-Nb-Zr and Ti-Nb-Zr-Sn coatings have been elaborated at room temperature by magnetron sputtering at a working pressure of 0.26 Pa. By using different targets and by changing the power applied to them during deposition, different chemical compositions have been obtained, with Nb content ranging from 0 to 33 at.%. The focus has been on identifying the crystallographic structure and the mechanical properties of the films depending on their chemical composition. XRD, TEM and resistivity measurements were performed to study the phase formation with respect to the Nb content. The stress induced during film growth has been evaluated *in-situ* using wafer curvature measurements and the mechanical properties were evaluated using nano-indentation and tensile tests. To assess the biocompatibility of the films, early cell behavior (cell adhesion, spreading and morphology) will be characterized and standardized cytotoxicity assay will be conducted.

Using XRD θ/2θ scans, the films have been found to be highly textured: the main peaks are 002 α and 110 β. XRD, TEM and resistivity show that with increasing Nb and Zr content, the phase evolves from hexagonal α phase to orthorhombic α'' martensite and then to cubic β phase. The curvature measurements have shown that at low Nb content, the film first develops a compressive stress that evolves during continuing growth into tensile stress. At high Nb content, the stress remains compressive throughout deposition. Preliminary *in vitro* biocompatibility tests show that osteoblast cells well adhere on the quaternary coatings after 72 h and manifest cell functional activity.

**DP-ThP-5 Development of Multilayer Hydroxyapatite (HA) - Silicon (Si) Coatings Deposited on Ti6Al4V by Magnetron Sputtering with Potential Biomedical Application**, ***Julián Andrés Lenis Rodas (julian.lenis@udea.edu.co)***, *K. Perez Zapata, F. Bolívar Osorio,* University of Antioquia, Colombia*; P. Rico, J. Gómez Ribelles,* University of Valencia, Spain

Titanium alloys, specifically Ti6Al4V, are widely used in the biomedical field because they have an adequate balance between mechanical properties, corrosion resistance and biocompatibility. However, when it is incorporated into the human body, unfavorable reactions can be obtained that do not allow adequate osseointegration, due to the formation of a fibrous and non-adherent layer between the biomaterial and the bone, which can trigger the failure or rejection of the implant. The purpose of this study was to evaluate the influence of the surface modification of Ti6Al4V with a Hydroxyapatite (HA) - Silicon (Si) coating on its in vitro biological response, also studying the effect of surface roughness. The deposition process was carried out by Magnetron Sputtering on Ti6Al4V surfaces with different roughness - RMS, 3.8 nm and 48.7 nm. The surface morphology of the coatings was observed by Scanning Electron Microscopy and Atomic Force Microscopy, the chemical composition was evaluated by means of EDS and micro-Raman spectroscopy. The biological response of the coatings was evaluated by MTT and cell adhesion assays, using mouse mesenchymal stem cells. The control in the process parameters allowed to obtain coatings with a good compositional balance (a Ca/P ratio close to 1.67 and characteristic vibrations of HA). RMS values of 27 ± 5 nm and 52 ± 6 nm were obtained for the coatings obtained on the Ti6Al4V with different roughness. The biological tests indicated a non-toxic behavior in the HA-Si coatings, in addition, the cellular adhesion of the Ti6Al4V was favored both by the incorporation of this system and by increasing its roughness.

**DP-ThP-6 Effective Antiviral Copper Coatings onto Thermoplastic Against SARS-CoV-2**, *C. Popescu,* IRCER, France*; M. Courant,* CHU Limoges, France*; E. Laborde,* IRCER, France*; S. Alain,* CHU Limoges, France*; V. Perin,* Kometa Technologies, France*; A. Castro,* CITRA, France*; L. Youssef,* IRCER, France*; T. Maerten,* Oerlikon-Balzers, France*;* ***Marjorie Cavarroc (marjorie.cavarroc@safrangroup.com)***, Safran, France*; D. Alain, A. Vardelle,* IRCER, France

The actual viral outbreak continues to have a tremendous impact on human health, social relations, and the economic situation worldwide. Eengineered metallic coatings can mitigate the viral transmission from the thermoplastic surfaces (fomites) touch points in transports. This goal is achievable by functionalizing thermoplastic surfaces with metals through innovative designs that inhibit or destroy the microorganisms. The life span of these functionalized surfaces depends on their physical-chemical properties and external factors (e.g., humidity, temperature, cleaning agents, etc.) that can modify the engineered surface. The presented work focus on copper-based thermoplastic surfaces obtained by different deposition methods to observe the influence of the chemical composition of the surface, but also the importance of coating structure and texture, to increase the SARS-CoV-2 inactivation rate. The in-vitro antiviral tests are realized in agreement with normalized protocols to qualify the antiviral surfaces (ISO 21702:2019). The obtained results show that the deposition method has a strong influence on both the microstructure and the surface chemistry of the engineered Cu films. The coatings enhanced grain dislocations increase the Cu ions release and their participation in the reactive oxidative species processes influences the viral growth time.

**DP-ThP-7 Antibacterial Graphene Coatings Electrophoretically Deposited on Nitinol Substrate**, ***Madhusmita Mallick (madhusmita1509@gmail.com)***, *K. Mitra, A. N,* Indian Institute of Technology (IIT) Madras, India

Graphene can be an effective antibacterial candidate owing to its bactericidal property. In this study, graphene coatings were prepared on Nitinol substrate through a cost-effective electrophoretic deposition method (EPD). The antibacterial activity of graphene-coated samples was investigated against two strains of gram-positive (S.Aureus) and gram-negative (E.Coli) bacterias by classic colony counting method, live/dead fluorescent microscopy and scanning electron microscopy (SEM) techniques. Here, bare nitinol substrate was chosen as a control sample.The results showed that the coatings exhibited stronger antibacterial activity against E. coli bacteria with thin membrane than S.

aureus bacteria with thick membrane. Furthermore, the antibacterial test suggested that oxidative stress mechanism is the main factor of antibacterial activity of EPD prepared graphene coatings.

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