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

Surface Coatings and Surface Modifications in Biological Environments II

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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.

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