Coatings for Biomedical and Healthcare Applications
Room Pacific F-G - 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, **Dr. Kerstin Thorwarth**, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

1:40pm **D1-2-MoA-1 Antibacterial Performance of DLC and Ag-doped DLC coatings with a Long Term Perspective***, **Maneesha Rupakula,*** Platit AG, Switzerland*; K. Sharma,* EPFL, Switzerland*; H. Bolvardi, B. Paul, G. Wahli,* Platit AG, Switzerland

DLC display properties such as high mechanical hardness, low coefficient of friction, high chemical inertness, and good biocompatibility. Due to their amorphous structure, doping with certain elements enhances functionality still preserving structural integrity. Ag doped DLC films form an interesting class of biomaterials being bactericidal along with other favourable physical properties. Where sterile or ultra-clean conditions need to be ensured, surfaces of components, instruments, parts of tactile and environmental surfaces can benefit from such hard biomaterials. For industrial relevance, 1) anti-bacterial response to both clinically relevant gram-positive and gram-negative bacterial strains and 2) antibacterial performance over longer-term needs to be explicitly studied and not inferred.

In this work, we addressed both antibacterial behaviour and its long-term effect over months. DLC films were prepared in a hybrid vapordeposition process to obtain Ag concentrations in DLC ranging 0 to 8.5%. DLC (No Ag) films display antifouling behaviour over bare substrate with antibacterial efficiency up to 30% for both gram-positive (S. aureus) and gram-negative (E. coli) bacterial strains. Hence, DLC (No Ag) films are considered intrinsically favourable as antibacterial surfaces. This passive antibacterial effect can vary widely when tuning mechanical film strength with change in carbon content. To obtain a constant efficiency with time, an active bactericidal effect with Ag doped DLC is necessary. At an optimal Ag-concentration of 6.9 % in DLC over DLC (No Ag), very high efficiencies of up to 99.6% were obtained for both types of bacterial strains. To motivate commercial implications of Ag-DLC the long-term antibacterial performance was also investigated. In aged samples (post de-oxidising treatment), the antibacterial efficiency was recovered up to 95% of its value pre-aging, encouraging an in-depth long-term study.

2:00pm **D1-2-MoA-2 TiN/NbN Superlattice Coatings Deposited by High Power Impulse Magnetron Sputtering Potential Candidate to Protect Medical Grade CoCrMo Alloys***, **Papken Hovsepian,*** Sheffield Hallam University, UK*; A. Ehiasarian, A. Sugumaran,* Sheffield Hallam University, United Kingdom*; I. Khan,* Zimmer- Biomet UK

In recent years significant progress has been made in the application of various ceramic, namely MeN functional coatings to engineer the surfaces of medical implants utilising metal-on-metal (MoM) articulation. TiN/NbN coatings were deposited on medical grade CoCrMo alloy by High Power Impulse Magnetron Sputtering, (HIPIMS). X-ray analysis revealed that the coatings exhibit single phase fcc crystal structure and (200) texture. LA diffraction analyses revealed the superlattice coating structure with bilayer thickness of 3.0 nm further confirmed by TEM imaging.

In dry sliding pin on disc tests TiN/NbN coatings exhibited friction coefficient of μ= 0.7 and wear coefficient of Kc = 1.4 × 10^{-14} m^3 N^{-1} m^{-1} which were significantly lower as compared to the bare alloy.

Coating impact load fatigue resistance was studied by applying 500 N load for 1 million impacts using CemeCon impact tester which revealed coating high durability.

In the case of TiN/NbN coating deposited on CoCrMo substrate where $E_{coating}$ / $E_{substrate}$ is as high as 1.81 indicating that the substrate does not provide the necessary load bearing support for the brittle thin film, the utilisation of the Berkovich indentation technique proved to be a potent approach to study coating material as well as structural response to applied concentrated load.

FIB/SEM analyses of the indented coatings revealed that in the hard-on-soft material systems cracks will initiate due to sub- coating substrate deformation and then propagate towards the coating surface. The FIB/SEM and low magnification XTEM analysis showed that an exceptionally strong TiN/NbN coating substrate adhesion bonding was achieved due to the utilisation of the HIPIMS pre-treatment.

High resolution XTEM analyses revealed first time that during the indentation a collective rotation and alignment of the individual layers of the superlattice stuck takes place without compromising coatings integrity which is clear evidence for the exceptionally high coating toughness.

In potentiodynamic polarization tests in 3% NaCl and Hank's solution TiN/NbN showed several orders of magnitude lower corrosion current and higher pitting potential compared to CoCrMo which guarantees excellent protection.

Inductively Coupled Plasma Mass Spectrometry analyses of TiN/NbN coated samples corroded in Hank's solution revealed that the leaching of harmful metal ions from CoCrMo was reduced to bellow the detection limit.

The high toughness of the superlattice structured TiN/NbNcoatings combined with their exceptionally high adhesion on medical grade CoCrMo and reliable barrier properties ranks them as a strong candidate for medical implant applications.

2:20pm **D1-2-MoA-3 3D Printed Ceramics Reinforced Ti6Al4V: Structural and Nano-Mechanical Characterization***, **Peter Apata Olubambi,*** *T. Tshephe,* University of Johannesburg, South Africa **INVITED**

Compositional formulations and improved materials processing methodologies are innovative approaches for confronting the challenges being faced by materials and biomedical engineers in designing and producing biocompatible components and implants with longer lifetimes having enhanced wear and corrosion resistances. In this study, the structural properties of 3D additively manufactured Ti6Al4V containing ZrO_2 printed through direct metal laser sintering technique at varying process parameters were investigated and reported. Results on the relationships between the micro-scale and nano-scale mechanical properties as well as the biocorrosion behaviours of the biocompatible composites in some selected simulated human systems are presented.

3:00pm **D1-2-MoA-5 A Remote Atmospheric Pressure Plasma-Assisted Textile Functionalization Process on Polymeric Scaffolds for Bone Tissue Engineering***, **Wei-Yu Chen,*** *J. Lee, T. An,* Taiwan Textile Research Institute, Taiwan*; A. Matthews,* University of Manchester, UK

The porous textile structure of nonwoven polylactic acid (PLA) possesses the potential of being applied to tissue engineering scaffolds. However, when adopting biodegradable polymers, including PLA, for bone tissue engineering scaffolds, the inert and hydrophobic surface properties of these materials not only lead to poor biocompatibility and osteoconductivity but also limit the efficiency of surface modification treatments, which include hydroxyapatite (HAp) deposition via alternate soaking processes. To develop a rapid, environmentally friendly and polymeric textile-suitable process to tackle these issues, a remote atmospheric pressure plasma (APP) system using a bespoke Pyrex chamber and acrylic acid monomer was utilised to deposit carboxylic acid functional groups onto the PLA surface, which are beneficial for performing the following alternate soaking process for HAp deposition. Being compared with the neat PLA, the plasma functionalized PLA exhibited a 16% improvement in hydrophilicity and showed better biocompatibility after HAp deposition. The stability of hydrophilicity and surface elemental composition of the APP-functionalized surface are also reported and the HAp-deposited PLA was examined by a scanning electron microscopy and energy dispersive X-ray analysis.

3:20pm **D1-2-MoA-6 Development of Modified Hydroxyapatite Composite Coating Prepared by the Thermal Spray***, **Jo-Han Yu,*** National Taipei University of Technology, Taipei Tech, Taiwan*; K. Feng,* Ming Chi University of Technology, Taiwan*; Y. Yang,* National Taipei University of Technology, Taipei Tech, Taiwan

This study shows the modified hydroxyapatite composite coating formed under different spray conditions by Flame Spray (FS). Pure crystalline HA has a low dissolution rate, which slows down the bone integration. However, bioactive glasses are a family of special glasses which are able to bond to bones and, if the glass composition is properly designed, even to soft tissues. In this experiment, the hydroxyapatite and bioactive glass will used Flame Spray (FS) to coating on 304 stainless steel surface. This experiment will be divide into two different parts for discussion. In the first part will analysis the microstructure, phase composition, mechanical properties and bonding test of the modified hydroxyapatite composite coating. Based on the results, the acetylene flow rate of 1.60 Nm^3/hr and the speed of spray gun is 250 mm/s, the spray times of Flame Spray (FS)

using 2 times to conducting the experiments;The second part is the biocompatibility test of the modified hydroxyapatite composite coating, cell attachment morphology observation and human simulated body fluid immersion test.

3:40pm **D1-2-MoA-7 New Generation of Thin Films for Protection of Stainless Steel Against Corrosion and Bacterial Contamination***, **Akram ALHUSSEIN**, A. BELGROUNE, E. KAADY,* University of Technology of Troyes, France*; L. AISSANI,* University of Khenchela, Algeria*; R. HABCHI,* Lebanese University, Lebanon*; S. Rtimi,* Federal Polytechnic School of Lausanne, Switzerland

Coatings present a great solution to protect a material and give it multifunctional properties. The objective of our research is the development of new generation of protective and multifunctional coatings. In our studies, the deposition rate is controlled to obtain a uniform film of 1-3 µm thickness. The influence of process parameters on the coating physicochemical properties (morphology, microstructure …) and functional performance (corrosion resistance, biomedical properties…) is evaluated.

In this work, thin films were developed to protect stainless steel widely used in different severe environments in particular for maritime and biomedical applications. We present many strategies used for enhancing the coating efficiency based on the substrate used, the doped elements and coating architecture.

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4:00pm **D1-2-MoA-8 Effects of Silver Acetate Additives on Antimicrobial and Corrosion Behaviors of Plasma Electrolytic Oxidation Coatings on AZ31B Magnesium Alloy***, **Yu-Tse Sung**,* Department of Materials Engineering, Ming Chi University of Technology, Taiwan*; C. Tseng,* Department of Materials Engineering & Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan

In this study, the bioceramic composite coatings on AZ31B magnesium alloy were prepared by using plasma electrolytic oxidation (PEO) in alkaline solutions with sodium phosphate, sodium silicate, potassium fluotitanate and silver acetate additions. The effect of silver acetate content on antimicrobial and corrosion behaviors of PEO coatings on AZ31B magnesium alloy was investigated. The antimicrobial properties of PEO coatings were carried out by measuring the numbers of *Escherichia coli* bacterial colony after various incubation durations. The potentiodynamic polarization measurements were conducted to evaluate the corrosion behaviors of PEO coatings in simulated body fluid (SBF) solutions. The experimental results show that the antimicrobial effect of the PEO coatings is significantly improved with increasing silver acetate additive. More interestingly, the PEO coating with 0.2 g/L silver acetate addition exhibits a 100% antibacterial efficiency to *Escherichia coli* after incubation in 60 minutes. However, the potentiodynamic polarization curves display that the PEO coatings, as compared to AZ31 magnesium alloy, exhibit higher corrosion resistances in SBF solutions. Furthermore, the PEO coating with 0.15 g/L silver acetate addition shows the optimal corrosion resistance due to its lowest corrosion current density (Icorr), highest passivation breakdown potential (E_b) and largest polarization resistance value (Rp). In summary, the antimicrobial and corrosion behaviors of PEO coatings on AZ31B magnesium alloy can be pronouncedly improved by silver acetate additions.

4:20pm **D1-2-MoA-9 Tribocorrosion and Biological Analysis of Surface Coated by Polypyrrole Film and Zinc on Titanium Surfaces Treated by Plasma Electrolytic Oxidation***, **Maria Helena Borges**,* University of Campinas, Brazil, University of Illinois College of Medicine Rockford, USA*; H. Kanniyappan,* University of Illinois College of Medicine Rockford, USA*; V. Barão,* University of Campinas, Brazil*; M. Mathew,* University of Chicago College of Medicine Rockford, USA

Although titanium materials are the primary choice for biomedical implant applications due to their properties, the degradation generated by the tribocorrosion process has been reported to influence the success of implants. To overcome these issues, thin film coatings, inorganic agents, and surface treatments have been widely applied. In this context, conductive polymers, such as Polypyrrole (PPy), have demonstrated a promising application for implants due to their electrochemical properties. In addition, surface treatments such as plasma electrolytic oxidation (PEO) enhance mechanical and biological performance, mainly when associated with PPy film. However, considering implant failures can also be related to deficiencies in the osseointegration process, the electrodeposition of zinc (Zn) on the surface may promote an osteogenic substrate. Therefore, we aim to (1) investigate the tribocorrosion behavior of the surfaces treated by PEO and coated with PPy+Zn; (2) evaluate the osseointegration potential of the surface by the Zn incorporation *in vitro*. For this, commercially pure titanium discs were allocated into 4 groups: (1) machined; (2) PEO-treated; (3) PEO-treated followed by electrodeposition of PPy (PEO+PPy); (4) PEO-treated followed by electrodeposition of PPy and Zn (PEO+PPy/Zn). For tribocorrosion, tests were performed in three different modes: (1) free potential, (2) potentiodynamic, and (3) potentiostatic. A pin-on-disk tribosystem was used, and the number of cycles (2,000), frequency (1 Hz), and temperature (37ºC) parameters were selected to simulate the oral environments. For *in vitro* cell culture assays, the osseointegration potential was evaluated using MG-63 cells, which can classify the cells by their viability (alamarBlue assay), the number of live cells to dead cells (live-dead stain), how well the nucleus remained intact (DAPI), and cell adhesion efficiency (SEM). In addition, the mineralization property of the surface was determined using the Alizarin Red Staining (7 and 14 days), and the osteogenic differentiation potential was determined using the alkaline phosphatase activity for the period of 7 and 14 days. Our findings demonstrate that the PPy and PPy+Zn coating plays an important role in enhancing the tribocorrosion resistance. Furthermore, the PEO+PPy/Zn surface is cytocompatible and promising to improve the osseointegration process of implants.

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