Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D3

Medical Devices, Biosensors, and Biodegradation

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The method effectiveness has been extensively demonstrated using different ultrathin films systems [2-4]. Chemical-vapour-deposition (CVD)-grown graphene films thickness was determined using MP-SPR and after first initial layer thickness was found to be 0.37nm / monolayer on a solid support [3]. Atomic Layer Deposition (ALD) (PICOSUN™ R-150) was used to deposit Platinum (Pt) and nanolaminate (Al_2O_3 and Pt) layers on a glass substrate. Target thickness of the layers were 11 nm for Pt, and altering 5nm each for nanolaminate. Thickness was found to be in good agreement with the target thicknesses. Stearic acid (SA) Langmuir Blodgett films showed approximately 2.5±0.2 nm thickness, and linear increment with increasing layer number [2]. The SPR curves (angular spectra) were analyzed using BioNavis LayerSolver software to determine layer thickness and refractive indexes. Additionally to layer properties MP-SPR measures in real-time interactions on a thin films. Protein and cell samples binding on a Plasma Sprayed hydroxyapatite coating was measured label free [4].

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

References

[1] Albers, Vikholm-Lundin, Chapter4 in Nano-Bio-Sensing, Springer 2010

[2] Granqvist et al., Langmuir,29(27),2013,8561-8571, 2013

[3] Jussila et al. Optica, Vol.3, No.2, 2016

[4] Vilardell et al. J. Funct. Biomater. 7, 23, 2016

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

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

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

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

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

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

Author Index

Bold page numbers indicate presenter