Coatings for Biomedical and Healthcare Applications
Room Sunrise - Session D1

Surface Coatings and Surface Modifications in Biological Environments

Moderators: Kerstin Thorwarth, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland, Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA, Argelia Almaguer-Flores, Universidad Nacional Autonoma de Mexico, Mexico

1:30pm **D1-1 Reactively Sputtered Iridium Oxide Films for Biomedical Electrode Coatings: Microstructural Dependence of the In-Vitro Electrochemical Performance**, *N Page, J Lucchi, J Buchan, T Scabarozi,* Rowan University, USA*; S Amini,* Johnson Matthey Inc., USA*; **Jeffrey Hettinger**,* Rowan University, USA

Iridium oxide films have been synthesized by reactive magnetron sputtering in an oxygen rich environment. The films have been deposited onto various substrate materials at temperatures of 20, 200, and 400°C. The partial pressure of oxygen required to synthesize iridium oxide is approximately 20% at an overall pressure of 10mTorr and is reduced as the substrate temperature is increased.

The synthesized films have been characterized using x-ray diffraction, electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The microstructure of the coatings depends on temperature, oxygen partial pressure and the substrate material. For room temperature depositions, the grains are generally less than 100nm in size. As the temperature is increased, the grain size increases. An interesting surface microstructure is observed at elevated oxygen partial pressures and are most notable in coatings deposited with a substrate temperature of 200°C. Images of cross-sections indicate that the microstructure is a surface microstructure and does not extend to the coating-substrate interface.

The electrochemical measurements were performed in phosphate buffered saline solution between 0.80V and -0.60V. The measured results indicate that the most complex microstructures improve the coating charge storage capacity by an order of magnitude. Similar features to those that grow at 200°C grow at room temperature with elevated oxygen partial pressures. These features lead to more modest increases in charge storage capacity. The additional microstructure increases the coating surface area and is associated with the emergence of the (011) diffraction peak.

1:50pm **D1-2 Nanostructured Surfaces based on Tantalum Oxide for Osseointegrated Metallic Implants***, **CristianaFilipa Almeida Alves**, J Oliveira, S Pires, L Marques,* University of Minho, Portugal*; D Schneider,* Fraunhofer Instituit für Werkstoffphysik und Schichttecnhologie, Germany*; A Cavaleiro,* University of Coimbra, Portugal*; S Carvalho,* University of Minho, Portugal

Tantalum (Ta) and tantalum oxide coatings have been proven as bioactive materials, so there are promising materials for promoting osseointegration and the performance of medical devices such as dental implants. A new approach has been used on this work. We propose the development of antibacterial and osseointegrated bioactive surfaces based on the synergetic effect of nanostructured and oxide surfaces of Ta-based materials.

In this work Ta-based coatings were deposited by DC magnetron sputtering onto Ti CP substrates in an Ar+O_2 atmosphere. Nanostructured anodic tantalum oxide was successfully prepared by electrochemical deposition.

Structural results show that the small increase of O content leads to a change of Ta phase from stable phase (α-Ta: bcc) to mixture with metastable phase (β-Ta: tetragonal) achieving the oxide phases with a large amount of O. Combined structural and mechanical results with DFT calculations shows that the increased addition of oxygen to the Ta phase, a decrease in the density of the crystal structures and increase in the elastic properties is observed, explained by the smaller atomic substitution of Ta and formation of stable TaO_x amorphous phases at grain boundaries.

Also, Ta surface were anodized and results show that the electrolyte, composed by H_2SO_4 and HF, in a 15-25V potential range allow us to control the Ta interconversion from nanopores to nanotubes array. Despite the capacity needed of HF to dissolve and create anodic oxide nanostructures (dissolution assisted by electric field), there is a clear dependence on H_2SO_4 concentration to obtain highly ordered nanostructures.

2:10pm **D1-3 Development of a Biocompatible Titanium Niobium Alloy Coating as a Buffer for Rigid Coatings on Polyetheretherketon***, **Markus König**, K Bergner, H Scheerer, G Andersohn, M Oechsner,* TU Darmstadt, Germany

For the treatment of spinal disk diseases more and more polyetheretherketon (PEEK) implants are used instead of titanium implants. This is due to the excellent cytotoxicity, radiological transparency and low elastic modulus (E_{PEEK} = 3,5 GPa). Nevertheless using PEEK is going along with some disadvantages like the low tendency for a fast and reliable osseointegration. To overcome this drawback a thin osteoconductive coating is needed. Therefore Physical Vapour Deposition (PDV) offers a frequently applied technique to create good adhering coatings on polymers. Most of these coatings are based on ceramics or metals like *hydroxyapatite* or titanium. These materials have a much higher modulus of elasticity (approx. 100 GPa) and a lower elongation. This is the reason why such composites fail through the "eggshell effect".

To overcome this problem a more elastic and biocompatible layer in between is needed. As a casted alloy titanium and niobium (60 wt% Ti - 40 wt% Nb) has an elastic modulus of 60 GPa and excellent biocompatible properties. Till this day it has been unknown if this characteristics could be produced with thin film techniques. It was possible to generate such coatings by physical PVD magnetron sputtering. This was realized by the investigation of target configuration, power and gas settings. The generated coatings were investigated by nanoindentation, micro-scratch tests as well as modified scratch tests to characterise their mechanical abilities. X-ray diffraction, glow discharge optical emission spectroscopy and energy dispersive X-ray spectroscopy were used to characterise the chemical composition and to prove that an alloy is achieved. The realized alloy coating has a composition of 60 wt% titanium and 40 wt% niobium with an elastic modulus of 63 ± 5,7 GPa. Hence, the mechanical strength of biocompatible coatings on PEEK could be enhanced.

2:30pm **D1-4 Development of Novel Long-Lasting S-Phase based Anti-Bacterial Coatings***, D Formosa, **Xiaoying Li**, H Dong,* The University of Birmingham, UK

It is well-known that biologically active Ag/Cu ions are strong bactericides and silver or copper nanoparticles have been used in polymer-based antibacterial coatings. However, their poor durability has limited their use in tribological applications. This problem has been largely addressed recently by developing novel plasma co-alloying of austenitic stainless steel surfaces with both nitrogen and Ag/Cu to form Ag/Cu doped hard and wear resistant S-phase. However, this technology is only applicable to austenitic stainless steel as the S-phase cannot be formed in other materials.

In this study, S-phase based anti-bacterial coatings have been, for the first time, developed using magnetron sputtering through co-deposition of austenitic stainless steel with Ag/Cu to form hard S-phase doped with Ag, Cu or both in monolayer and multilayer structures. These coatings where tested and optimised using multiple techniques such as – transmission electron microscopy, X-Ray diffraction, corrosion and wear testing, scratch and fretting techniques and anti-bacterial tests amongst others.

It has been found that it is possible to produce dense corrosion resistant S-phase microstructure with high adhesion to different substrates. Co-depositing S-phase with Ag and Cu dopants brings about significant anti-bacterial efficacy to the traditionally inactive S-phase surface. This was achieved while preserving the advantageous properties of the S-phase microstructure. As opposed to the popular diffusion based S-phase production such as plasma nitriding, this technology can also be applied on all kinds of surfaces, including low-cost steel surfaces, polymers and ceramics.

2:50pm **D1-5 Single-step, Environmentally-Friendly, Biological Functionalisation through Radicals generated by Plasma Surface Modification of Biomedical Devices***, **Marcela Bilek**, E Kosobrodova, A Kondyurin, B Akhavan, M Santos, E Wakelin, G Yeo, C Tran, D McKenzie, A Weiss,* University of Sydney, Australia*; M Ng, S Wise,* Heart Research Institute, Australia **INVITED**

Plasma Immersion Ion Implantation (PIII) is a process in which a bias voltage is applied to an object immersed in plasma, accelerating ions towards it. These ions are implanted into the surface creating highly reactive radicals in the sub surface region. For polymeric materials, the radicals are mobile within the subsurface so that they may be utilized to covalently immobilize bioactive molecules on the surface upon contact [1]. Where the surface to be functionalized is non-polymeric a carbon containing precursor gas is added so that a plasma polymer is deposited under ion bombardment. Both of these approaches as well as a new variation of these processes that enables the energetic ion implantation of complex interconnected 3D polymeric networks, such as tissue engineering scaffolds.

Short-lived radicals (with lifetimes of less than a day) as well as long-lived radicals with lifetimes of over a year are created [2]. Their diffusion is temperature activated [3] and kinetic theory shows that the depth of the treatment determines the lifetime of the long-lived radicals [1]. Covalent immobilization of functional (including biologically functional) molecules is then achieved by simple immersion or incubation of the surface in a solution containing the functional molecules to be immobilized. This eliminates the need for multiple stage linker chemistry and the associated solvent disposal and variable yield problems. The use of this approach to surface immobilize bioactive peptides, antibodies, enzymes, single stranded DNA and extra-cellular matrix proteins [4] onto the external surfaces of materials, including three-dimensional structures of biomedical devices, such as cardiovascular stents, scaffolds for tissue restoration and implantable prostheses, will be described. The benefits for and recent progress towards commercial applications in implantable biomedical and diagnostic devices will be reviewed.

References:

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[2] Kosobrodova EA, et al, *NIMB* (2012) **280**:26-35

[3] Wakelin EA, et al, *ACS Appl. Mater & Interfaces* (2015) **7**:26340-26345

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Key words: plasma immersion ion implantation (PIII), plasma immersion ion implantation and deposition (PIII&D), biological surface functionalisation, radicals, biomedical diagnostics, implantable biomedical devices, cardiovascular stents, tissue engineering scaffolds.

3:30pm **D1-7 Deposition and Characterisation of Silver Nanocomposite Coatings on Orthopaedic Grade Cobalt Chromium Alloys and the Related Antimicrobial Effects***, **Liuquan Yang**,* Wallwork Cambridge Ltd, UK*; L Richards,* MatOrtho Limited, UK*; A Misha, J Shelton,* Queen Mary University of London, UK*; S Collins,* MatOrtho Limited, UK*; S Banfield, L Espitalier,* Wallwork Cambridge Ltd, UK*; H Hothi, A Hart,* Royal National Orthopaedic Hospital, UK*; J Housden,* Wallwork Cambridge Ltd, UK

Silver containing materials have shown novel antimicrobial properties in various applications historically. Hard wearing PVD silver nanocomposite coatings have the ability to self-lubricate at high temperature and benefit from antimicrobial effect. This study focuses on the deposition of three different contents of silver nanocomposite coatings deposited on cobalt chromium (CoCr) alloy by electron beam physical vapour deposition (EBPVD) and the related characterisations. The coating structures are studied in terms of scratch test, nano-indentation, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), X-ray photoelectron spectroscopy (XPS) and optical surface profilometry (OSP). The specific surface area, surface roughness and morphology of the silver particles are analysed and the coatings tested in vitro for antimicrobial effectiveness and wear characteristics against ultra-high molecular weight polyethylene (UHMWPE). The results have shown the silver nanocomposite hard wearing coatings are promising candidates in orthopaedic applications and may lower the risk of infection. Further investigations will optimise the silver coatings and will be subject to simulator tests and clinical trials.

3:50pm **D1-8 Oral Bacteria Adhesion on Saliva Coated and Uncoated Stainless Steel Surfaces: Experimental Characterisation and Modelling***, **Jinju Chen**, S Chinnaraj, Y Ammar, J Pahala Gedara, N Jakubovics,* Newcastle University, UK

Biofilms refer to bacteria growing within a matrix of extracellular polymeric substances attached to surfaces, which have significant impact to a wide range of industries and environment. The initial bacteria attachment is important for biofilm formation, which can be affected by various materials surface characteristics such as surface roughness, surface hydrophobicity, and surface chemistry. The total interaction energy required for bacteria to adhere to surfaces can be determined by extended DLVO theory (XDLVO) which considers Lifshitz van der Waals interactions, electrostatic interactions and acid-base interactions. The extended DLVO model can further be improved by considering the surface roughness of the materials. However, there is lack of experimental work and modelling of bacteria adhesion on patterned surfaces which are relevant to many medical implants.

In this study, streptococcus gordonii DL-1, a typical cocci shaped bacteria found in oral cavity, was cultured on the patterned stainless steel. The surface coverage of attached cells was calculated using MATLAB code. An in-house C++ code was developed to compute the bacteria deposition by implementing the surface roughness enhanced XDLVO. The simulated results qualitatively agree with the experimental measurement and both have shown that patterned surfaces would promote bacteria adhesion. In addition, it has demonstrated that the saliva coating does not have much effect on the initial attachment of streptococcus gordonii.

4:10pm **D1-9 Towards Antibacterial yet Biocompatible and Bioactive Surfaces***, **Dmitry Shtansky**, I Sukhorukova, A Sheveyko, E Levashov,* National University of Science and Technology "MISiS", Russian Federation

The fabrication of antibacterial yet biocompatible and bioactive surfaces is a challenge that biological and biomedical community has faced for many years, while no "dream material" has been developed so far. Various strategies for development of bioactive and bactericidal films with various antibacterial components (Ag, B, antibiotic, bacteriophages) providing long-lasting antibacterial effect are considered [1-4]. The substrates with different topography were produced via selective laser sintering, pulsed electro-erosion treatment, chemical etching, sandblasting, and laser treatment. Multicomponent biocompatable nanostructured films with different content of antibacterial components were deposited on substrates with different topography and roughness using PVD methods (magnetron and ion sputtering, ion implantation). Different functional treatments to provide antibacterial functionality including saturation with antibiotics or bacteriophages were fulfilled. In addition, thick (up to 30 µm) multicomponent biocompatible yet antibacterial coatings with high surface roughness (R_a > 6 µm) were obtained by pulsed electrospark deposition [5,6]. The obtained results show that under optimal surface chemistry and topography conditions the material can be biocompatible, bioactive and bactericidal.

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4:30pm **D1-10 Characteristics of Plasma Polymerization Films using HMDSO Precursor on 316L Stainless Steel***, **Si-Bu Wang**, J Lee, Y Lee,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan

This study focused on the characterization of the organic film deposited on 316L stainless steel substrate using a plasma polymerization process with hexamethyldisiloxane (HMDSO) precursor. The organic films were fabricated under different HMDSO-O_2 gas ratios and the heating temperature of the monomer. The plasma characteristics during the plasma polymerization process were studied by an optical emission spectrometer. The structure and bonding of the deposited films were analyzed by a Fourier Transform Infrared Spectroscopy (FTIR). The scratch test was employed to evaluate the adhesion properties of coatings. Preliminary biocompatibility studies were carried out using MG-63 cell line (human osteosarcoma) to investigate cell-material interaction. The results of cell viability and toxicity are presented.

It can be found that the plasma polymerization grown films were free of pinholes and showed an excellent adhesion quality to the substrate. Good biocompatibility was also observed for the organic coating. Effects of HMDSO-O_2 gas ratio and the heating temperature of the monomer on the plasma status, structure, film thickness, mechanical property and biocompatibility of the films deposited on 316L stainless steel substrate were further discussed in this work.

4:50pm **D1-11 Structure and Biocompatibility of Fluorine-containing TaCN Thin Films***, **JangHsing Hsieh**, H Lin,* Ming Chi University of Technology, Taiwan*; S Liu,* National Taipei University of Technology, Taiwan

TaN thin film coatings are known to have good mechanical properties, impact toughness, as well as good biocompactibility. However, the friction coefficient of these films is sometimes too high, or the hemocompatibility is poor. The purpose of this study is to reduce the friction coefficient and lower the surface energy of TaN coating by introducing CFx into/onto the nitride coatings. CFx–doped TaN films, with and without CFx top layer, were deposited on silicon and tool steel substrates by magnetron sputtering. During the deposition process, C_2F_6 gas with various flow rates was added. During the deposition of 30 nm CF_x top layer on some samples, the power to Ta target was shut off. After deposition, these films were then characterized using XRD, XPS, FTIR, FESEM, as well as a tribometer. The tribo-tests were carried out with and without argon flow. Surface energies of the films were also analyzed with contact angle measurement system. According to structural analysis, TaN phase would transform to Ta(FCN) with the increase of the fluoride gas flow rate, which would cause the decrease of friction coefficient and surface energy. According to the results obtained from tribotesting, it is found the increase of CF_x would reduce the effects of moisture and oxygen on friction coefficient. The prepared films may have good hemocompatibility and wear-resistance.

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