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

Surface Coating and Modification for Use in Biological Environments II

Moderator: Mathew T. Mathew, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

1:40pm **D1-2-MoA-1 Recent Development of Biocompatible Thin Film Metallic Glass Materials***, **Jyh-Wei Lee**,* Ming Chi University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan*; Y Yang,* National Taipei University of Technology, Taiwan*; C Lin,* National Taiwan University, Taiwan **INVITED**

The thin film metallic glass (TFMG) materials have been intensively studied due to their promising physical and mechanical properties, such as high strength, flexibility, and excellent corrosion resistance. Recently, the biomedical applications of TFMGs also attracted lots of attentions from researchers. Improved sharpness and non-stick effects of the dermatome and syringe needles have been reported, respectively, by the coating of thin film metallic glass. In this work, several Zr-, Ti- and Fe-based TFMGs were fabricated using magnetron sputtering method. The corrosion resistance and in-vitro biocompatibility tests of TFMGs were studied. The antimicrobial test of some Cu or Ag containing TFMGs was also evaluated. The in-vivo animal test on Zr-Ti-Si and Fe-Zr-Nb TFMGs was further investigated. In addition, fracture resistance evluation of dental Ni-Ti rotary instruments with TFMG coating was conducted. It is found that excellent anti-corrosion properties were observed for these TFMGs. Remarkable antimicrobial performance was obtained for the Cu or Ag containing TFMGs. In-vitro test showed that the TFMGs had good proliferation and differentiation of cultured cell. The in-vivo animal test also indicated that no allergy, toxicity or carcinogenic reaction was caused by the TFMGs to the rats. The Ti-based TFMG coating can effectively improve the fatigue fracture resistance of dental Ni-Ti rotary files. We can conclude that the biocompatible Zr-, Ti- and Fe-based TFMGs show very promising application on the dental and orthodontic surgical tools.

2:40pm **D1-2-MoA-4 Antibacterial and Biocompatible Properties of Ga-doped TaON Thin Films***, **Jang-Hsing Hsieh**, Q Liu,* Ming Chi University of Technology, Taiwan*; C Li,* National Yang Ming University, Taiwan

Recently, gallium ions have been studied for its multi-functional bio-activity. While gallium has no known function in human physiology, the chemical properties that it shares with iron allow it to bind to iron-containing proteins (Trojan Horse effect), including the iron transport protein transferrin. Thus, malignant cells and microorganisms may be tricked into incorporating gallium in place of iron for iron-dependent processes essential for bacterial viability and growth. Hence, rather than facilitate iron-dependent cellular function, gallium disrupts it. As a result, the interaction between gallium and iron-proteins can be exploited for therapeutic purposes in cancers and bactericidal treatments. Accordingly, it is of great interest to know how Ga can be doped into surface coatings.

In this study, the deposition processes of tunable TaOxNy-Ga thin film coatings were studied systematically. Following this, the resultant mechanical, structural, and, bio-related properties were examined, in terms of O/N ratio, surface roughness and Ga contents. However, due to low melting point of Ga (~29 ^{o}C), it is relatively difficult to sputter Ga into those oxynitride coatings. Therefore, Ga_2O_3 target was used in this study to provide oxygen and Ga. According to the results, it was learned that small amount of oxygen (2~5%) and gallium (1~3%) in the coatings could be beneficial to the improvement of mechanical and antibacterial properties. The enhanced dissolution of Ga ions was observed with the addition of oxygen. The highest hardness could reach 30 GPa, while an antibacterial efficiency of >90% could be found after 48 hrs of immersion. The films showed good biocompatibility with MG63 cells.

3:00pm **D1-2-MoA-5 TiO_2 Nanotubes Produced in Aqueous Electrolytes with CMC for Biomaterials Application***, **Robinson Aguirre Ocampo**, M Echeverry-Rendón, S Robledo, F Echeverría,* Universidad de Antioquia, Colombia

Nanotubular structures were produced on the c.p. Titanium surface by anodization in an aqueous electrolyte that contains carboxymethylcellulose (CMC) and NaF. The internal diameter obtained at voltages of 20, 10 and 2 V was about 100, 48 and 9.5 nm, respectively. Those diameters were measured using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Scientific reports about nanotube produced by anodization with internal diameters upper than 30 nm are very common, however, reports about lower nanotube diameters (<20 nm) are scarce. Several heat treatments at 200, 350 and 600 °C were made to produce nanotubes with different TiO_2 polymorphs (Anatase, Rutile), at 200 °C no phase change was observed, at 350 °C the nanotubes change from amorphous phase to Anatase, and at 600 °C the rutile phase was predominant. These phases were corroborated by XRD and Micro-Raman microscopy. All the tested surfaces were superhydrophilic (high surface free energy), and the superhydrophilic behavior is maintained after at least 25 days, regardless of the heat treatment. The aim of produce nanotubes with different diameters and various heat treatments was to correlate the nanotube characteristics (morphology, internal diameter, composition) and the biologic behavior (cell adhesion and proliferation and antibacterial properties). The heat treated samples showed higher antibacterial properties in contrast to the as anodized samples. All nanotube coatings of TiO_2 were non-cytotoxic, nevertheless the anodization parameter or electrolyte composition used. However, some differences in terms of cell adhesion were found. Based on those results, these coatings can be applied as drug carriers, surface modification of biomaterial devices and catalyst, among others.

3:20pm **D1-2-MoA-6 Electrochemical Evaluation of Titanium Oxide Coatings Deposited on Magnesium Alloys***, B Millan-Ramos,* Universidad Nacional Autonoma de Mexico, México*; J Victoria-Hernandez, S Yi,* Magnesium Innovation Centre, Helmholtz-Zentrum, Germany*; D Letzig,* Magnesium Innovation Centre, Helmholtz-Zentrum, Germany, Germany*; **Phaedra Silva-Bermudez**,* Instituto Nacional de Rehabilitación, Mexico*; S Rodil,* Universidad Nacional Autonoma de Mexico, México

Titanium oxide (TiO_2) has been recognized as the active layer responsible for the good biocompatibility and osteogenic properties of the Ti-based medical alloys used for dental and orthopedic applications. Meanwhile, magnesium (Mg) and its alloys are currently widely researched for orthopedic applications, since their mechanical properties are more adequate to balance load transfer between bone and implant, but also due to its biodegradability. Extensive mechanical, in-vitro and in-vivo studies have been done to improve the biomedical performance of Mg alloys through alloying, processing conditions and surface modifications, including coating deposition. The main purpose of such modifications is to extent the degradation rate of the alloy in order to match it with bone self-healing time. In this work, we are investigating the use of titanium oxide coatings deposited by reactive magnetron sputtering on high purity Mg alloys.

Here, we present the electrochemical response of TiO_2-coated Mg-alloys in simulated physiological fluids. The results indicate that independently of the TiO_2 film thickness (60 - 250 nm) and the use of a Ti-buffer layer, the corrosion rate of the Mg alloy is not significantly reduced. Such response is probably associated to specific chemical reactions occurring between Mg and Ti that were not expected.

4:00pm **D1-2-MoA-8 Metallization of Polymers for Medical Applications***, **Aarati Chacko**, H Hug,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; S Gauter,* Christian-Albrechts-University Kiel, Germany*; K Thorwarth,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Metallization of polymers has been of interest for years, as a means to achieve barrier coatings in packaging, biocompatible interfaces for medical implants, or to produce light-weight alternatives to metal parts in the automotive and aerospace industries, to cite a few examples. As the performance requirements of metalized plastics increase, so too must our understanding of plasma-polymer and metal-polymer interactions that occur in coating processes. High Power Impulse Magnetron Sputtering (HiPIMS) is a physical vapor coating method that allows one to span a whole range of energetic regimes; close to direct current sputtering, with low metallic ion discharge, up to almost fully ionized discharges. This versatile technique is our method of choice to study and tailor the substrate-film interphase region responsible for 'good' and long-lived coating adhesion.

In our study we vary the pulse-on/off time, thus controlling the time allowed for surface processes to occur between metal-species fluxes. We evaluate the chemical state of our interface using XPS and gauge the practical adhesion of the resulting films using a modified ASTM D4541 pull-off test. In addition, we study the effect of sample pre-treatment on adhesion, also using the above methods. The test metal-polymer system for this study is titanium on PEEK, which has shown exemplary adhesion in the case of orthopedic implants for use in spinal fusion surgery.

4:20pm **D1-2-MoA-9 Characteristics of a Composite Ceramic Coating Fabricated on Mg-1.2Zn-0.5Ca-0.5Mn Alloy Towards Biodegradable Bone Implants*, Hamdy Ibrahim,*** University of Tennessee at Chattanooga, USA*; D Dean,* Ohio State University, USA*; M Elahinia,* University of Toledo, USA

INTRODUCTION: Mg and its alloys possess a biodegradable nature that has recently made them attractive for developing biomedical devices that are expected to degrade and bioresorb completely *in-vivo* after the healing of the body tissue. In addition to their biodegradable nature, Mg alloys are biocompatible, and they have low density and modulus of elasticity, close to the bone. We have developed a patent-pending alloy, Mg-1.2Zn-0.5Ca-0.5Mn produced using biocompatible alloying elements, and a heat treatment process that is likely to provide the needed mechanical stability during bone healing and reliably resorb following the healing of a reconstructed skeletal segment. Our goal is to investigate the use of a composite ceramic-based coating to delay device corrosion (weakening) for 4-6 months.

METHODS: We heat-treated Mg-1.2Zn-0.5Ca-0.5Mn alloy samples to achieve significant mechanical strength and then coated them using plasma electrolyte oxidation (PEO) and layer-by-layer coating techniques to achieve corrosion resistance. The coated samples were characterized for their morphological and chemical properties using SEM, EDS and XRD methods. Finally, the corrosion characteristics before and after coating were determined using Potentiodynamic polarization test conducted in a simulated body fluid (SBF).

RESULTS: PEO-coated samples show pitting and pores, a common observation following PEO coating, and a tight junction with the subsequent layer-by-layer coatings. The composite coated samples showed a major enhancement in the corrosion resistance compared to the only PEO-coated and uncoated samples. The XRD patterns showed the presence of the incorporated compounds on the coating surface in addition to the presence of biocompatible corrosion products on the surface after corrosion such as hydroxyapatite (HA) and magnesium hydroxide ($Mg(OH)_2$). The use of heat treatment followed by composite ceramic coating may be beneficial for the fabrication of Mg-1.2Zn-0.5Ca-0.5Mn skeletal fixation devices with predictable resorption rates.

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