Coatings for Biomedical and Healthcare Applications
Room Pacific Salon 3 - Session D2-TuA

Bio-corrosion and Bio-tribology

Moderators: Jessica Jennings, University of Memphis, USA, **Steve Bull**, Newcastle University

1:40pm **D2-TuA-1 Bio-Tribocorrosive Behavior of the Contact M30NW Stainless Steel against HDPE Reinforced with MoS_2 Particles. New Polymer Implant: Promising Material?**, *A Salem, M Guezmil, W Bensalah, S Mezlini,* Université de Monastir, Tunisia*; **Jean Géringer**,* Mines Saint-Etienne, France

Some new polymer composites are under investigation in order to enhance the biocompatible usage of new biomaterials. This paper deals with the tribological behavior of High Density PolyEthylene/molybdenum disulphide (MoS_2-HDPE) composites against M30NW stainless steel. As received HDPE pellets were milled and blended with MoS_2 particles using a ball milling machine. The reinforced HDPE specimens with different contents of MoS_2 were elaborated using a compression molding machine. Tribological characterization including wear rate and friction coefficient was investigated using a linear reciprocating pin-on-disc tribometer under dry conditions. Tribocorrosion tests were carried out in the presence of bovine serum solution. It is highlighted that the use of MoS_2 enhances the tribological performances of HDPE composites compared to the unfilled polymer under dry and lubricated conditions. In both cases, an optimal content of MoS_2 was around 4 wt.%. Morphological and chemical investigations using SEM and EDS analyses were carried out on the composite discs after wear tests. Thus the wear scenario was discussed in relation to the MoS_2 content.

2:00pm **D2-TuA-2 Evaluation of the Adhesion of Electrosprayed and Solution-Cast Chitosan Coatings on Titanium Surfaces**, *V Suresh, E Chng, J Bumgardner, **Ranganathan Gopalakrishnan**,* University of Memphis, USA **INVITED**

Biomedical implant devices for dental/craniofacial and orthopedic applications are a reliable and effective means for repairing/re-storing function of damaged, diseased or missing tissues. Despite the success of these devices, there are still challenges in their use with respect to improving their integration into boney tissues, promoting healing and resisting/preventing infection. Electrospray coating technologies provide an additive manufacturing route to endow implant surfaces with new properties to improve their performance by controlled deposition of desired materials, compounds and/or agents in the form of nano- or micro-particles on the surface of implant devices under relatively mild conditions. This ensures that the biomaterials do not get denatured under high temperature or harsh chemical environments commonly employed in many coating methods. They also provide a means to control the structure of coatings with high precision that allows the functionalization of complex 3D geometries of the implants with a range of physical and bioactive properties. Devices such as dental implants, total joint replacement devices, bone plates and screws that cannot be easily coated by other manufacturing methodologies such as solution casting, sputter coatings, or electrochemical treatments can be robustly handled by the electrospray technique. This project focuses on assessing the adhesion of electrosprayed chitosan coatings on model titanium surfaces and screws to explore their potential as an implant treatment technology. Currently, the most widely used technique for implant coating with biomaterials is solution casting. This method limits the coverage of chitosan on complex surfaces of implants, and provides little control on the thickness of the coating and leads to excessive wastage. This research also evaluates the effectiveness of the electrospray as a delivery method of aerosolized chitosan to coat complex implants with precise thickness control, multilayer coatings for controlled drug delivery and to reduce wastage. Adhesion strength values are reported and compared between electrosprayed and solution cast chitosan coatings.

2:40pm **D2-TuA-4 Study of the Mechanical and Tribological Properties of the TaN with Ti Inclusion Multilayer Films on Si Substrate**, ***Ernesto García,*** Cátedras-CONACyT, Universidad de Guadalajara, México*; J Berumen,* ITESO, Universidad Jesuita de Guadalajara, Tlaquepaque, Jalisco, México*; M Flores-Martinez,* Universidad de Guadalajara, México*; E Camps,* Instituto Nacional de Investigaciones Nucleares, México*; S Muhl,* Instituto de Investigaciones en Materiales-UNAM, México

The hip prosthesis surfaces are exposed to high mechanical, chemical and tribological stress conditions. For that binary and ternary transition metallic nitride films have been studied in order to improve the wear and corrosion resistance of the metallic surfaces of the prosthesis. This work shows the first studies of the TaN with Ti inclusion multilayers films. These were produced using DC magnetron cosputtering with a Ta and Ti targets in an N_2/Ar atmosphere in a multilayer arrangement with similar thickness, incremental layer and decremented layer thickness on a silicon substrate. The films were structural, chemical and topologically characterized, using X-Ray diffraction (in theta-2 theta and in-plane configuration), Raman spectroscopy and Electronic microscopy, respectively. The mechanical properties were studied using nanoindentation (at 10 mN) and scratch test (from 0 to 8N) with a Rockwell C indenter. The tribological characterization was carried out with a linear reciprocating with a Rockwell C indenter, with at 0.5, 1 and 2 N of load and 5 cycles of 5 mm of length. The wear track produced for the scratch and the tribological test were studied with optical and electronic microscopy. The layers had a combined structure of a cubic of TaN and hexagonal and cubic of Ta. The coating presented a lower Hardness than the reported for the TaN films. The coating with the incremental arrangement presented a better tribological performance but with lower hardness.

3:00pm **D2-TuA-5 Enhancement of Tribocorrosion Properties of Ti6Al4V by Formation of a Carbide-Derived Carbon (CDC) Surface Layer**, ***Kai-yuan Cheng,*** University of Illinois at Chicago, USA*; R Nagaraj, D Bijukumar, M Mathew,* University of Illinois College of Medicine, USA*; M McNallan,* University of Illinois at Chicago, USA

Metal implant materials not only face corrosion or friction individually but the synergism of tribology and corrosion, which has been called "tribocorrosion". Especially, on the bearing of hip implant in the synovial fluid, the usual CoCrMo alloy endures severe tribocrrosion reaction, sometimes resulting in the formation of wear and corrosion products which cause the adverse local tissue reaction. In 2011, a graphitic tribolayer was discovered on retrieved hip implants at Rush Medical Center, which suggested that the tribolayer might offer lubrication and corrosion protection. Therefore, a coating of graphitic material might be beneficial to the performance of orthopedic implants.

Carbide-derived carbon (CDC) is a primarily graphitic material formed on silicon carbide, which improved tribological performance in non-biomedical applications. If CDC can be applied on the metal substrate, its high lubrication and chemical inertness should provide the same improvement as the graphitic tribolayer found on the retrieved hip implant. To produce a CDC layer on a metal, the metal is first carburized to form a surface layer of metal carbide, and subsequently the carbide is decomposed to form CDC. In this study, Ti6Al4V alloy was chosen as our substrate due to its high affinity to form carbides on its surface and its poor tribocorrosion property, by which CDC's protection can be demonstrated. As long as CDC can properly protect Ti6Al4V alloy, it is possible to reproduce the same effect on other metal surfaces.

In this presentation, recent tribocorrosion results obtained in the hip simulator at Rockford Medical Center, CDC treated metal shows a smaller voltage drop during(ΔE_{CDC}= -0.2±0.047(V) < $\Delta E_{Ti6Al4V}$= -0.89± 0.13(V)) testing in an open-circuit potential condition, a smaller induced current(ΔI_{CDC}= -4.8E-6±4.4E-6 (A) < $\Delta I_{Ti6Al4V}$= -3.94E-4±8.02E-5 (A)) when tested under potentiostatic conditions, a smaller wear loss(ΔV_{CDC}= -0.001±5.85E-4(mm^3) < $\Delta V_{Ti6Al4V}$= -0.43±0.025(mm^3)) and smaller values of friction coefficient(μ_{CDC}= 0.0045±0.0025 < $\mu_{Ti6Al4V}$= 0.47±0.135). The biocompatibility tests have shown CDC is as biocompatible as the Ti6Al4V substrate. In general, the CDC protected Ti6Al4V performs better in tribocorrosion without sacrificing biocompatibility.

4:00pm **D2-TuA-8 Considerations when using Additive Manufacturing to make Medical Devices**, ***Alejandro Espinoza Orías,*** Rush University Medical Center, USA **INVITED**

Additive Manufacturing has demonstrated to be and gone beyond being a disruptive technology as many industries have adopted it to mass-produce parts on demand. In the medical arena, however, there are some concepts that part manufacturers need to be familiar with before going to mass production. A big part of the orthopedic market is that of hip and knee implants that have seen steady growth in the last decade. Corrosion is a natural process and changes the properties of metallic structures. In the case of orthopedic implants, such as total hip replacements, titanium alloys are the most frequently used metal due to their elevated resistance to corrosion, compared to other alloys suitable for implantation in the body. Some of these considerations are as diverse as the patient population meant to benefit from AM: patient privacy, metallurgy, mechanical properties and cleanliness. The aspects of bio-corrosion and bio-tribology have received little attention when new additively manufactured implants hit the market. A big reason for this is the 510(k) process that allows manufacturers to 'grandfather-in' the designs. However, we know little about the differences in metallurgy that are related to the additive manufacturing process that has key contrasts to that of traditional subtractive manufacturing. The most relevant aspect of utility from the additive manufacturing point of view is the direct ability to print highly rough and porous surfaces that are meant for bone ingrowth. While this manufacturing method is capable of producing high-resolution surface finishes with or without built-in designed porosity, not much is known about the surface interaction properties of said finished surfaces. The need for better and more accurate methods to describe bio corrosion and bio tribological aspects of additively manufactured implants makes this type of characterization crucial since the durability of the implant is in play. Current traditionally manufactured designs, last about 15 years not without their own survivability issues. It remains to be seen if the materials and the processes involved in additive manufactured can match the same type of performance benchmarks of the standard manufactured implants.

4:40pm **D2-TuA-10 Nanostructured Surfaces for (Bio)sensors***, **Vitezslav Stranak**,* University of South Bohemia, Czech Republic*; R Bogdanowicz,* Gdansk University of Technology, Poland*; P Sezemsky, V Prysiazhnyi, J Kratochvil,* University of South Bohemia, Czech Republic*; M Smietana,* Warsaw University of Technology, Poland*; O Kylian,* Charles University, Czech Republic*; Z Hubicka, M Cada,* Institute of Physics CAS, v. v. i., Czech Republic

The contribution reports our study of nanostructured surfaces preferentially used for bio-sensing applications. Nanostructured surfaces were prepared by low-temperature plasma assisted deposition employing magnetron sputtering of bulk target. The advantages of nanostructures for sensor applications have been demonstrated several times. Here we focus on two approaches: (i) the first one utilizes homogeneous transparent conductive oxide (TCO) films for Lossy Mode Resonance (LMR) sensors while (ii) the second employs Ag nanoparticles for detection and signal calibration of matrix assisted laser desorption/ionization mass spectrometry.

Bio-sensors working on LMR principle represent rather new concept which appeared a few years ago. The LMR sensors, equipped by precisely tailored TCO film (in our case indium doped tin oxide - ITO) are based on the optical fibre and allow optical as well as electrochemical sensing. The optical sensitivity is achieved by spectral shift of transmission spectra of the light passing through the optical fibre, while the electrochemical effects can occur on the sensor surface. Our main aim represents tailoring of the ITO film deposition to achieve relevant optical and electrochemical properties of ITO with adequate LMR and electrochemical response [1]. The detection of substances as, e.g. ketoprofen [2], will be reported, too.

The second part will be devoted to nanostructures for independent mass-to-charge calibration of laser desorption/ionization mass spectrometry (LDI MS). Properly tailored Ag nanostructured surface - formed as homogeneous thin film, isolated nanoislands, and spherical nanoparticles - can effectively substitute protonation agent for low-mass molecules instead of conventionally used matrices. Beside the surface characterization, the impact of LDI MS laser, irradiating the nanostructured surfaces responsible for Ag cluster production, will be discussed [3]. It is the nanoparticle size and the surface coverage that play a key role and have to be optimized.

[1] V. Stranak, R. Bogdanowicz, P. Sezemsky, H. Wulff, A. Kruth et al, Surf. Coat. Technol. 335, (2018), 126.

[2] R. Bogdanowicz, P. Niedziałkowski, M. Sobaszek, D. Burnat, W. Białobrzeska et al, Sensors 18, (2018), 1361.

[3] V. Prysiazhnyi, F. Dycka, J. Kratochvil, V. Stranak, P. Ksirova et al. J. Vac. Sci. Technol. B 37, (2019), 012906.

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Author Index

Bold page numbers indicate presenter