Coatings for Biomedical and Healthcare Applications
Room Pacific F-G - Session D2-TuM

Medical Devices: Bio-Tribo-Corrosion, Diagnostics, 3D Printing

Moderators: Dr. Hamdy Ibrahim, University of Tennessee at Chattanooga, USA, **Margaret Stack**, University of Strathclyde, UK

8:00am **D2-TuM-1 Empowering PVD-Coatings to Control the Time Dependent Chemical and Microstructural Coating Properties in Aqueous Electrolytes***, **Holger Hoche,*** Center for Structural Materials, TU-Darmstadt, Germany*; T. Ulrich,* Center for Structural Materials, TU Darmstadt, Germany*; P. Polcik,* Plansee Composite Materials, Germany*; M. Oechsner,* Center for Structural Materials, TU-Darmstadt, Germany **INVITED**

Intelligent PVD coatings, which can change their chemical composition and their surface structure in aqueous electrolytes have a great potential for various medical applications. Therefore the coating material must be able to maintain the corrosion reistance and simultanously release specific chemical species.

To achieve this, the authors developed a novel alloying concept for PVD coatings, where TiN-based coatings were alloyed with Mg and MgGd, respectively. Thereby, the corrosion protection capability of corrosive substrate materials, e.g. magnesium or mild steel, can be improved significantly [1]. Depending on the chemical composition of the coating, an adjustment of the corrosion resistance in NaCl electrolytes between 24h and 1000h is possible. Moreover, the developed alloying concept enables to get control of the time dependent chemical and structural properties in aqueous electrolytes: The chemical stability of the coating is determined the proportion of Mg and Gd in the entire TiN matrix: Under a corrosive load, the coating depletes of Mg and consequently, the chemical composition and the surface microstructure changes.

For the present study, TiN+Mg and TiN+MgGd coatings, respectively, are deposited using standard PVD magnetron sputtering technology. Therefore, TiMg and TiMgGd targets were produced using spark plasma sintering. The effect of the mentioned alloying concept on the time dependent chemical and structural changes during exposure of the specimens in NaCl electrolytes is comprehensively investigated. The underlying mechanisms and the resulting properties will be discussed.

[1] T. Ulrich, C. Pusch, H. Hoche, P. Polcik, M. Oechsner, Surface and Coatings Technology 422 (2021) 127496.

8:40am **D2-TuM-3 Early Detection of Fretting-Corrosion at the Hip Modular Junction Interface by Acoustic Emission Non-Invasive Technique***, **Bill Keaty,** Y. Sun,* University of Illinois at Chicago, USA*; M. Mathew,* University of Illinois - Chicago, USA*; D. Ozevin, J. Eapen, T. Zhang,* University of Illinois at Chicago, USA

Total hip replacement (THR) is becoming an increasingly common surgical procedure globally, as it is an end-stage treatment for patients suffering from osteoarthritis or trauma[1]. Early failure is a common occurrence in THRs due to tribocorrosion processes. As a result, a diagnostic method is necessary to catch early failure of THR before irreversible damage occurs. It was reported that the possible feasibility of acoustic emission (AE) technique can detect material degradation at the THR head-cup interfaces[2]. However, no investigation has been done at the modular junction interface, where fretting-corrosion occurs. It was hypothesized that the acoustic emission data could be correlated to the varying level of THR damage at the modular junctions.

A series of fretting-corrosion experiments were conducted with a custom-made fretting rig capable of collecting simultaneous mechanical, electrochemical, and AE data. ZrO2-Ti6Al4V couples were chosen to represent THR femoral head-neck interfaces for the fretting test. To investigate the efficacy of acoustic emission of detecting fretting-corrosion damages, the samples were subject to three different potentials to simulate (i) new implant: no corrosion at Ecathodic (ii) well function implant: normal corrosion at Eoc (iii) and damaged implant: accelerated corrosion at Eanodic. Bovine calf serum was selected as the electrolyte to simulate the synovial fluids. The standard electrochemical protocol was followed in the fretting under potentiostatic conditions.

The results showed that anodic potential conditions had the most significant increase in current during fretting of ±0.03 mA compared to Eoc conditions with a current increase of ±0.005 mA. This data agrees with the expected trend that the samples exposed to accelerated Eanodic corrosion will have a significant current increase while fretting. Mechanical data was obtained, expressed in the form of force vs. displacement as a friction loop, with an energy ratio of <0.2 for the entire testing (3600 cycles), indicating the partial slip fretting region[3]. The trend in-situ AE data displayed a pulse-like acoustic emission fluctuation, indicating a strong correlation between the fretting-corrosion processes and acoustic emission results. This is an ongoing investigation; the study will focus on linking the AE data and THR fretting-corrosion damages associated with the mechanistic transitions. This could be extremely helpful in the early prediction of THR failure in orthopedic implant patients and clinical practices.

[1]J. Geringer et al., *Metals and Surface Engineering*, 2011 [2]C. Lee et al., *J of the Mech Beh of Bio Mat*, 2019 [3]Fouvry et al, *Wear*, 1997

9:00am **D2-TuM-4 Corrosion Evaluation of Plasma Electrolytic Oxidation Coatings on Titanium Alloys For Biomedical Implant Application***, E. Sondgeroth, K. Cheng, Y. Sun,* UIC School of Medicine at Rockford, USA*; C. Takoudies,* UIC School of Medicine, USA*; E. Vries,* Faculty of Engineering Technology , University of Twente, The Netherlands, USA*; D. Matthews, N. Bolink,* Faculty of Engineering Technology , University of Twente, The Netherlands*; A. Yerokhin,* Department of Materials, University of Manchester, United Kingdom*; **Mathew Mathew,*** UIC school of medicine at Rockford, USA

Titanium is a widely used biomaterial in biomedical implants partly due to its good corrosion resistance which is chiefly attributed to the nano-scale passive layer on its surface(1). While the rates of corrosion for titanium implants currently seem to be low, the incorporation of mechanical wear in a corrosion environment such as the fretting-corrosion seen in a human femoroacetabular joint can result in devastating damage to titanium implants(2). Thus, coating technology may enhance the resistance to tribocorrosion damage. The objective of this study was to test the efficacy of Plasma Electrolytic Oxidation (PEO) coatings on titanium implants compared to bare titanium.

PEO was conducted under different conditions to produce six sample coating groups of varying electrolyte concentrations and thicknesses: $NaAlO_2$ + Na_3PO_4, $NaAlO_2$ + Na_3PO_4 (18 um thickness), $NaAlO_2$ + Na_3PO_4 + Al_2O_3, $NaAlO_2$ + Na_3PO_4 + PTFE NP_5, $NaAlO_2$ + Na_3PO_4 + PTFE NP_5 (thick), and $NaAlO_2$ + Na_3PO_4 + Al. The samples were washed for 10 mins each in isopropanol and DI water. Corrosion testing was conducted in Bovine calf serum 30 g/L (pH 7.4) to simulate synovial fluid and CP and EIS were collected. CP data was graphed as Potential versus Current Density and interpolated to find I_{corr} and E_{corr} for each test group. EIS data was plotted as Nyquist and Bode plots and fitted via a Rapid Electrochemical Assessment of Paint electrical circuit model to estimate each sample's corrosion resistance and coating capacitance.

The I_{corr} was 1.002 ±0.55μA/cm^2, 2.38±0.005 μA/cm^2, 0.88 ±0.48 μA/cm^2, 0.91±0.1 μA/cm^2, 0.41 ±0.31 μA/cm^2, and 0.069±0.0007 μA/cm^2 and E_{corr} was -0.39±0.17 V, -0.40±0.03 V, -0.36±0.15 V, -0.4±0.08 V, -0.47±0.03 V, -0.51±0.04 V, -0.53±0.02 V for each group, respectively. The data shows mild partial improvement in corrosion, especially corrosion potential, in the coated samples as compared to bare Ti. Overall, the results indicate that the coating assists in improving corrosion resistance. EIS data analysis also partially agrees with the improved corrosion resistance. It is worth noting that, the chemistry of the surface and structure of the coating will be influencing the parameters of the corrosion resistance. Particularly in the current study, the coatings displayed a severe porous nature, which may adversely affect the corrosion and wear properties. The hypothesis is partially validated, as the coating enhanced the corrosion resistance of the implant surface. The studies will continue to evaluate the surface properties and underlying mechanisms.

9:20am **D2-TuM-5 Large-Scale Metallic Nanotubes Array (MeNTA) with Plasmonic Nanoparticles for SERS Application***, **Alfreda Krisna Altama,** J. Chu,* National Taiwan University of Science and Technology, Taiwan*; P. Yiu,* Ming Chi University of Technology, Taiwan*; W. Chiang,* National Taiwan University of Science and Technology, Taiwan

The limitations in reproducing large-scale and highly-sensitive surface-enhanced Raman scattering (SERS) substrates are a major problem for practical applications. In this work, we report on our works about a periodic three-dimensional (3D) metallic nanostructure array, referred to as MeNTA fabricated using PVD processes developed for large-scale semiconductor engineering. Specifically, the MeNTAs were fabricated using metallic glass alloy, providing high strength, ductility, and good biocompatibility. For further development, over the MeNTAs deposited a uniform coating of gold nanoparticles (NPs) to form a high-sensitivity

AuNP@MeNTAs 3D-SERS substrate. Using crystal violet (CV) as a probe molecule, the performance of an AuNP@MeNTA 3D-SERS substrate can be provided. Here we found a very low detection limit with a comparable enhancement factor. The SERS performance did not degrade for more than a week after installation, thereby demonstrating high stability and repeatability. This research provides useful guidelines for the low-cost fabrication of SERS substrates of high sensitivity.

9:40am **D2-TuM-6 Carbide-derived Carbon (CDC) for Implant Application: Tribocorrosion Kinetics and Mechanisms***, **Kyle Kinnerk**,* Department of Biomedical Engineering, University of Illinois at Chicago, USA*; Y. Sun, M. Daly,* Department of Civil, materials, and Environmental Engineering, University of Illinois at Chicago, USA*; M. Wimmer,* Department of Orthopedic Surgery, Rush University Medical Center, USA*; M. McNallan,* Department of Civil, materials, and Environmental Engineering, University of Illinois at Chicago, USA*; M. Mathew,* Department of Biomedical Sciences, UIC College of Medicine at Rockford, USA

Between 2000 and 2014, the estimated annual incidence of primary total hip replacement per 100,000 in the U.S. in the 55-70 year age range increased by 194.3% [1]. Previously, we fabricated carbide-derived carbon (CDC) on Ti6Al4V, and our finding indicated that CDC can provide superior protection to the substrate in a tribocorrosive environment. The objective of this work is to test CDC under three different electrochemical conditions, cyclic polarization (CP), OCP, and potentiostatic (PS), with the surface characterized by SEM-EDS and 3D profiler.

CDC was prepared on a Ti6Al4V substrate via the electrolysis approach[2]. Ti6Al4V was polished until the surface had a mirror-like finish (Ra<25 nm). Alumina was used as the pin to simulate a ceramic counter body, and bovine calf serum (BCS) was selected to emulate biological fluids. Two groups of samples were tested, alumina (Al_2O_3)-Ti6Al4V (control group) and alumina-CDC, using a custom tribometer with reciprocal sliding for 3600 cycles. A standard electrochemical protocol was followed, and CP, OCP, PS were usedfor the sliding stages. Electrochemical impedance spectroscopy (EIS) was conducted before and after the testing stage to analyze the local corrosion kinetics. SEM/EDS was used to observe the wear scar and obtain the surface composition, 3D profiler will be used to measure the wear volume, and ICPMS will be used to measure the metal ions concentration released into the BCS solution.

Based on the potentiodynamic results under sliding conditions, the CDC coated sample showed approximately 126-fold smaller carbon density variation ($6.301x10^{-6}$ A/cm^2) than the bare titanium alloy ($7.577x10^{-4}$A/cm^2), implying that CDC has a smaller corrosion weight loss (K_c). The OCP results agree with the potentiodynamic results, where the potential drop of CDC (0.194V) is smaller than Ti6Al4V (0.7V), meaning that CDC can provide protection to the substrate material under tribocorrosive environment. Furthermore, SEM-EDS results indicate that CDC still remained on the surface after tribocorrosion testing for both electrochemical conditions. Therefore, it is possible that CDC can be smeared over the surface by mechanical motion and act as a solid lubricant at the interface. Potentiostatic condition will be included to fully evaluate CDC's tribocorrosion performance, and more characterization techniques will be employed to reveal the protection mechanism of CDC. In this work, we found that CDC can significantly improve the substrate's tribocorrosive resistance, showing that CDC is promising in further implant applications.

[1] M. Sloan et al., *J. Bone Jt. Surg.,* 2018 [2]Y. Sun et al., *Surf. Coat. Technol.,* 2021

10:00am **D2-TuM-7 PEKK as Biomaterials Under Fretting Corrosion Solicitations: May This Biopolymer Be Considered as New Hip Implant Component?***, **Jean Geringer**, J. Monnatte,* Mines Saint-Etienne, France*; G. Planche,* EPIC sarl, France*; J. Porteus,* Oxford Polymers, USA

Some materials dedicated to orthopaedic implants are well used from more than 40 years. About hip implants some PAEK, poly Aryl Ether Ketone, materials may have a right impact on the lifetime. PEEK, poly Ether Ether Ketone actually is under investigations. However PEKK, poly Ether Ketone Ketone, needs some improvements concerning Friction/Fretting corrosion resistance. From the fundamental point of view, PEKK was under investigations through this study about fretting corrosion investigations. Some fundamental investigations under these tribological conditions are not quite well described. This work aims at providing some fundamental results on tribology/tribocorrosion.

A typical fretting corrosion machine, Fig 1, allowed to manage 16 hours of experiments. Titanium alloy, Ti-6Al-4V, was the counter part in bovine serum. The displacement amplitude was sinusoidal with the amplitude of +-40µm.

This study aimed at establishing the fretting map and at drawing thanks to OCP, Open Circuit Potential, evolution the A ratio (Dissipated energy over the total energy) vs. OCP drop. This approach is well improved and the suggested ranking of contact was well achieved in accordance with previous results [1].

Under hip implants mechanical constraints PEKK material showed good performance under fretting corrosion solicitations compared to UHMWPE for example. Further investigations need to be performed in order to assess the capability of using as implants.

Figure 1

10:20am **D2-TuM-8 Fretting-corrosion (<5µm) Performance of Carbide-derived Carbon (CDC) Surface Modification for Hip Implants***, **Yani Sun**, M. Daly, M. McNallan,* Department of Civil, Materials and Environmental Engineering, University of Illinois at Chicago, USA*; M. Mathew,* Department of Biomedical Sciences, UIC College of Medicine at Rockford, USA

Fretting-corrosion at the taper junction is one of the main causes of early failure of total hip replacement (THR)[1]. Previously, we have proved that carbide-derived carbon (CDC) can protect Ti6Al4V from tribocorrosive damages[2]. However, the fretting-corrosion behavior of CDC still remains unknown. Also, experimental fretting setups used in the literature simulate motions of 50 µm or higher[3], which might not simulate micromotions at the taper junction that leads to partial-slip fretting. Therefore, we aim to develop a device simulating a motion <5 µm while simultaneously collecting electrochemical data, and test CDC's fretting-corrosion behavior.

The fretting-corrosion apparatus mainly consists of a stepper motor, a force sensor, and a corrosion cell connected to a potentiostat. Two groups were designed as (i) ZrO_2 pin on the Ti6Al4V as the control group and (ii) ZrO_2 pin on the CDC. Bovine calf serum (BCS) with protein content of 30 g/L was selected as the electrolyte at 37±1°C. A normal load of 83 N was applied, and the pin was controlled to move with an amplitude of 2 µm at 1 Hz for 3600 cycles. A typical protocol was followed to monitor the evolution of open-circuit potential (OCP). After the fretting-corrosion testing, the exposed area was characterized by SEM/EDS.

As a result, friction loops of both groups show a narrow elliptical shape, and the energy ratios of both groups remained below 0.2 throughout the entire stage, indicating a fretting regime of partial slip according to Fouvry et al.[4]. Moreover, CDC possesses higher OCP (-0.076 V) than Ti6Al4V (-0.541 V) during the fretting stage, suggesting that CDC has a higher resistance to corrosion. The fluctuations of OCP caused by fretting motions of CDC is approximately 0.005 mV, which is smaller than that of Ti6Al4V (0.03 mV), suggesting that CDC can provide protection to the substrate under the fretting-corrosion conditions. Based on the SEM images, the main damage showing on the Ti6Al4V disk is abrasive wear with typical ploughing features, which might be because of the higher hardness of ZrO_2 than the Ti alloy. Less damages were observed on the CDC surface and CDC still presents on the surface after the testing, implying that CDC might act as a solid lubricant and get smeared over the surface by the mechanical wear and thus protect the substrate from fretting-corrosion damages. Also, TEM will be utilized in the following study to reveal detailed mechanism and structural information.

[1]S. Yu et al. *J. Clin. Orthop. Trauma* 2020 [2]Sun, Y et al. *Surf. Coat. Technol.,* 2021. [3]J. Geringer et al., *Tribocorrosion Passive Met. Coat,* 2011 [4]S. Fouvry et al., *Wear*, 1995

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