Surface Engineering of Biomaterials, Devices and Regenerative Materials: Health, Food, and Agriculture Applications

Room Palm 1-2 - Session MD1-1-MoM

Coatings and Surfaces for Medical Devices: Mechanical, Corrosion, Tribocorrosion, and Surface Processing I

Moderators: Jean Geringer, Ecole Nationale Superieure des Mines, France, **Mathew T. Mathew**, University of Illinois College of Medicine at Rockford and Rush University Medical Center, USA

10:00am **MD1-1-MoM-1 NaOh Etching and Oxygen Plasma Treatments on Surface Characteristics and Their Potential to Activate Micro-Arc Oxidized TiO_2 Biomedical Coatings***, **Paulo Noronha Lisboa-Filho [paulo.lisboa@unesp.br]**,* UNESP, Brazil **INVITED**

Activation treatments such as NaOH etching or O_2 plasma can play an essential role in surface conjugation of titanium with biomolecules, providing a better interaction at the bone-implant interface. However, their application on complex titanium dioxide (TiO_2) surfaces is still not explored. In this contribution, bioactive and porous TiO_2 coatings produced by micro-arc oxidation (MAO) were treated with NaOH etching or O_2 plasma and then placed in contact with a reactive isocyanate test compound to evaluate the potential of molecule conjugation. Results suggested that O_2 plasma treatment has only changed the surface chemistry of the coating through carbon contaminants removal, plasma-driven oxidation and generation of functional OH species, including reactive carboxyl groups. This chemical modification by plasma has made the surface superhydrophilic. After NaOH etching, the coating became rougher and also superhydrophilic, containing titanate structures doped with sodium and calcium on its surface and inside the inner pores. Upon reaction with butyl isocyanate, the O_2 plasma-treated surfaces seem to better provide molecule conjugation, introducing characteristic conjugation bonds, and also making MAO coatings more hydrophobic due to the surface-terminated methyl chains from isocyanate. This proof-of-concept study has demonstrated the promising grafting potential given by O_2 plasma on complex TiO_2 surfaces.

10:40am **MD1-1-MoM-3 Influence of Microstructures on the Corrosion Behavior of Cobalt-Chromium Alloys Under Different Ortho Joint Conditions***, **Mathew T. Mathew [mtmathew@uic.edu]**, Avirup Sinha, Sujoy Ghosh, Maansi Thapa, Remya Ramachandran, Nicki Ta,* University of Illinois at Chicago, USA

Cobalt-Chromium-Molybdenum (CoCrMo) alloys have been used in various biomedical applications, including hip and knee implants, making them highly essential in orthopedics. A major concern regarding these implants is their long-term corrosion resistance, as corrosion can have a negative impact on patient health. Corrosion resistance is impacted by a variety of factors, such as the alloy's microstructure and the environmental conditions that can affect the release of metal ions. In this study, two different microstructures of CoCrMo were tested including homogeneous and banded samples. Each microstructure was tested under three different conditions: normal, inflammatory, and infectious. To stimulate these environments, 30 g/L protein was used for normal conditions, 0.5 mM hydrogen peroxide for inflammation, and 15 µg/L LPS for infectious conditions. To test the long term effects of these conditions, 24 hour corrosion experiments were performed using a three-electrode electrochemical set up. The electrochemical testing protocol included the sequence of open circuit potential, potentiostatic run, electrochemical impedance spectroscopy, and cyclic polarization. For banded samples the experiments were run at a constant potential of -0.7V and for homogeneous samples, it was run at -0.68V. The banded structure exhibited higher current values than the homogeneous structure, indicating that CoCrMo alloys with a homogeneous microstructure have greater corrosion resistance. Furthermore, among normal, inflammatory, and infectious conditions, the inflammatory condition resulted in the greatest alloy loss (µg) for both banded and homogeneous structures. Specifically, the banded structure showed a loss of 37.53 µg, while the homogenous structure exhibited a loss of 5.69 µg, indicating inflammatory conditions have the least corrosion resistance.

11:00am **MD1-1-MoM-4 Synergistic Fretting–Corrosion Mechanisms in DLC Coatings***, **Tomasz Liskiewicz [T.Liskiewicz@mmu.ac.uk]**,* Manchester Metropolitan University, UK*; Samuel McMaster,* Anglia Ruskin University, UK*; Michael Bryant,* University of Birmingham, UK*; Thawhid Khan,* University of Sheffield, UK*; Yu Yan,* University of Science and Technology Beijing, China*; Ben Beake,* Micro Materials Ltd, UK **INVITED**

This study investigates the synergistic interactions between fretting wear and electrochemical crevice corrosion in diamond-like carbon (DLC) coating systems on AISI 316L substrate under physiologically representative conditions. Particular emphasis is placed on understanding how albumin influences fretting–corrosion mechanisms, given their critical role in many engineering and biomedical environments. A combined experimental methodology is employed, integrating micro-mechanical characterisation (instrumented indentation and scratch testing) with fretting experiments employing in-situ electrochemical characterisation to assess coating durability, damage initiation, and interfacial degradation. Electrochemical techniques, including open-circuit potential monitoring, potentiodynamic polarisation, and electrochemical impedance spectroscopy, are applied in situ during fretting to capture the evolving interaction between mechanical and electrochemical degradation processes.

Fretting was replicated by applying micro-motion to the Al2O3 ball relative to the coated plate under a dead weight normal load. A maximum Hertzian contact pressure of 800 MPa was used for the tests, at a fretting displacement amplitude of 100 µm, giving a gross slip fretting regime. Each fretting test lasted 60 minutes resulting in 3600 cycles at a frequency of 1 Hz. Detailed surface and subsurface analyses using scanning electron microscopy, focused ion beam cross-sectioning, and energy-dispersive X-ray spectroscopy reveal progressive coating damage involving micro-cracking, interfacial delamination, and tribologically induced graphitisation of the DLC layer. Results demonstrate that fretting accelerates corrosion through mechanical disruption of the coating–substrate interface, while corrosion promotes further fretting damage via under-film attack and crack propagation, establishing a genuine fretting-corrosion synergy.

A mechanistic model is proposed in which mechanical defect initiation, electrochemical attack, and debris generation act in a feedback loop, driving progressive coating degradation. These insights highlight the importance of considering protein–surface interactions and combined degradation modes when designing DLC coatings for demanding fretting–corrosion service conditions in biomedical and engineering applications.

11:40am **MD1-1-MoM-6 Mechanisms of Fretting Corrosion in Titanium-based Biomedical Modular Implant Interfaces***, **Avirup Sinha [asinha38@uic.edu]**,* University of Illinois - Chicago, USA

Fretting corrosion is observed at modular junctions under load, where micro-motions lead to material loss and release of metallic ions or debris. Depending on applied load and displacement amplitude, fretting progresses through partial slip, mixed, and gross slip regime. In this study, fretting corrosion behavior was investigated under two contact configurations: metal on metal (Ti-6Al-4V on Ti-6Al-4V) and metal on ceramic (Ti-6Al-4V on ZrO2) in Bovin Calf Serum (BCS). BCS used in the experiment reflect two conditions: normal and infectious. Experiments were performed using 83 N normal load with a displacement amplitude of 5 µm at 1 Hz. Electrochemical protocols include sequential measurements of open circuit potential (OCP), potentiostatic (PS), and electrochemical impedance spectroscopy (EIS) which are synchronized with fretting motion. The test condition includes 10.9 mm diameter mirror polished disk and a 3 mm diameter pin with 20 ml of electrolyte used for each trial.This approach allows systematic evaluation of how contact pair and electrolyte chemistry influences the synergistic effects of wear and corrosion. The results are expected to advance the understanding of fretting corrosion in modular implants and support the design of materials and interfaces with improved in-vivo durability.

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