Quartz crystal mass monitoring to study tribofilm formation and retention in self-mating CoCrMo systems

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Statement of Purpose: Tribochemical reactions have been cited as an important wear mechanism in metal-on-metal (MoM) joints [1]. Earlier findings pointed to the occurrence of a carbon rich tribofilm containing graphitic material in well-functioning metal hip joints [2]. Presumably, the tribofilm forms due to interaction between the metal surface and proteins from the surrounding environment. Although the theoretical benefits of such interfacial material have been discussed, pathways of tribofilm formation and its impact on implant tribology are not well understood. Part of the problem is to generate a contentious tribofilm for in-vitro tests. Recent findings have shown that an electrochemical process in the presence of protein generates tribofilm-like material on the metal surface, suggesting that similar events contribute to the tribofilm formation in-vivo [3]. It was the purpose of this study to investigate the wear and friction properties of CoCrMo surface with and without a carbon rich tribofilm. Therefore, a new test rig with a quartz crystal micro-balance (QCM) as mass detector was employed. QCM is a standard technique to observe mass changes of substances through frequency changes of a quartz crystal in real time.

Methods: Quartz crystal samples were sputter coated with CoCrMo alloy allowing the use of a QCM as mass change detector. The chemical composition and microstructure of the sputter coating was adjusted to be identical to the previously reported nanocrystalline subsurface generated in metal hip joints in-vivo [4]. A pin-on-disk type tribometer was built around the QCM detector. The counter bodies were three cylindrical pins made from CoCrMo alloy rubbing against the CoCrMo sputter coating. Multidirectional motion and an initial surface pressure of 300 MPa were applied. Normal force, friction force, and mass changes on a µg-level were recorded. Three different test conditions were tested: 1) polished CoCrMo coating in distilled water, 2) polished CoCrMo coating in bovine calf serum (BCS - 30g/L protein) and 3) electrochemically applied continuous carbon rich tribofilm tested in BCS .

Results: A carbon-rich film formed at 0.85 V vs. SCE at 100 ng/mm^2 leading to mass gain, instead of loss (Fig.1).

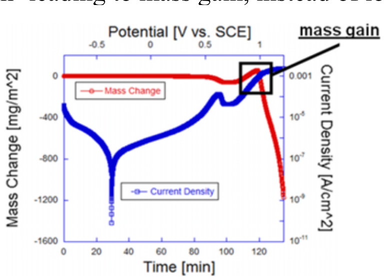

Figure 1. Potentio-dynamic curve and responding mass change of CoCrMo in BCS (mass gain at 0.85V)

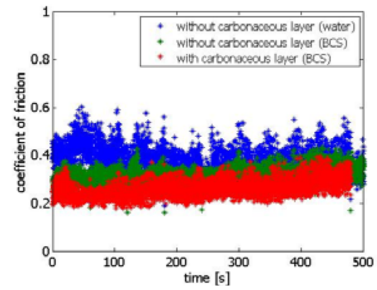

Figure 2. Coefficient of friction measured in tests 1-3

Using EELS and Raman spectroscopy a similar composition to tribofilms formed in vivo could be shown. Besides carbon and nitrogen, films exhibited traces of cobalt and chromium as well as the characteristic Raman double peak as reported in [2] indicating graphitic material.

Friction was variable and scattered within each experiment, but clearly differed between test conditions (Fig. 2). The highest coefficient of friction was observed for the polished CoCrMo coating in water, followed by polished CoCrMo coating in BCS . The lowest coefficient of friction was found for tribofilm coated samples tested in BCS. Here, during the short period of low friction, a mass loss of 100 nm/mm^2 was detected which correlates with the thickness of the pre-applied tribofilm. After the removal of the tribofilm (as confirmed by microscopy) friction in test 3) increased to values of test 2).

Conclusions: This study utilized a quartz crystal micro-balance as a mass detector, which allows in-situ measurements of mass loss and gain. Interestingly, a carbonaceous film of the same composition as in vivo could be generated purely by electrochemistry. The tribological test indicated improved friction behavior for the time that the film was present. This is in agreement with the earlier assumption of a beneficial influence of the partially graphitic tribofilm on friction. However, the effect was not durable. Presumably, the contact pressure was too high to maintain the tribofilm. More conforming contact conditions, as those in MoM hips, seem to provide better conditions for tribofilm formation – as long no severe contact conditions (edge loading, stripe wear) occur. In summary, the results suggest that the tribofilm formation is dependent on ion-protein interactions (as they may occur during tribocorrosive processes) and once formed it influences friction beneficially.

References: [1] Wimmer MA. J. Orthop. Res. 2010;28:436–443 [2] Liao Y. Science. 2011;334:1687–1690 [3] Martin EJ. Langmuir. 2012; in press [4] Pourzal R. J. Mech. Behav. Biomed. Mat. 2009;2,186–191

Acknowledgments: Work conducted at NW University. Study was funded by NIH (RC2-AR058993) and NSF FDN 116095). CoCrMo alloy was kindly donated by ATI Allvac