The Effect of Simulated Inflammatory Conditions on the Corrosion and Fretting Corrosion of CoCrMo alloy

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Introduction: Cobalt-chromium-molybdenum (CoCrMo) alloy is widely used in orthopedic devices. Ions and particles released from CoCrMo have been recognized as a major concern [1]. Recently, inflammatory cell induced corrosion of CoCrMo alloy has been documented in our laboratory [2]. This mechanism of corrosion results from stimulated immune and inflammatory cells releasing reactive oxygen species such as hydrogen peroxide (H2O2), utilizing Fenton reactions, and acid to amplify corrosion processes. How simulated inflammatory based H2O2, Fenton reactions and acid affect CoCrMo corrosion is not fully understood. The goal of this study is to assess the effects of simulated inflammatory species on the corrosion and fretting corrosion behavior and surface oxide structure of CoCrMo alloy.

Methods: Fretting corrosion test: CoCr/CoCr pin-on-disk combinations (ASTM F-1537) were used (n=3) [3]. The surface condition of these samples consisted of sanding to 600 grit finish. Three solutions were used to simulate the in vivo conditions: 1. PBS, 2. PBS with 0.01M H2O2 and 0.1mM Fe3+, and 3. PBS with HCl (pH=3). All tests were performed at a fixed load of 6 N, and fixed fretting amplitude (50 μm) and frequency (1.25 Hz). The baseline current (w/ no fretting) and fretting current were recorded and analyzed in all tests.

Potential-Dependent Tests: During fretting, the potential was varied from -800 mV to +600 mV and both baseline and fretting currents were captured. Fretting was performed for 200 s at each voltage.

Long-term Tests: A long term fretting test was conducted on one sample sequentially in PBS with H2O2, PBS solution with HCl, PBS solution at 600 mV, PBS solution with H2O2 at 600 mV. Fretting was performed for at least 1.5 h in each solution. This potential was selected because it is the OCP of CoCrMo when exposed to simulated inflammatory solution conditions. Damage of fretting interfaces was investigated using Scanning Electron Microscope (SEM)

Electrochemical AFM (ECAFM) study: Surface oxide structure was studied using ECAFM. Disks of CoCrMo alloy were mechanically polished up to 600 grit followed by polishing sequentially using 1, 0.3 and 0.05 um alumina suspensions. A CoCrMo sample was placed in the electrochemical fluid cell in the AFM (details of the system can be found elsewhere [4]). A three electrode system was used for the electrochemical tests with CoCrMo severing as the working electrode, chlorided Ag wire as the quasi-reference electrode and Pt wire as the counter electrode. Voltages (from 0.1 V to 0.65 V) were applied to the surface of CoCrMo alloy immersed in PBS. Current and surface morphology changes were captured.

Results: Fretting currents above the baseline (Fig. 1) were observed at voltages above -0.4 V in PBS and PBS with acid solution. In solutions with H2O2 and Fe3+, fretting currents only arose above 0.2 V while
the baseline current was at least 10 times larger than the other two conditions. Currents increased more than 100 times in the fretting condition compared to non-fretting condition in PBS and PBS with acid solution. The passive state was observed to remain present at voltages higher than 0.4 V in acidic PBS (pH = 3) whereas pH 7.4 PBS exhibited transpassive breakdown of the oxide. Pitting corrosion and surface dissolution were observed in the long-term fretting test under inflammatory conditions (Fig. 2). When the voltage was 0.65V, dissolution of the oxide film occurred and increased surface roughness was observed using ECAFM (Fig. 3). Currents increased by 2 to 3 orders of magnitude during the first 10 minutes of exposure (Fig. 4) while the oxide film kept on dissolving and reforming.

![Figure 1 Comparison of fretting and baseline current in different solutions.](image1)

![Figure 2 Severe pitting, fatigue corrosion and dissolution were observed after long-term fretting corrosion under inflammatory condition.](image2)
Figure 3. Time-dependent surface morphology changes of CoCrMo at 0.65 V in PBS.
Discussion: Simulated inflammatory solution conditions greatly affect the corrosion and fretting corrosion behavior of CoCrMo alloy. Baseline currents show large increases in simulated inflammatory solutions which contain H2O2 and result in large positive shifts in OCP. Additionally, oxide films are not protective (no fretting current observed) from -0.6 V to 0.2 V in H2O2/PBS solutions. Corrosion damage (pitting corrosion) similar to that found in retrieval studies was observed after long term fretting corrosion tests in simulated inflammatory solutions and voltages. Dissolution and reforming of CoCrMo oxides were observed under physiologically attainable potentials (0.65 V).

Significance: Corrosion and fretting corrosion susceptibility of CoCrMo alloy is significantly affected by simulated inflammatory conditions. With H2O2 and Fe3+ present, static corrosion current densities rise and oxides are less protective under fretting conditions, whereas passivation of oxide films occurs in pH 3 solutions. Pitting corrosion was observed after long-term fretting corrosion in simulated inflammatory solutions.

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