Tribocorrosion in Hard-on-Hard Total Hip Replacement Bearing Couples

Andrew R. Beadling, Michael G. Bryant, Duncan Dowson, Anne Neville.
Institute of Functional Surfaces, Leeds, United Kingdom.

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Introduction: During articulation of a Hard-on-Hard (HoH) bearing couple with a metallic component, the passive oxide film on the surface of the component can become damaged. This oxide which forms spontaneously in air is present on most metallic biomaterials and provides the desirable qualities of corrosion resistance and biocompatibility to modern biomedical alloys. This damage results in exposure of the bulk material to synovial fluid, which acts as an electrolyte. The total degradation of a device is therefore a complex mix of mechanical wear and corrosive phenomena on the active surface as the passive film is continuously disturbed and reformed. Synergistic effects can also take place, enhancing material loss both through wear and corrosion [1]. The ability to predict the performance of such a device therefore needs a greater understanding of the interaction between the tribology and electrochemistry during sliding. In order to investigate these phenomena an anatomically representative hip simulator has been instrumented with a three-electrode electrochemical cell [2, 3].

Methods: Clinical HoH bearing couples (Metal-on-Metal, MoM) were tested to one million cycles in a ProSim Deep Flexion Hip Simulator. The components were cemented into plastic fixtures to isolate them from the simulator, using laboratory grade PMMA bone cement. The metallic components were High Carbon (HC) Cobalt-Chromium (CoCrMo) alloy. The hip simulator was instrumented with a three-electrode electrochemical cell comprising of the metallic components as the Working Electrode (WE) and completed by a Thermo Scientific Combination Redox/ORP Silver/Silver Chloride (Ag/AgCl) Reference Electrode (RE) and Platinum Counter Electrode (CE). The Open Circuit Potential (OCP, Ecorr) was monitored continuously over the course of a test to give a qualitative assessment of corrosive processes taking place during articulation. Periodically the resistance to polarisation (Rp) was determined through linear sweep voltammetry (± 25 mV Ecorr) in order to quantify the corrosion current (Icorr) and thus the total material loss at the exposed WE surface over the course of the test. The mass of material lost as a result of corrosion was calculated using Faraday’s Law, shown in Eq. 1 and converted to a volume loss. As CoCr is an alloy, the values used for Atomic Mass and Valence Number were calculated using a weighted average according to the alloy composition which assumes proportional oxidation during corrosion. Error was calculated using values for Cobalt and Chromium to account for a possible preferential release of those elements.
Equation 1: Faraday’s Law.

A twin-peak loading profile was used in part reference to ISO 14242-1 [4]. Bearings were tested either under a standard walking cycle or subjected to 0.8 mm microseparation. 36mm bearings were tested previously by Hesketh et al. [3]. Tests were performed with Foetal Bovine Serum as the lubricant, diluted to 17g/L total protein content using PBS. 0.03% Sodium Azide was also added to retard bacterial growth. The serum was changed at 333,000 cycle intervals.

**Results:** The OCP for MoM bearings tested up to 1 MCycles can be seen in Figure 1. A 36mm bearing was tested under a standard walking cycle to 0.8 MCycles and 28mm bearings were tested under both standard walking cycle and microseparation to 1 MCycles. Following an initial period of relatively noble OCP for all bearings (approx. 0 to -50mV), the OCP dropped immediately and significantly upon the initiation of sliding. All bearings dropped to approx. -300 to -400 mV and remained relatively stable for a short period of time. Following that the OCP for the 36mm bearing gradually shifted back towards pre-sliding noble potentials where it stayed for the rest of the test. The OCP for the 28mm bearing under walking conditions remained reasonably stable at around -200 to -300mV over the entire test with brief periods outside this range. The 28mm bearing subjected to microseparation dropped much lower to approx. -600mV and remained lower than the other two bearings over the entire test.
Figure 1: Open Circuit Potential (Ecorr) for 36 and 28mm HC CoCr MoM Bearings tested to 1 MCycles under standard Walking cycle and Microsep conditions.

The cumulative volume loss purely as a result of oxidation at the WE surface for the 28mm bearings can be seen in Figure 2. For the bearing under walking conditions the wear rate remained relatively stable of the first one million cycles, resulting in a total volume loss due to corrosion of 0.234mm$^3$. The wear rate for the microseparating bearing varied wildly over the first million cycles and resulted in a total volume loss almost an order of magnitude higher at 2.044mm$^3$. 
Figure 2: Total Faradaic Volume Loss as a result of Oxidation at the WE surface for 28mm HC CoCrMoM Bearings tested to 1 MCycles under standard Walking cycle and Microsep Conditions.

**Discussion:** For all bearings tested, a cathodic shift in OCP was noted upon the initiation of sliding. The cause of such a cathodic shift is generally regarded as an increase in corrosive degradation. The behaviour of OCP of the entire test was different for all three tests, giving a qualitative assessment of different levels and mechanisms of corrosion taking place. For the 36mm bearing, the shift early shift to more noble potentials may be indicative of a ‘wear induced passivation’ as a result of bearing tribology and so called ‘tribochemical reaction layers’ [5]. This shift was not noted in the 28mm bearing tested under walking conditions, possibly as a result of the lubrication regime being operating in the severely mixed region whereas a 36mm bearing will be closer to a fluid-film regime. The 28mm bearings remained relatively stable under standard walking, whereas under microseparation the OCP dropped much lower and varied much more over the course of the test. This may indicate an increased but much more unstable level of corrosion taking place.

When comparing the increase in wear as a result of applying microseparation, various previous studies have reported a slight increase to a three or four-fold increase over the first million cycles [6-8]. Volume lost purely as a result of corrosion at the exposed WE surface appeared to be almost an order of magnitude higher for the 28mm bearings tested within this study. Previous studies have largely only considered a ‘wear’ process when analysing the performance of such bearings. This may indicate that corrosion plays a much more significant role in degradation at the bearing surface during adverse loading conditions than previously thought.

**Significance:**
- Metal-on-Metal bearings depassivate during sliding resulting in an increased level of material loss due to corrosive phenomena.
- The depassivation mechanisms and severity of corrosion vary depending on the tribological conditions of articulation.
- During the first million cycles the corrosive degradation appears much more significant as a result of microseparation than previously considered.

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