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The Effect of Microseparation on Corrosion Rates of Metal-on-Metal Total Hip Replacements

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ABSTRACT

The poor performance of Metal-on-Metal (MoM) bearings has to date been blamed on "adverse loading" conditions. Studies have focused on the effect of cup inclination and microseparation on gravimetric wear rates and highlighted the importance of surgical technique when implanting such devices. Up to four fold increase in the wear rates of MoM bearings subjected to microseparation has been reported during the bedding-in period. The contribution of corrosive processes to overall material degradation during adverse loading has not previously been investigated. In the present study 28 mm HC CoCrMo alloy Total Hip Replacements were tested to 1 Mcycles under standard gait and severe microseparation conditions in an electrochemically instrumented hip simulator. An order of magnitude increase in material lost as a result of oxidation was noted (0.234 to 2.044 mm^3/Mcycle) during microseparation. Corrosive degradation may therefore be a much more significant contribution to poor bearing performance under adverse loading than previously considered.

Key words: Total Hip Replacement, Metal-on-Metal, CoCrMo, Microseparation, Tribocorrosion

INTRODUCTION

Since 2008, there has been a rapid downturn in the use of a MoM bearing combination in Total Hip Arthroplasty operations. Their resurgence in popularity over the preceding decades was due to an increased knowledge of the tribology of such bearings and clinical studies demonstrating favorable long-term survivorship rates of first-generation devices.[1–3] During the development of second-generation and resurfacing MoM devices, hip simulation was used to benchmark their wear rate against the existing Metal-on-Polymer (MoP) gold standard. Wear rates of orders of magnitude smaller than MoP bearings of similar diameters were often reported,[4,5] with the smaller wear debris produced thought to lie outside the range required to initiate osteolysis.[6] These drastically improved wear rates were attributed to improved tribology via a shift toward the fluid-film lubrication regime.[7,8] Since their introduction however these prostheses have demonstrated higher than acceptable failure rates, with one particular device having a revision rate as high as 24.2% at seven years.[9] Adverse Reaction to Metal Debris (ARMD) is a general term to cover soft tissue conditions that are thought to be related to the release of metallic debris and ions, resulting in the early failure of MoM devices though metallosis, pseudotumors and Aseptic Lymphocyte Dominated Vasculitis-Associated Lesions (ALVAL).

The mechanical depassivation and subsequent repassivation of a passive oxide film was first noted on stainless steels[10] and applies to most metallic biomaterials. These alloys owe their corrosion resistance and biocompatibility to such a protective oxide, which can become damaged during articulation due to cyclic abrasion of the surfaces. Exposure of the reactive bulk alloy to the synovial fluid results in corrosive material loss. The accelerated material loss as a result of wear accelerated corrosion is termed tribocorrosion. The degradation of MoM Total Hip Replacements (THRs) is therefore a complex mix of mechanical wear and corrosive phenomena as well as synergistic effects. First proposed by Watson *et al.*[11] the total material loss can therefore be expressed as pure wear (W_0), pure corrosion (C_0) and their synergistic effects (S). The synergies can be further broken down to corrosion enhanced wear (dWc) and wear enhanced corrosion (dCw), as shown in Equation 1.The ability to predict and optimize the performance of a MoM device therefore needs a greater understanding of the interaction between the tribology and electrochemistry during sliding.

$$T = W_0 + C_0 + (dW_c + dC_w) \tag{1}$$

The performance of MoM devices has received much scrutiny in recent years, with simple configuration tribometer studies demonstrating the importance and significance of corrosive processes to the overall alloy degradation.[12,13] Further studies investigating the use of electrochemically instrumented hip simulators have demonstrated the depassivation of the alloy and accelerated corrosion during sliding.[14,15] One study suggested that during a standard ideal walking cycle for a 36 mm MoM bearing, corrosion accounted for as much as 12-14% of the total material loss.[16] This does not include accelerated mechanical wear caused by corrosive processes, which have been attributed as wear processes. Other work in the area has investigated the significance of so called tribochemical reaction layers, the result of tribological and electrochemical interactions with the proteinaceous lubricants necessary to MoM performance.[17–19] Assessment of these devices is therefore a complex, multi-disciplined field and cannot be simplified to just wear rates.

Other work in the field has examined the sensitivity of MoM bearings to various breakdowns in lubrication, typically caused by malpositioned components. One such scenario is the case of microseparation, first observed in fluoroscopic studies of MoP and MoM implants[20,21] and later applied to explain so called “stripe wear” of Ceramic-on-Ceramic devices.[22] When a device is undergoing microseparation, the femoral and acetabular bearing components shift to separate centers of rotation during the walking cycle. This causes a separation of the surfaces which results in a collision upon the following heel-strike, often along the rim of the acetabular component, before normal articulation resumes.

These “adverse loading” conditions have been observed to cause an increased wear rate for MoM devices. The importance of surgical technique during implantation of MoM bearings has therefore been stressed within the literature. Williams *et al.*[23] reported a non-statistically significant increase in wear rate from 2.03 (±2.60) to 2.70 (±2.20) mm^3/Mcycle for 28 mm bearings subjected to microseparation over the first million cycles. Beyond the bedding-in phase overall wear volume after five million cycles was shown to increase from approximately 3 to 8 mm^3. Leslie *et al.*[24] reported on the combination of a high cup inclination angle (55°) and microseparation for a 39 mm surface replacement device. During the first million cycles wear rates increased from approximately 2.5 to 7.0 mm^3/Mcycle. Al-Hajjar *et al.*[25] reported an increase from approximately 1.2 to 4.62 mm^3/Mcycle for 28 mm MoM bearings subjected to microseparation over the first two million cycles of articulation. The demonstrated increased wear rates have largely been attributed solely to the breakdown in lubrication and an overriding “wear” process for MoM devices.[26] To the authors knowledge no investigation into the effect of adverse loading on the electrochemical processes at the bearing surface has been conducted to date. This study therefore aims to examine the case of severe microseparation for a 28 mm MoM bearing couple and investigate its effect on corrosive degradation of the alloy.

EXPERIMENTAL PROCEDURE

A commercially available Simulation Solutions ProSim† Deep Flexion Single-Station Hip Simulator has been instrumented with a three-electrode electrochemical cell. A schematic of the test cell can be seen in Figure 1. Plastic fixtures and laboratory grade Polymethyl Methacrylate (PMMA) bone cement was used to hold the components. This was done in order to isolate them from the rest of the rig. The working electrode (WE) was formed by making a connection to the rear of the acetabular cup using conductive epoxy resin. Care was taken to prevent this connection becoming exposed to the electrolyte using silicone sealant. The WE also comprised the femoral head when the two components were in contact, which was assumed to be constant over a standard gait cycle.

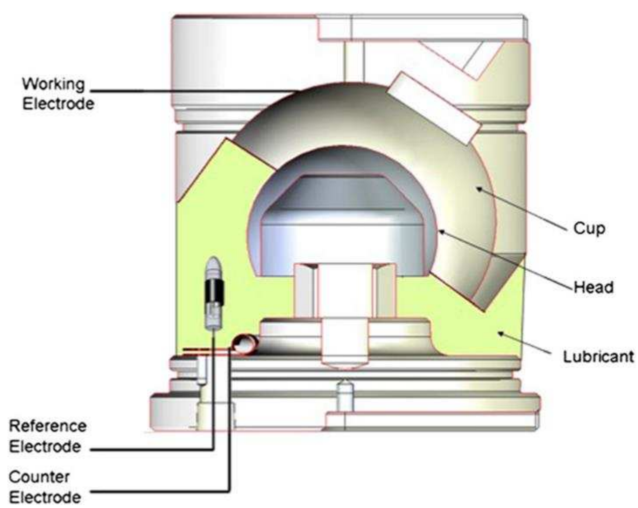

Figure 1: Schematic of Hip Simulator test cell instrumented with a three electrode electrochemical cell.

† Trade Name.

A Thermo Scientific† combination electrode was used to complete the electrochemical cell. This consisted of a Silver / Silver Chloride (Ag/AgCl) reference electrode (RE) and platinum counter electrode (CE). All electrochemical tests were conducted using a Metrohm Autolab† PGSTAT101 potentiostat.

Clinical High Carbon Cobalt-Chromium-Molybdenum (CoCrMo) alloy components were tested to one million cycles. This is commonly accepted to equate to one year *in vivo*. 28 mm diameter bearings were selected as one of the most common sizes used clinically. A standard twin-peak loading cycle was used at a frequency of 1 Hz. The loading cycle comprised of 3 kN and 300 N peak and swing-phase loads respectively, +30° -15° Flexion / Extension and ±10° Internal / External rotation in part reference to ISO-14242 Part One.[27] Bearings were tested under either standard walking cycle conditions or subjected to 0.8 mm microseparation. The microseparation was effected by applying a negative load during the swing phase to separate the head and cup. The different conditions shall henceforth be referred to as "Standard Gait" and "Microseparation". All tests were performed at 37 °C with Fetal Bovine Serum (FBS) as the lubricant. This was diluted to a 17 g/L total protein content with Phosphate Buffered Saline (PBS). 0.03% Sodium Azide was also added in order to retard bacterial growth and the lubricant was changed every 333,000 cycles.

The Open Circuit Potential (OCP, E_{corr}) was monitored continuously over the course of each test to give a qualitative assessment of the reactions taking place on the exposed surface of the working electrode. Every 10,000 cycles the resistance to polarization (R_p) was determined using Linear Sweep Voltammetry (±25 mV vs. E_{corr} at 1 mV/s). Corrosion currents (I_{corr}) were calculated using the Stern-Geary equation (Equation 2).[28] This was done in order to quantify the material degradation as a result of corrosion. The Tafel constants β_a and β_c were both assumed to be 120 mV throughout the test as per the qualification set previously by Hesketh *et al.*[13,15]

$$I_{corr} = \frac{\beta_a \beta_c}{2.303 R_p (\beta_a + \beta_c)} \tag{2}$$

The corrosion current was then integrated with respect to time in order to give a total charge transfer (Equation 3). Faraday's Law (Equation 4) was used to convert the charge transfer to a mass loss and further to a volume loss as a result of oxidation at the working electrode surface. Due to the assumptions commonly made for pure metals there is some uncertainty in applying Faraday's Law to an alloy. As HC CoCrMo has three main constituent elements, each with different molar masses and half-cell valence numbers, how the data is interpreted can be critical. A weighted average molar mass (66.66) and valence number (2.79) was used based on the approximate percentage alloy composition (Co ≈ 64%, Cr ≈ 43%, Mo ≈ 6%). This assumes a stoichiometric release of ions for the WE surface which may not be the case. Upper and lower error bars therefore represent the values for Cobalt (58.9, 2) and Chromium (51.99, 3) respectively to account for possible preferential release of those elements.

† Trade Name.

$$Q = \int_0^t I_{corr}\, dt \tag{3}$$

Where: Q = Charge Transfer (C)
I_{corr} = Corrosion Current
T = time (s)

$$m = \frac{MQ}{nF} \tag{4}$$

Where: m = Mass loss from oxidation
M = Atomic Mass
n = Valence number
F = Faraday's Constant (96,490 C/mole)

Periodically the WE was also anodically polarized (+50 mV vs. E_{corr}) for 10 seconds and the resultant anodic current transient was sampled at high frequency (100 Hz). An analogue voltage signal was also taken from the hip simulator load cell and sampled at the same rate by the potentiostat. The resultant current is governed by the Butler-Volmer equation (Equation 5) and enables monitoring of the depassivation/repassivation kinetics during a cycle in an attempt to link the tribology of the cycle to the electrochemistry.

$$I = I_{corr}\left\{exp\left(\frac{\alpha_a nF\eta}{RT}\right) - exp\left(-\frac{a_c nF\eta}{RT}\right)\right\} \tag{5}$$

Where: I = Current as a result of applied potential (A)
α_a = Anodic charge transfer coefficient
α_c = Cathodic charge transfer coefficient
η = Applied Overpotential (V)
R = Ideal Gas Constant
T = Temperature (Kelvin)

RESULTS & DISCUSSION

Open Circuit Potential

The Open Circuit Potential (E_{corr}) for both "Standard Gait" and "Microseparation" conditions over the course of the tests can be seen in Figure 2. Initially during a static phase E_{corr} remained relatively noble at approximately -43 and -25 mV under both conditions. Upon the initiation of sliding an abrupt decrease in E_{corr} was noted for both "Standard Gait" and "Microseparation", decreasing to -330 and -350 mV respectively. The OCP gives a qualitative assessment of the reactions taking place on the exposed WE surface. Cathodic shifts in OCP for depassivated alloys are generally regarded to represent an increase in the rate of corrosion taking place as a result of removal of the protective oxide. Cathodic shifts upon sliding have been observed previously for CoCr sliding couples both in tribometer studies[12,29] and in hip simulators.[15,16]

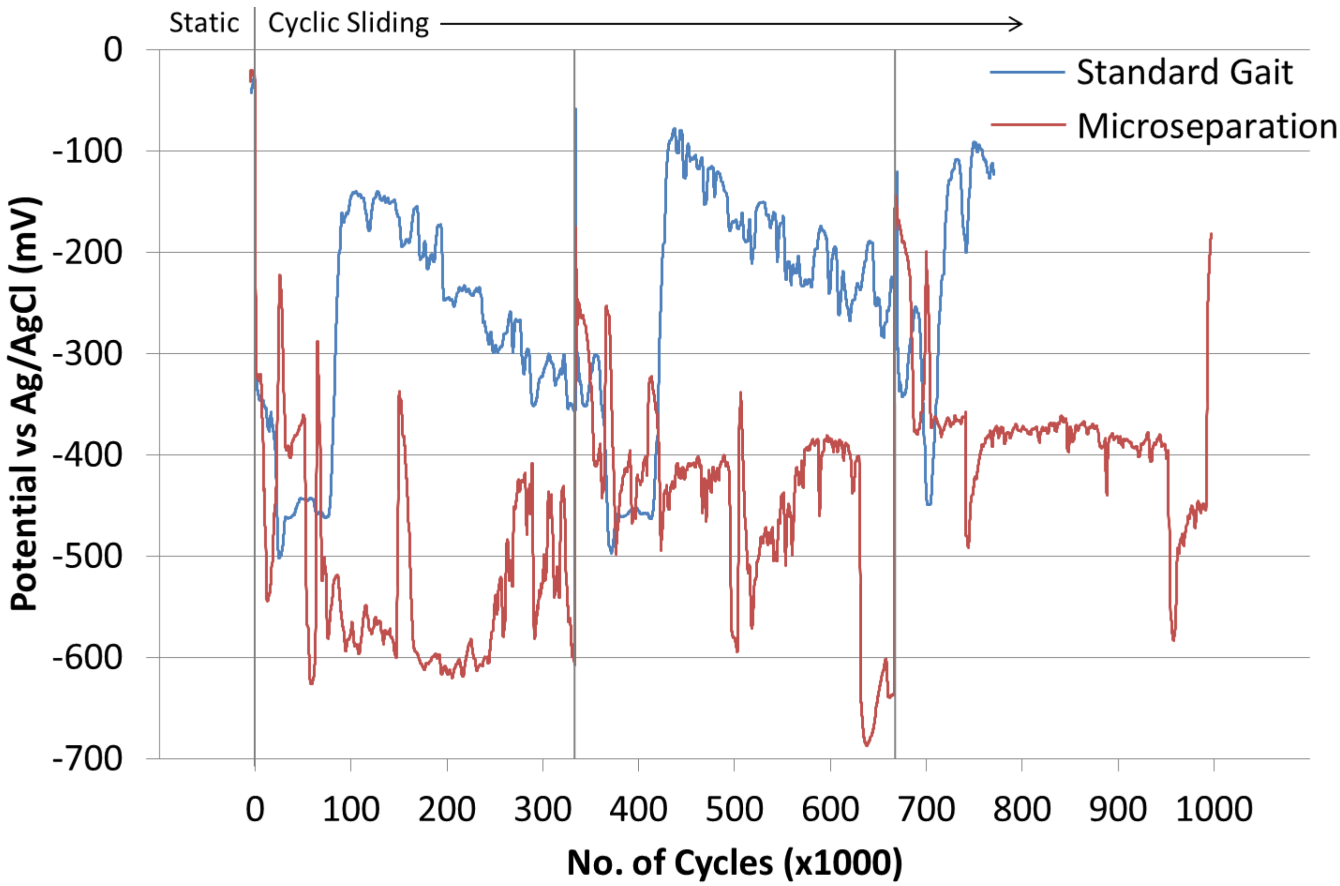

Figure 2: The Open Circuit Potential (E_{corr}) of 28 mm HC CoCrMo bearings subjected to standard gait cycle and 0.8 mm microseparation for 1 MCycles.

Both tests continue to fall to approximately -500 and -540 mV where "Standard Gait" remains until suddenly rising back to almost pre-sliding levels of -150 mv at around 100,000 cycles. Over the remaining time before the first serum change at 333,000 cycles the E_{corr} gradually fell to approximately -350 mV. This pattern of an initial fall from static conditions, a sharp rise and then a further gradual fall is repeated over the next two serum changes. An anodic shift during sliding has been observed previously for 36mm MoM bearings.[15] This was attributed to the formation of Tribochemical Reaction Layers on the bearing surface, which have been studied extensively by other authors.[17,18,30] Termed a "wear-induced" passivation, the formation of the film was thought to protect the material from degradation during ideal articulation.

The E_{corr} of the "Microseparation" test behaved differently with high initial fluctuations before falling and remaining relatively stable at approximately -600, -450 and -400 mV during the three serum phases of the test. Periodically the E_{corr} became unstable and varied between approximately -320 and -700 mV over the entire test. The stable "wear-induced" passivation was not observed under "Microseparation," which was generally observed to be much more transient with sudden Anodic and Cathodic shifts over the entire test. This may represent a rapidly changing contact and be a result of the unstable articulation conditions caused by collision upon heel-strike. As such the formation of a protective tribochemical layer may not have been possible. After the initial drop the OCP on average was much lower under "Microseparation" than under "Standard Gait." This may indicate more material loss as a result of corrosive processes during the adverse loading cycle recreated here.

Corrosive Material Loss

The corrosion currents (I_{corr}) calculated from the periodic determination of polarization resistance (R_p) can be seen in Figure 3. Upon the initiation of sliding a fall in R_p was noted with a corresponding increase in I_{corr} for both test cases. Under "Standard Gait" conditions the corrosion current remained relatively stable between 7.14 and 9.87 µA over the entire test. Following 770,000 cycles an average corrosion current was used to project I_{corr} values over the remaining part of the test due to data lost as a result of a software crash.

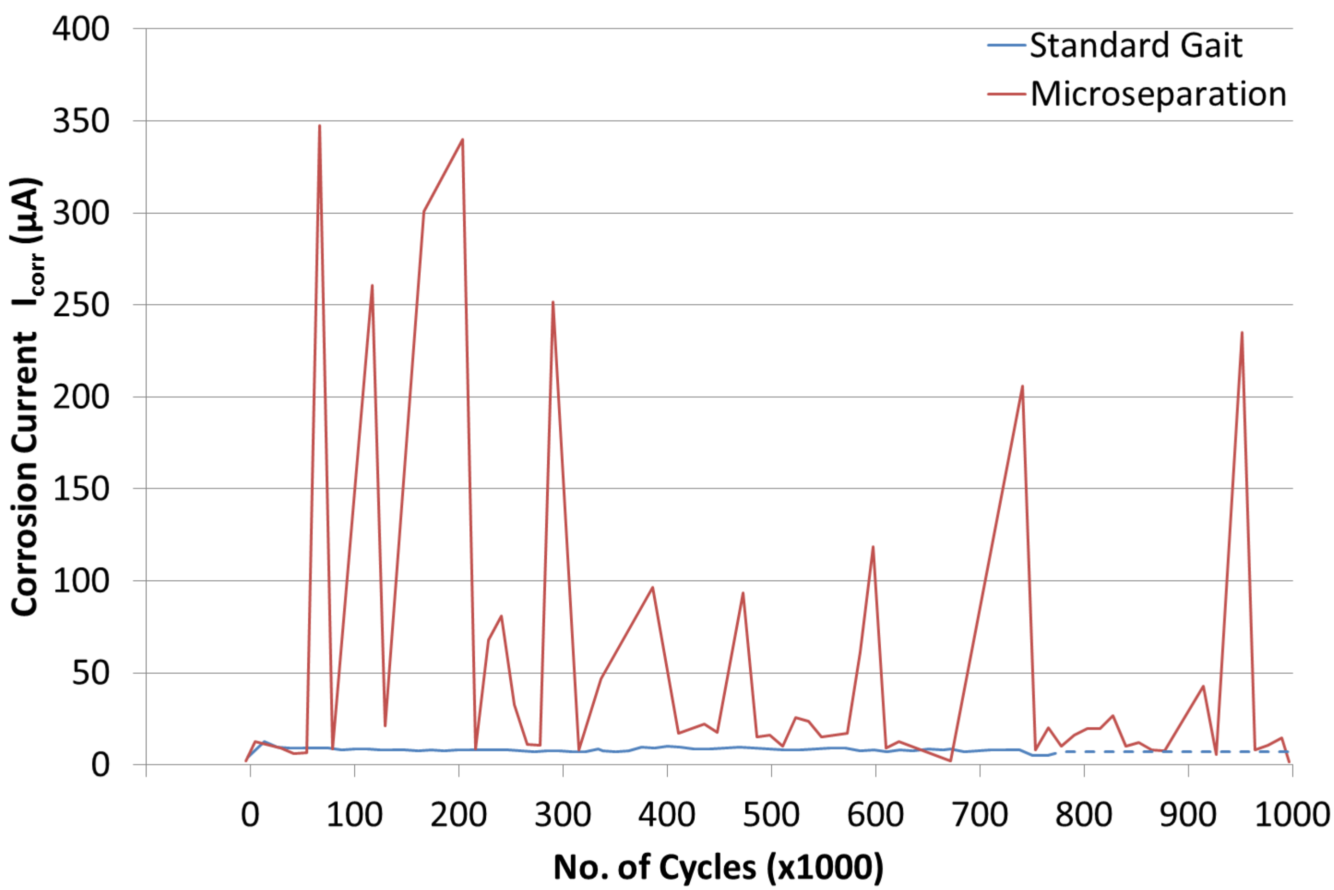

Figure 3: The Corrosion Current (I_{corr}) for 28 mm HC CoCrMo bearings subjected to standard gait cycle and 0.8 mm microseparation for 1 MCycles.

Initially I_{corr} for the "Microseparation" case appeared similar to "Standard Gait" with a low and stable current. At around 70,000 cycles however I_{corr} was observed to spike to 350 µA. Over the entire test the I_{corr} presented a transient behavior and on average appeared an order of magnitude higher than for "Standard Gait" conditions.

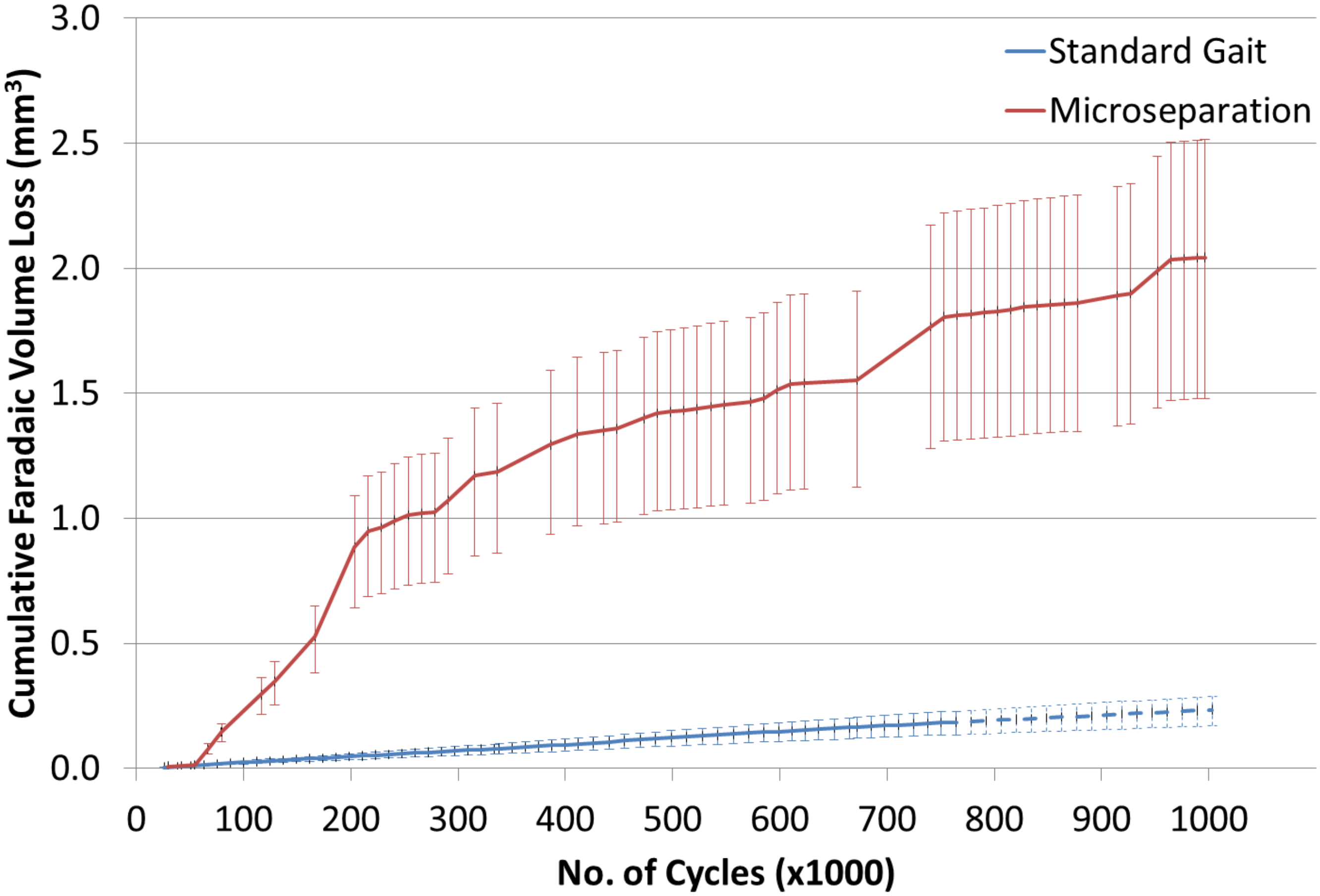

Figure 4: Cumulative Faradaic Volume Loss as a result of oxidation for 28 mm HC CoCrMo bearings subjected to standard gait cycle and 0.8 mm microseparation.

The cumulative Faradaic volume loss calculated using Faraday's Law (Equation 4) for both "Standard Gait" and "Microseparation" can be seen in Figure 4. Under "Standard Gait" the rate of material loss remained consistent over the duration of sliding, as a result of the fairly stable I_{corr}. The cumulative volume loss due to oxidation over the first million cycles was 0.234 mm^3. These bearings are generally considered to be performing well with an overall wear rate of less than 1 mm^3/Mcycle. Corrosive loss under standard gait could therefore be as much as a fifth of total wear.

Under "Microseparation" the rate of material loss was much more variable, due to the transient nature of I_{corr} over the first million cycles. The cumulative volume loss due to oxidation over the first million cycles was 2.044 mm^3, an order of magnitude increase vs. "Standard Gait" and double what is considered a well performing bearing.

Anodic Current Transient

An example of the resultant anodic current transients over three cycles of “Standard Gait” and “Microseparation” can be seen in Figure 5. These transients describe the kinetics of anodic dissolution at the surface of the WE under a small imposed potential (+ 50 mV E_{corr}). When the passive film becomes damaged, either thinned or removed entirely thus exposing the bulk alloy, a spike in current will be seen as the film is repaired and/or ions are lost to the electrolyte.

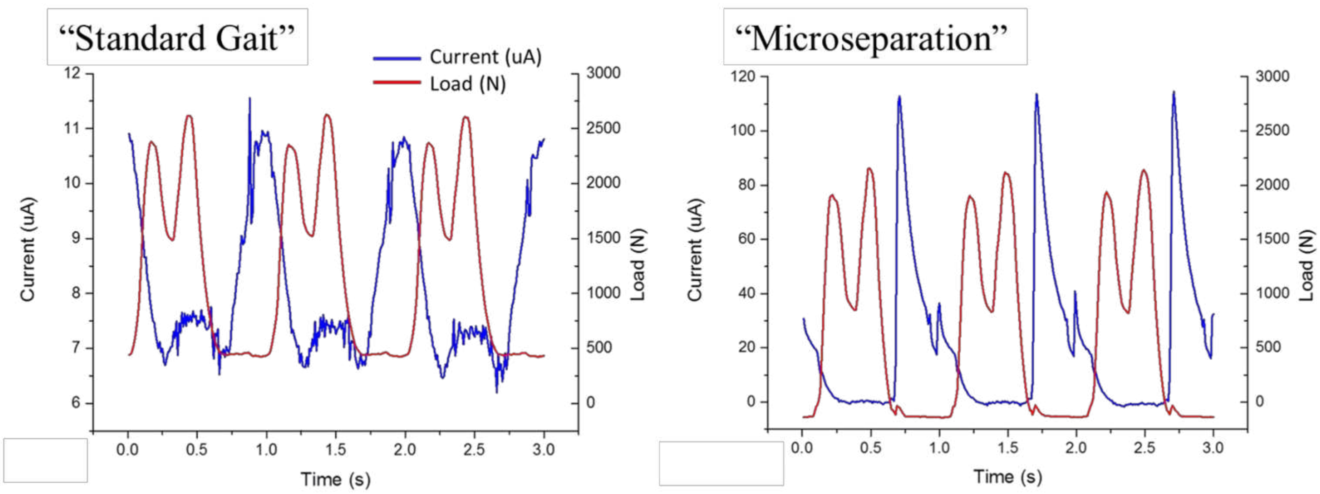

Figure 5: Anodic Current Transients (+50 mV vs E_{corr}) during three cycles of "Standard Gait" and "Microseparation".

A clear periodicity in the anodic current transient was consistently noted for both tests, suggesting a link between the tribology and resultant corrosion. For the “Standard Gait” test case, the anodic current appeared to mimic a dual peak profile, similar to that of the loading curve. A base level of current was established at between 6.5 and 7 µA suggesting a form of continuous depassivation over a cycle. Peaks in current of approximately 7.5 and 11 µA were observed to occur after heel-strike and toe-off loading peaks respectively.

For “Microseparation” a different transient profile was observed with a single peak of approximately 115 µA occurring after the toe-off unloading event. The anodic current then rapidly declines to zero and does not re-initiate during the subsequent loading cycle, only peaking again after unloading.

CONCLUSIONS

It has been demonstrated that MoM bearings depassivate during articulation leading to increased material degradation due to corrosive phenomena. The articulation conditions can have a drastic effect on the level of material lost due to tribocorrosion and thus corrosive phenomena may be much more critical to overall material loss under adverse loading conditions. There also appears to be a clear link between the tribology of an articulating bearing and the depassivation and repassivation of the passive oxide, and thus the material degradation.

Future Work

Although the degradation during the “bedding-in” phase under microseparation has been examined further work is needed to investigate the performance beyond 1 MCycles and thus over the entire service-life of these devices.

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