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Biotribocorrosion of metal-on-metal hip replacements: How surface degradation can influence metal ion formation

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ABSTRACT

To investigate the combined effects of wear and corrosion on the performance of metal-on-metal total hip replacements, tribocorrosion tests were performed on 36 mm diameter joint replacements in an instrumented hip simulator. Corrosion related damage contributed significantly to material loss and to the formation of metal ions, and varied throughout the tests. Changes in corrosion rate were attributed to the formation of tribochemical reaction layers. Cyclic variations in corrosion current may be influenced by elastohydrodynamic film thickness, and the presence of these cycles can indicate when the most severe contact is taking place. Additionally, current hip simulator testing procedures, which adequately accelerate the rate of mechanical wear, were found to under-estimate the amount of corrosion damage expected to take place *in vivo*.

1. Introduction

Tribological performance of Metal-On-Metal (MoM) Total Hip Replacements (THRs) is affected by six major variables; radius, clearance and surface finish, loading cycle, motion, viscosity and boundary lubricating properties of the proteins. Of these variables only the radius, clearance and surface finish can be influenced by the design. The objective is to minimise MoM contact, by separating the opposing surface asperities with a fluid lubricating film. Manipulation of these three factors can control the lubricating film thickness, and hence the wear rate [1,2]. It is very difficult to ensure fluid film lubrication throughout a complete cycle of motion but it has been found that, by increasing the femoral head diameter from 16 mm or 22 mm to >28 mm, a shift from boundary lubrication to mixed lubrication can be achieved [3]. Modern, large diameter MoM hip replacements operate predominantly in the mixed lubrication regime. It is thought that this is facilitated through the action of isoviscous elastohydrodynamic lubrication, but there is some degree of MoM contact leading to wear [2,4]. The wear rate varies throughout each cycle and is governed by the local ratio of effective film thickness of ideally smooth surfaces to the combined roughness of the opposing surface known as the lambda ratio (Λ). The importance of lubricating film thickness on the wear of MoM THRs was demonstrated though analysis of over 70 experiments spanning 5 laboratories [2]. This showed material loss to be inversely proportional to lubricating film thickness to the power 1 and 1.5 approximately, for running in and steady state conditions respectively.

Current MoM hip replacements are typically made from alloys of cobalt, chromium and molybdenum (CoCrMo). These alloys are passive in nature due to the spontaneous formation of a protective oxide layer in air. The oxide layer is predominantly Cr_2O_3 and to a lesser extent oxides of Mo and Co [5–7]. It has been shown through angle resolved XPS that the oxide film thickness increases linearly from 1.8 nm–3.1 nm with an applied potential between 0 and 0.3 V. At greater potentials the increase in thickness is more dramatic owing to the increased cationic fraction of Mo and Co oxides. Co was shown to be the major species dominating active dissolution, and consequently was found to exist in depleting concentration towards the surface of the oxide layer [6,7]. In tribological conditions, the oxide layer present on CoCrMo alloys can be broken down by mechanical wear. When the oxide layer is compromised, the base alloy is susceptible to increased anodic dissolution and the alloy is considered to be electrochemically active; this process is called depassivation. Under reciprocating tribological contact, the passive film is continuously removed and reformed, causing a shifting equilibrium between the two. Experiments have shown that when this occurs, the total material loss is a combination of mechanical wear, corrosion and the synergy between the two [8–11]. Synergy arises as a combination of the effects of wear-on-corrosion and corrosion-on-wear. The effects of wear-on corrosion arise through mechanical depassivation of the material surface, as well as the generation of particulate debris, which may corrode whilst still in contact with the surface. It is worth noting that the mean debris size and the predicted elastohydrodynamic film thickness are similar in magnitude, a few tens of nanometres [2,4,12].

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Experiments have shown that the total charge arising from anodic currents, measured on stainless steel under sliding, correlate well with the total wear volume over a range of experimental conditions [8]. Tribometer studies have exhibited that corrosion reactions contribute significantly to the total degradation of the alloy. By cathodically inhibiting any corrosion reactions and therefore any synergistic reactions too, the total degradation of CoCrMo can be reduced by around 20–50%, depending on the experimental conditions [10,11,13]. When CoCrMo was subject to micro-indentation the surface was plastically deformed and electrochemical noise measurements revealed a peak in anodic current as a result of cracks formed in the passive layer. When the indenter was removed, a considerably greater anodic current was observed as a result of the exposure of the depassivated alloy.

The aim of this paper is to enhance the understanding of simultaneous affects of wear and corrosion governing the degradation of MoM hip bearing surfaces during the running-in period. It intends to establish how variations in the predicted EHL film thickness relate to the electrochemical degradation of the hip through ionisation of the bearing surface. Furthermore, it will attempt to quantify the relative release of metal ions from both particle dissolution and surface depassivation. By using an electrochemically-instrumented simulator, a more detailed understanding of the mechanisms leading to ion and particle formation can be obtained. Emphasis is placed on the importance of viewing the bearing surface as a complex environment in which electrochemical reactions must be considered alongside tribological conditions, in particular elastohydrodynamic lubrication.

2. Experimental methodology

2.1. Equipment setup

In this study, two 36 mm diameter high-carbon (HC) CoCr (ASTM F1537) head/cup pairs were investigated in a Prosim Deep-Flexion hip simulator under biaxial motion of 30° flexion, 15° extension, ±10°axial rotation (axial rotation was out of phase by approximately 0.25 s) and a cup inclination angle of 45°. The tests were conducted in identical conditions and are referred to as test 1 and test 2, although they represent two repetitions of the same test configuration. A standard twin-peak loading cycle was used with a peak load of 3 kN and a swing phase of 150 N at a frequency of 1 Hz. All the bearing surfaces had an initial roughness of between 4 and 7 nm and diametrical clearances between 83 and 86 μm. The lubricant used was foetal bovine serum, diluted to a total protein content of 18 g/l with phosphate-buffered-saline (PBS) and 0.03% sodium azide giving a conductivity of 14.6 mS/m. Tests were run at 37 °C, and the pH of the buffered serum remained at pH 7.4 throughout the test. Tests were run for 1 million cycles in total, but were stopped every 333,000 cycles to permit replacement of the serum solution. In order to minimise disturbance to growth of the tribologically produced surface film (termed tribofilm), the test samples were not removed from the simulator when the serum was replaced. Tribofilms are also referred to as tribochemical reaction layers [14–16], and their formation and composition will form the basis of a future study. Serum was drained from the simulator and the test cell, then refilled and rinsed with distilled water 3 times before refilling with fresh serum. At this point a sample of the used serum was taken for ion analysis by inductively-coupled-plasma-mass-spectroscopy (ICP-MS). For *in situ* electrochemical testing of the joint, the simulator was instrumented with a 3-electrode electrochemical cell, details of which are provided elsewhere [17]. The working electrode connexion was made to the back of the acetabular cup which, in the case of MoM contact, resulted in a working electrode comprised of the exposed head and cup bearing surfaces. A combined Ag/AgCl reference- and platinum counter-electrode was inserted into the gaiter containing the serum solution. The distance between the reference/counter electrodes was kept at a minimum to mitigate the effects of solution resistance on electrochemical measurements. Following testing, surfaces were rinsed with distilled water, weighed and the roughness and roundness of the bearing surfaces was tested using a Taylor Hobson Talysurf PGI 800. Finally, surfaces were cleaned vigorously with a solution of 5% nitric acid, to remove most of the adherent protein layer, before repeated profilometry and mass loss measurements were undertaken. The overall experimental procedure is shown in Fig. 1.

2.2. Electrochemical measurements

For the first 900,000 cycles of testing the open-circuit-potential (OCP) was monitored. The OCP arises from the simultaneous anodic and cathodic reactions taking place at the bearing surface, and gives an indication as to whether the surfaces are passive or active. When monitoring OCP the surface is in free-corrosion conditions, and no net current flows between the working electrode and counter electrode.

Every 10,000 cycles Linear-polarisation-resistance (LPR) tests were undertaken, every 10,000 s, to determine the polarisation resistance (R_p). Polarisation was made from −50 mV to +50 mV with respect to OCP, at a scan rate of 0.067 mV/s.

Anodic and cathodic polarisation was performed to determine the Tafel constants β_a and β_c, necessary for converting R_p into a corrosion rate, as shown in Eq. (1). The cathodic scan was performed from +50 mV to −250 mV (Vs OCP) and the anodic scan was performed from −50 mV to +250 mV (Vs OCP). Cathodic scans were performed first, following which the OCP was allowed to equilibrate prior to the anodic scan. All electrochemical testing was undertaken using an Autolab PGStat 101.

$$i_{corr} = \frac{\beta_a \beta_c}{2.303 R_p(\beta_a + \beta_c)} \tag{1}$$

At approximately 100,000, 200,000 and 300,000 cycles into each 1/3 million cycles, the current under potentiostatic polarisation was measured. Each polarisation test was performed at +100 mV (Vs OCP), and was sustained for just 100 s to minimise the effects of accelerated anodic dissolution on the surface. The current produced by a corroding surface under an applied potential is governed by the Butler–Volmer equation Eq. (2):

$$i = i_{corr}\{exp-(\alpha nF\eta/RT)-exp((1-\alpha)nF\eta/RT)\} \tag{2}$$

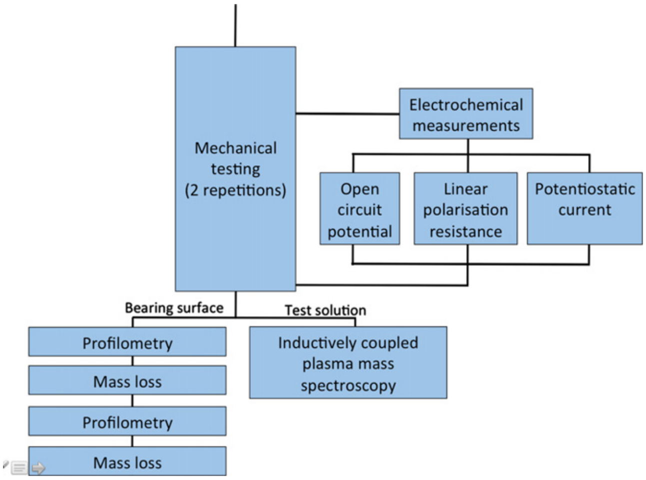

Fig. 1. Flow chart of experimental procedure.

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