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Real-time corrosion measurements to assess biotribocorrosion mechanisms with a hip simulator

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ABSTRACT

Due to the reduced wear compared to the metal-on-polyethylene implant, second generation metal-on-metal hip prostheses have been widely used as the replacement in younger patients in recent years. Osteolysis induced by polyethylene wear debris was a major concern with metal-on-polyethylene hip replacements. In metal-on-metal total joint replacements, however, there has been concern about the incidents of pseudo tumours as a result of the production of very fine wear debris and the associated production of metallic ions of Co and Cr. The origins of the metallic ions may be from two potential sources: from the bearing surface and from the dissolution of wear debris produced by the tribological action or the production of ions by depassivation of the CoCr alloys.

Although there has been extensive work on simulation of wear processes in hip joint replacements through hip simulators running over prolonged periods and mapping the wear rates, to date there have been several attempts to measure the interactions (biotribocorrosion) between corrosion and tribology *in-situ* in simulated body fluids using a hip simulator. This paper describes the instrumentation of an integrated hip joint simulator to provide electrochemical measurements in real-time. The open circuit potential and polarization experiment results are reported and the importance of these measurements to gain an understanding of the origins of metal ions and to complement the wealth of wear data available is discussed.

1. Introduction

There are two main categories of joint replacements, according to the characteristics of the bearing materials: hard-on-soft and hard-on-hard systems. Metal-on-polyethylene (MoP) type bearing systems fall into the hard-on-soft category. A number of studies have shown that polyethylene wear debris can lead to osteolysis and result in failure and the need for revision operations [1–3]. Metal-on-metal (MoM) hip replacements present a hard-on-hard bearing interface. MoM hip replacements and hip resurfacing replacements were reintroduced in the last decade due to the considerable reduction in volumetric wear, theoretical advantages and indications of promising clinical survival results [4,5]. Particularly for younger patients, MoM implants have been seen to offer promise in terms of enhanced wear resistance, decreased risk of dislocation (when using large diameter variations) and increased range of motion.

Extremely sever clinical problems have been seen in MoM hip replacements after relatively short times leading to significant debate in the community and through the general media about their safety. There are reports of pseudotumour formation as a result of localized areas of particulate debris and metallic ion [6]. MoM implants are now found to be in the centre of a huge debate where there are still a number of unknowns. The most pertinent are being where the metal ions originate from. The current paper can make a contribution to the understanding of MoM performance. A hip simulator has been instrumented to enable the ion generation as a result of the depassivation of the acetabular cup and femoral head to be quantified by electrochemical measurements *in-situ*.

The progress going on at the tribological interface in a hip simulator (and ultimately *in vivo*) are essentially tribocorrosion. Tribocorrosion is defined as the chemical, electrochemical and mechanical processes leading to a degradation of materials in tribological contacts operating in a corrosive environment [7,8]. The mechanism of damage is not restricted to hip joints but occurs anywhere where there is a tribological influence (erosion, sliding, wear, abrasion, etc.) in conjunction with a corrosive fluid. Neville et al. examined erosion–corrosion behaviour for materials under slurry conditions where mechanical impact by particles temporarily removes the passive film and corrosion can occur [9,10]. In many ways the damage, which is a combination of

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Nomenclature

c	radial clearance
C'	weight loss due to pure corrosion
C_E	erosion effect on corrosion
CE	counter electrode
E	weight loss due to erosion
E'	effective elastic modulus
E_1	elastic modulus of the femoral head
E_2	elastic modulus of the cup
E_c	corrosion effect on erosion
h_{min}	minimum film thickness
ICP	inductively coupled plasma
MoM	metal-on-metal
MoP	metal-on-polyethylene
OCP	open circuit potential
R_1	radius of the femoral head
R_2	radius of the cup
Ra_c	surface roughness of the cup
Ra_h	surface roughness of the femoral head
R_x	equivalent radius
RE	reference electrode
S	synergy
TWL	total weight loss
W	weight loss due to pure mechanical damage
WE	working electrode
XPS	X-ray photoelectron spectroscopy
η	viscosity of synovial fluid
u	entraining velocity
λ	lambda ratio

mechanical and electrochemical processes, was analogous to the biotribocorrosion experienced by hip joints. Material degradation was evaluated and a description of the components of the damage was used to separate material loss (Eq. (1)) caused by mechanical impact, electrochemical processes and their interactions. Many other authors in tribocorrosion use Eqs. (1)–(3) in different forms to assess the components of damage in processes where tribology and corrosion interact.

$$TWL = W + C' + S \tag{1}$$

$$S = W_C + C_W \tag{2}$$

$$TWL = W + C' + W_C + C_W \tag{3}$$

TWL is the total weight loss in a wear-corrosion environment. The pure material degradation caused by mechanical wear is shown as W. C' is the material loss due to the electrochemical corrosion process only. S is the synergy effect which involves W_C (the corrosion effect on wear) and C_W (the wear effect on corrosion).

There are also a few research focused on a thin layer formed on the bearing surface as a result of operating in the simulated and real conditions. The nature of the thin layer so called tribofilm was under investigation. Liao et al. found that the film is carbon rich and had graphitic properties [11]. Wimmer, Cann and other researchers noticed protein precipitates on the bearing surface containing calcium, oxygen, phosphors, *etc.* [12–14]. The authors also found organometllic formation on sample surfaces in tribometer tests [15]. This tribofilm not only can lubricate the tribological contacts but also can regulate ion release.

The *in-situ* electrochemical measurements in the hip simulator are used to assist in the understanding of two key aspects of hip joint tribocorrosion: (a) the release of ions from the surface due to the motion/contact depassivation of the head/cup; (b) understanding the interactions between the surface and the lubricant to form the so-called tribofilm.

2. Experimentation and materials

The ball-in-socket geometry presented by hip joints is often presented by a ball of equivalent radius R near the plane surface of a semi-infinite solid. The equivalent radius can be calculated from:

$$\frac{1}{R_x} = \frac{1}{R_1} + \frac{1}{R_2} \tag{4}$$

where R_1 and R_2 are the radii of the femoral head and acetabular cup, respectively. The difference between R_2 and R_1 is the radial clearance, c. For all tests in this paper, the normal diameters of the femoral heads were 36 mm and the diametrical clearances $2c$ were in the range of 95–105 μm.

The minimum film thicknesses (h_{min}) were calculated using the Hamrock and Dowson equation [16].

$$\frac{h_{min}}{R_x} = 2.75\left(\frac{\eta u}{E' R_x}\right)^{0.65}\left(\frac{w}{E' {R_x}^2}\right)^{-0.21} \tag{5}$$

where η is the viscosity of synovial fluid:

The entraining velocity is u ($u = (u_1 + u_2/2)$) and w is the load. R_x is the equivalent radius for a ball on-plane model. E' is an effective elastic modulus $1/E' = 1/2((1-\nu_1^2)/(E') + (1-\nu_1^2)/(E'))$. The minimum film thickness is related to the head radius and radial clearance in a certain lubricant.

The predicted minimum film thickness, together with the composite surface roughness of the bearing surfaces $(Ra_h^2 + Ra_c^2)^{0.5}$ was used to predict the lambda ratio, λ, which is a dimensionless parameter indicating the severity of contact and the lubricating regime of the system.

$$\lambda = \frac{h_{min}}{(Ra_h^2 + Ra_c^2)^{0.5}} \tag{6}$$

where Ra_h and Ra_c are the surface roughness (R_a) values for the head and the cup, respectively. It has been shown [17] that if the lambda ratio is greater than 3, fluid film lubrication is predominant. A value below 1 indicates that the boundary lubrication prevails, and between 1 and 3, the system is operating in a mixed lubrication regime. MoM bearings are believed to operate in the mixed lubrication regime most of the time, depending on the loading conditions and speed [18], although a large percentage of the load is supported by elastohydrodynamic films. It means that at the interface, there are asperity contacts between the metallic femoral head and metallic acetabular cup with an interfacial fluid film between asperity contacts.

Detailed set up can be seen in another paper [19]. 25% (v/v) bovine serum supplemented with 0.1% (w/v) sodium azide to retard bacterial growth was used as the lubricant. To reduce the effect of bacteria, the longest test was carried out for 125 h (450,000 cycles) without pause. Short tests were also conducted for 30,000 cycles. During each test, serum was not replaced until the test finished ensuring that conditions were not affected by replacing serum during testing. The frequency of the motion was controlled at 1 Hz. For each condition, 3 samples (cup and head couple) were studied for repeatability. The clearance was controlled at 100 ± 5 μm.

After each test, the hip implant couple was weighed to determine the total loss of CoCrMo from the prosthesis. The serum samples were