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Fretting corrosion characteristics of polished collarless tapered stems in a simulated biological environment



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ABSTRACT

The role fretting-corrosion plays on the degradation and formation of debris within the stem cement interface was investigated. Electrochemical measurements of potential and polarisation resistance, along with solution mass spectroscopy were employed. Optical, Scanning Electron and Transmission Electron Microscopy with Energy Dispersive X-Ray Spectroscopy techniques were utilised to observe surface morphology after fretting-corrosion tests. Electrochemical measurements indicated dynamic loading resulted in de-passivation of the metallic surface. Solution mass spectroscopy indicted high concentrations of cobalt were released from the interface, accounting for 94% of all metallic ions released into the environment. Detailed imagery of fretting-corrosion product indicated a chromium and oxygen layer on the metallic and bone cement surface owing to the electrochemical stability of species released as a result of fretting-corrosion.

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1. Introduction

Although a recent decline in the number of cemented Total Hip Replacements (THR) has been seen in UK registry figures, the method of cementing femoral stems still remains an extensively practiced technique in patients aged 65 and over, with superior short term results been observed for cemented THR [1]. During THR, the medullary canal is reamed to size using a series of reamers and rasps and a poly methyl-methacrylate (PMMA) cement restrictor placed at the bottom of the canal and the PMMA bone cement is introduced and pressurised in a retrograde fashion with respect to the distal portions of the femur. The femoral stem is then introduced into the PMMA bone cement, until the desired position is met and the remaining cement cleaned away to leave the bone cement mantle. This introduction of the stem into the bone cement has been shown to result in interactions at the stem–cement interfaces, undesirable from both a mechanical loading and electrochemical point of view, resulting in the release of metallic and PMMA bone cement wear debris, along with potentially toxic metal ions into the biological system [2–6].

The subject of mechanically-induced crevice corrosion of cemented femoral stems was a topic first brought to light by Willert et al. [7] in the 1970s describing the early failure of cemented Titanium (Ti) Muller Straight stems. However, recently interest has been renewed due to the cases reported by Donnell

et al. and Bolland et al. [8,9]. Both cases describe the early failure of cemented collarless polished tapered cobalt chromium alloy stems coupled with a metal-on-metal (MoM) articulation due to localised corrosion of the cemented regions of the femoral stem resulting in extensive soft tissue necrosis as a result of the metal ion release.

To date there have been only a few studies that have attempted to understand and quantify the occurrence of fretting-corrosion at the stem cement interface [10–13]. However many studies have assumed a simplified model in order to gain an insight into the complex fretting-corrosion interactions existing at the stem–cement interface [14,15]. Furthermore, the influence of such variables as galvanic coupling, bone cement type and variation in loading still remain unknown. Consequently, the purpose of this study was to characterise and quantify the general electrochemical response at the stem/cement interface as well as any tribochemical reactions occurring within the interface and the influence fretting-corrosion has on the external environment.

2. Materials and methods

2.1. Electrodes and solution

Low carbon CoCrMo Ultima TPS™ (DePuy International, Leeds, UK) collarless polished femoral stems ($n=3$) were utilised as the working electrode (WE) in this study (Table 1). Each femoral stem went through a forging process and was then mechanically polished

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to a surface roughness of $R_a \approx 0.05 \mu\text{m}$. Samples were then cleaned and passivated by DePuy International (Leeds, UK) in order to replicate surface treatment post manufacturing. A Thermo-scientific Sureflow Redox combination electrode, consisting of a Ag/AgCl reference electrode and Pt counter electrode was also employed. The solution used for electrochemical measurements was 0.9% NaCl solution (pH 7.4, 8 ppm O_2), which was made up from analytical grade reagent and deionised water.

2.2. Setup for fatigue and fretting corrosion measurements

A novel test method was developed and conducted in part reference to ISO 7206-4 to evaluate the mechanically enhanced corrosion mechanisms at the stem–cement interfaces of fully cemented femoral components. Firstly, a collarless polished LC CoCrMo stemmed component was cemented into a specially designed polymer mould using SmartSet[®] HV bone cement (DePuy International, Leeds, UK). Once polymerisation of the cement had occurred, the fully cemented stem was removed from the polymer mould, orientated at 10° flexion and 9° abduction to achieve torsional forces experienced *in-vivo* and placed into the test fixtures. The stem–cement component was then set in place using a lab grade PMMA resin. The protruding part of the specimen was then encased in a flexible silicon gaiter and immersed in 600 mL of 0.9% NaCl solution at $37 \pm 1^\circ\text{C}$. Initially a static load of 200 N was applied to the femoral stem for 24 h in order to simulate a time of no load bearing after surgery and also to let the system achieve equilibrium before cyclic testing in order to understand the initial passivation mechanics. After

24 h, a cyclic load of 200 N–2300 N at 1 Hz for 1 million cycles was applied to the stem through a $\varnothing 28$ mm LC CoCrMo femoral head and UHMWPE liner for 1 million cycles. Care was taken to seal the modular taper interfaces so to eliminate any additional effects. The head and liner interfaces were not immersed to ensure they did not contribute to the electrochemical signal. An integrated thrust bearing was also utilised with the intention to mitigate any de-passivation at the loading interface and loads not coincident with the axis of the testing machine. Fig. 1 demonstrates the test setup utilised in this study.

2.3. Electrochemical measurements and corrosion morphologies observations

An integrated 3-electrode electrochemical cell was employed in order to monitor the electrochemical responses at the stem/cement interface as a result of dynamic loading. Intermittent Open Circuit Potential (OCP) values and Linear Polarisation Resistance (LPR) measurements were recorded every 30 and 3600 s respectively. LPR measurements were conducted using a PGSTAT101 potentiostat/galvanostat (Metrohm Autolab B.V, Utrecht, NL) from $\pm 50 \text{ mV}_{\text{OCP}}$ at a scan rate of 0.25 mV/s in order to quantify the fretting corrosion characteristics at the stem–cement interfaces. Corrosion current was then calculated from experimentally obtained R_p values using the Stern–Geary equation [16] and plotted as a function of time.

Upon completion of each test the electrolyte was drained into a sterile polyethylene bottle and stored in the freezer until analysis to prevent further degradation of the solution. Prior to analysis, samples were defrosted for 24 h. 1 mL of bulk electrolyte was then extracted using a polymer tipped pipette and stabilised in 9 mL of 2% HNO_3 . Inductively coupled plasma mass spectrometry (ICP-MS) was utilised to determine concentrations of Co^{2+} , Cr^{3+} and Mo^{2+} released during free corrosion conditions as a result of mass transfer from the crevice to the bulk electrolyte. Isotope Co 59, Cr, 52 and Mo 96 were used in order to quantify the amount of metal ions released from the metal–cement interface. Cr 52 was

Table 1
Chemical composition for materials according to the American Society for Testing and Methods.

Material	C	Co	Cr	Mo	Fe	Ni
LC CoCrMo	0.05	Bal.	27.4	5.7	0.17	0.1

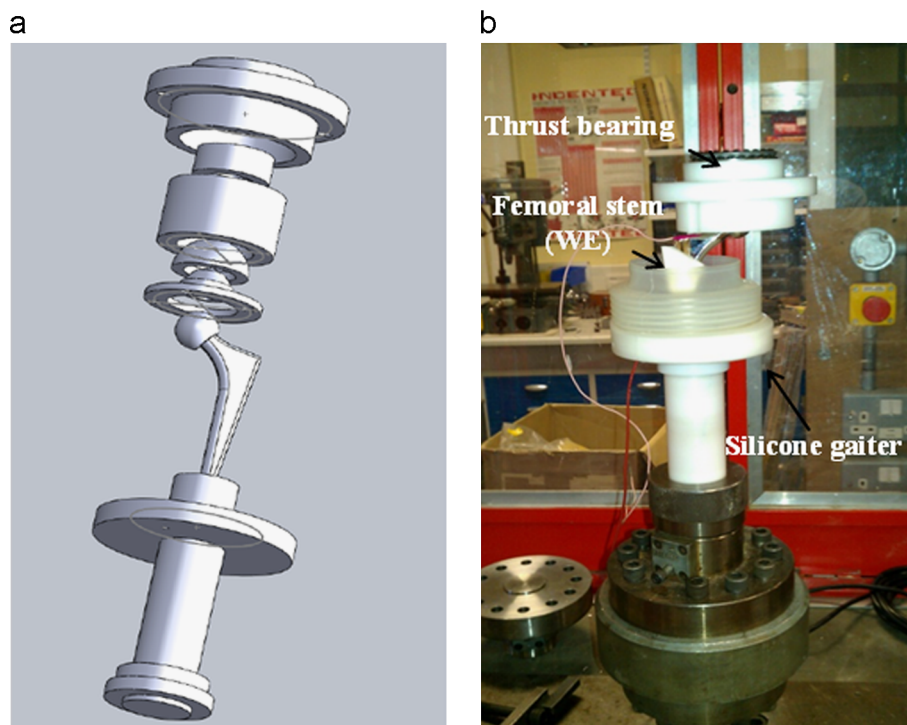


Fig. 1. (a) CAD and (b) Image of test setup utilised in order to simulate a gait cycle.

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