

Sub-surface characterisation of tribological contact zone of metal hip prostheses

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Abstract. Many metal on metal joint failures have been associated with adverse local tissue reactions due to the response of the body to wear debris and corrosion products, released from the bearing surface or the taper interface. Both a carbonaceous layer and an oxide film are reported on the CoCrMo metal joints, which play important roles in the wear resistance of the material. However, there is a lack of quantitative data on the structure and distribution of the carbonaceous layer and the oxide film. The current work provides a detailed investigation of the surface damage on retrieved CoCrMo taper interfaces. In addition, systematic differences in the starting surface structure of biomedical CoCrMo were studied through a comparison of a standard mechanical polished (MP) and an electropolished (EP) surface after reciprocating test. Site-specific FIB/TEM cross-sections show the evidence of the carbonaceous layer and the oxide film on both CoCrMo taper interfaces and MP, EP CoCrMo, ranging from 5 -500 nm depending on the location. The amorphous carbonaceous layer exhibits a π * peak in the EEL spectra, with trace of Ca and N. The oxide film on the taper interfaces has a porous texture and HRTEM indicates chromium oxide nano-crystals in an amorphous background, however, only a very thin oxide film (~ 2 nm) exists on MP and EP CoCrMo after reciprocating test.

1. Introduction

Metal debris and metal ions released from CoCrMo alloys is the subject of considerable interest due to the higher than expected failure rate of metal on metal (MoM) hip replacements [1, 2]. The Medicines and Healthcare Products Regulatory Agency (UK) and the Food and Drug Administration (US) issued alerts for all MoM hip replacement in 2010 and 2011, respectively, with concerns on the adverse local tissue reactions (ALTR) to metal ions, resulting dramatic drop of the MoM market in recent years. Metal ions and debris release is not only derived from the bearing surfaces, but can also arise from the taper interface between the head and stem components of modular total hip replacements [3]. Release of material from this interface has been linked to ALTR from MoM and Metal on Polymer (MoP) joints. It is well known that an oxide film is present on the surface of CoCrMo and plays an important role in the corrosion resistance of CoCrMo alloy. In addition, a tribo-layer due to tribochemical reactions has been widely observed in MoM prostheses by several authors [4, 5]. Despite the importance of these layers, there has been a relative lack of quantitative data on the structure of these layers. Furthermore, the effect of the starting structure of the CoCrMo alloy on the subsequent wear behaviour has not been established. In the current study, detailed analyses of near surface layers on the taper interfaces, as well as the biomedical grade CoCrMo with different surface finish (MP and EP) under reciprocating wear test, are provided using extensive site-specific transmission electron



microscopy (TEM) with associated high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS).

2. Experimental procedure

The taper interfaces of two retrieved femoral heads were studied. The two femoral heads were a 40 mm (Case1) and a 44 mm (Case 2) diameter zero offset low Friction Ion Treatment (LFIT™) CoCrMo anatomic heads which were both retrieved after 4 years *in vivo*. The bearing was a MoP articulation against a zero degree X3 polyethylene liner in a Trident HA (hydroxyapatite) coated acetabular shell made of Ti6Al4V ELI (Extra Low Interstitial). The stem was an Accolade Femoral stem, made of a β -titanium alloy (TMZF: titanium, molybdenum, zirconium and iron). Ethical approval was granted by the National Research Ethics Service Committee South Central-Southampton A. The samples were sterilised and stored separately in 10% buffered formalin.

The cast biomedical grade CoCrMo alloy of the reciprocating wear test was obtained from Finsbury Orthopaedics Ltd (UK). The chemical analysis revealed that the material matched the specifications required for the ASTM F75 standard. All CoCrMo were subjected to a mechanical polish, including those to be electro-polished. The electro-polishing was undertaken by a specialist electro-polishing company (Anopol Ltd., Birmingham, UK). Mechanical polished and electro-polished CoCrMo, namely MP and EP CoCrMo, were under reciprocating sliding test performing on a reciprocating ball-on-plate UMT tribometer (Bruker, USA), using 25 vol% bovine serum albumin (BSA) solution at room temperature. A wear track length of 10 mm, reciprocating at 600 rpm (02 m/s) under various loads (i.e. 2N and 4N) were chosen as the standard test parameter.

Site-specific TEM cross-sections of taper interfaces and wear tracks of MP and EP CoCrMo were prepared using a Quanta 200D FIB-SEM (FEI, the Netherlands). HRTEM with Cs corrector (Jeol R005, Jeol, Japan) in conjunction with electron energy loss spectroscopy (EELS, Gatan, USA) was employed to analyse the near surface structure.

3. Results and discussion

The initial surface finish was different on the taper interfaces and the MP, EP surfaces. A rough surface exhibiting the machining marks from the manufacture process could be seen on the taper interfaces. The EP CoCrMo has a highly polished surface free of residual deformation, whereas the MP CoCrMo has a highly polished surface with residual deformation comprising ϵ -martensite plates, mechanical twins and a high dislocation density. Despite the difference in surface finish, both carbonaceous layer and oxide film were observed from the taper interfaces and the MP, EP CoCrMo, as shown in Fig.1a and Fig.1b (sub-layer in the carbonaceous layer in Fig.1b is due to re-deposition of Pt). The thickness of the carbonaceous layer varied from region to region on the taper interfaces, ranging from 20 nm to 500 nm. A difference in the thickness of the carbonaceous layer was also seen on the MP and EP CoCrMo after reciprocating test at various loads, with ~ 30 nm for MP-2N, ~ 500 nm for MP-4N, ~ 40 nm for EP-2N and ~ 10 nm for EP-4N. Interestingly a thinner carbonaceous layer was seen for EP-4N compared with EP-2N. In addition, the carbonaceous layer on the taper interfaces and the MP CoCrMo samples was detectable. The carbonaceous layer was predominantly amorphous but with some small crystals in range of ~ 2 nm were observed (as shown in Fig.1c and circles in Fig.1e). Those nano-crystals were believed to be chromium oxide trapped in the carbonaceous layer.

The oxide film observed on the taper interfaces showed a porous structure (Fig.1a), ranging from 10 - 100 nm from region to region. HRTEM image (Fig.1d) showed nano-crystals ~ 2 nm embedded in the amorphous material. These nano-crystals were confirmed to be chromium oxide by EELS (spectrum 4 in Fig.2). A thin layer of oxide film of ~ 2 nm was observed from the MP and EP CoCrMo sample after reciprocating test, as shown in Fig.1e. HRTEM image indicated that the oxide film was a thin layer of nano-crystals and EEL spectrum (spectrum 3 in Fig.1) confirmed they were chromium oxides.

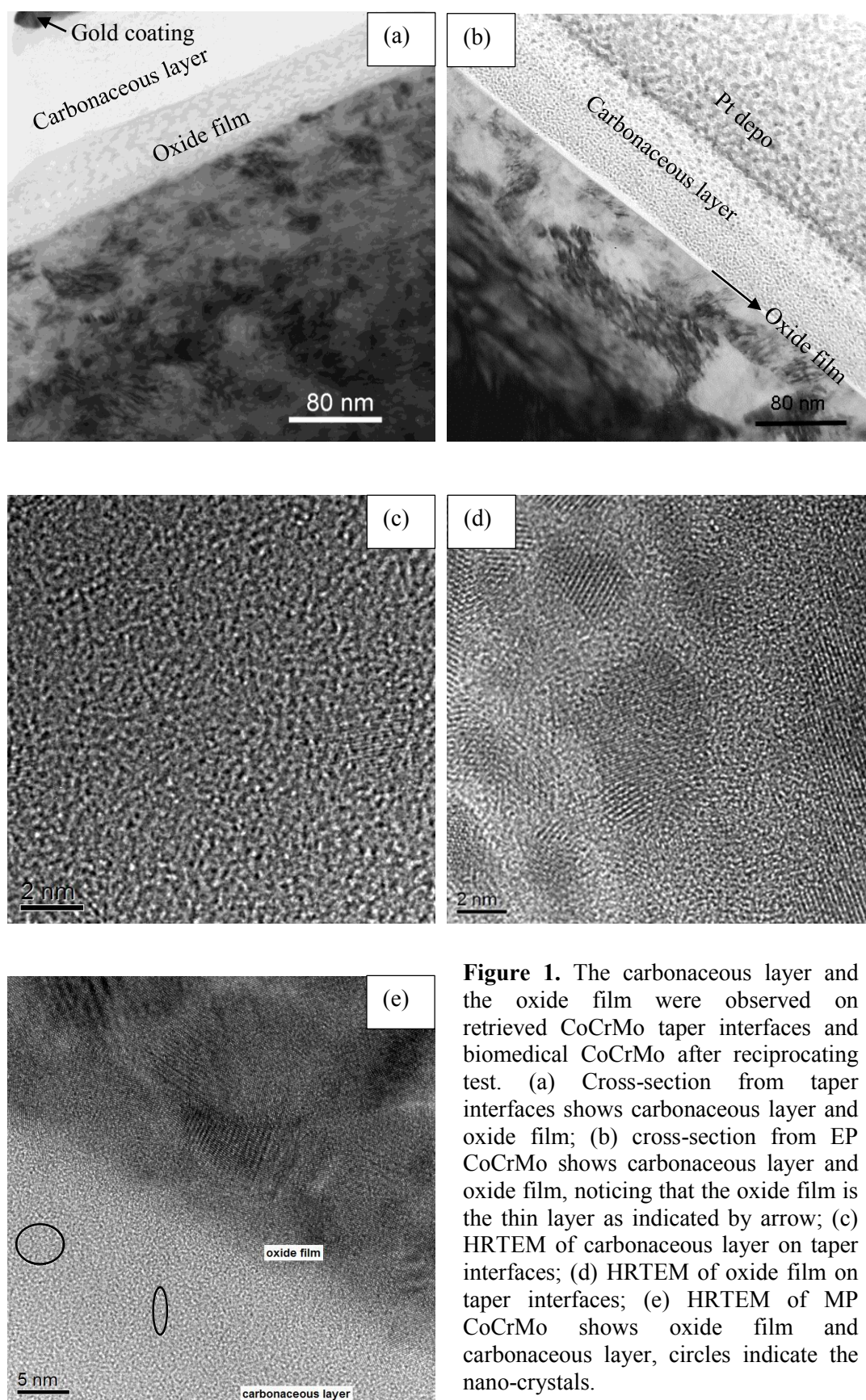


Figure 1. The carbonaceous layer and the oxide film were observed on retrieved CoCrMo taper interfaces and biomedical CoCrMo after reciprocating test. (a) Cross-section from taper interfaces shows carbonaceous layer and oxide film; (b) cross-section from EP CoCrMo shows carbonaceous layer and oxide film, noticing that the oxide film is the thin layer as indicated by arrow; (c) HRTEM of carbonaceous layer on taper interfaces; (d) HRTEM of oxide film on taper interfaces; (e) HRTEM of MP CoCrMo shows oxide film and carbonaceous layer, circles indicate the nano-crystals.

The thickness and the structure difference of the oxide film on the taper interfaces and the MP, EP CoCrMo could be due to the surface finish. On the taper interfaces, the initial oxide film was thick because of the rough surface finish, which acted as the contact zone and the tribochemical reactions could be the reason to form later thick and porous oxide film. However, with a highly polished surface finish, there was a thin/no oxide film on as-polished surface, which led to a thin oxide layer (~ 2 nm) on the MP and EP CoCrMo after reciprocating test.

The EEL spectrum from the carbonaceous layer on the taper interface (spectrum 1 in Fig.2) showed C-K, Ca-L, N-K and O-K edges. No Cr-L edges were observed, even though small (<2 nm) chromium oxide particles were present inside the carbonaceous layer (Fig.1c). The carbonaceous layer on the MP CoCrMo gave a similar result, spectrum 2 in Fig.2 although the Ca-L peak was more pronounced in this case. The oxide film on the MP CoCrMo, EEL spectrum (spectrum 3 in Fig.2) showed not only O-K and Cr-L edges, but also C-K, Ca-L and N-K edges. The oxide film was only ~ 2 nm such that the spectrum probably contained a signal from the nearby carbonaceous layer. Spectrum 4 in Fig.2 was from the oxide film on the taper interface, showing C-K, O-K and Cr-L edges. A π^* peak was observed in all C-K edges.

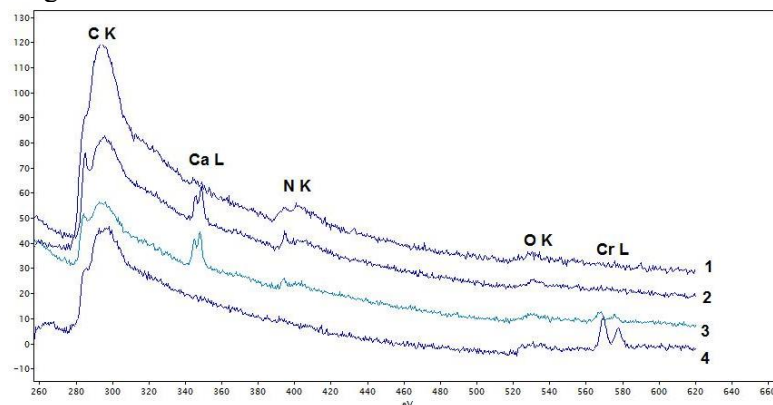


Figure 2. EEL spectra of carbonaceous layer on taper interface (1), oxide film on MP CoCrMo (2), carbonaceous layer on MP CoCrMo (3) and oxide film on taper interface (4).

4. Conclusions

The electropolishing produced a surface free of residual deformation, whereas the mechanical polishing resulted in significant residual deformation in the surface, as seen in the taper interfaces and MP CoCrMo after reciprocating test. Both carbonaceous layer and oxide film were observed from the taper interfaces and the MP and EP CoCrMo after reciprocating test. The amorphous carbonaceous layer exhibit a π^* peak in the EEL spectra, with trace of Ca and N. In addition, the carbonaceous layer on the taper interfaces and the MP CoCrMo after reciprocating test were thick and detectable, whereas a thin carbonaceous layer was seen on the EP CoCrMo after reciprocating test. The oxide film on taper interface has a porous structure and HRTEM indicated chromium oxide nano-crystals in an amorphous background, however, only a very thin oxide film (~ 2 nm) exists on MP and EP CoCrMo after reciprocating test.

References

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