

An Analysis of Corrosion Products caused by Fretting/Wear-Accelerated Crevice Corrosion on Retrieved Co-Cr-Mo Implants

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Statement of Purpose: The deposition of corrosion products outside of crevices formed between modular orthopaedic implant components has long been observed and described under both laboratory and clinical conditions [1, 2]. Properly identifying the origin of the corrosion and wear product deposits in the neck area of metal-on-metal hip implants [3] requires a comprehensive electrochemical and mechanical analysis of these complex systems that have two distinct metal-metal crevices. One crevice is the long and narrow opening between the articulating surfaces, which can be termed a ‘polished’ crevice. The other crevice can be formed – depending on design features and care/skills of assembly – at the taper junction, which may show the characteristics of a corroded or ‘etched’ crevice which can be accelerated by micromotion [4, 5] (Figure 1). In this study, we analyzed two different types of deposits, to learn more about their composition and potential origin.

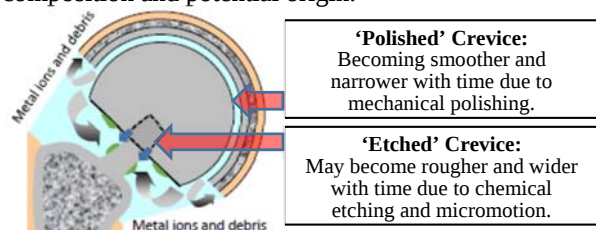


Figure 1. Different types of crevices in MoM implants.

Methods: The elemental and chemical compositions of two potential corrosion product deposits from CoCrMo alloy hip explants (provided by Anderson Orthopedic Research Institute) were analyzed by XPS. Deposit A was removed from a MoP hip as an almost intact piece with a relatively smooth underside where it had been in contact with the hip implant that showed evidence of considerable wear. This smooth underside surface had mixed light and dark areas (Figure 2.a). Deposit B was from a MoM hip stem, and was a stickier, more film-like layer (Figure 2. b & c). A sample was removed by sliding a new razor blade over the surface. The sample was of various colors from near white to a dull green.

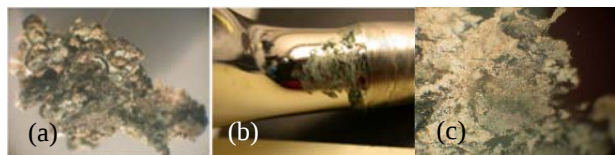


Figure 2: (a) Deposit A and (b and c) - Deposit B

The XPS analysis was performed over an elliptical area irradiated by the low-energy (1487 eV) monochromatic aluminum K α x-ray with a major axis of 1.0 mm and a minor axis of 0.5 mm. The depth of the analyzed volume was about 8 nm, determined by the small mean-free path of the emitted photoelectrons. The elemental survey spectra cover the binding energy range from 0 to 1100 eV, with a step size of 0.5 eV. Each sample was also ion etched using a PHI 04-303 Ion Sputter Gun.

Results and Discussion: An example of the elemental analysis results of the samples are shown in Figure 3.

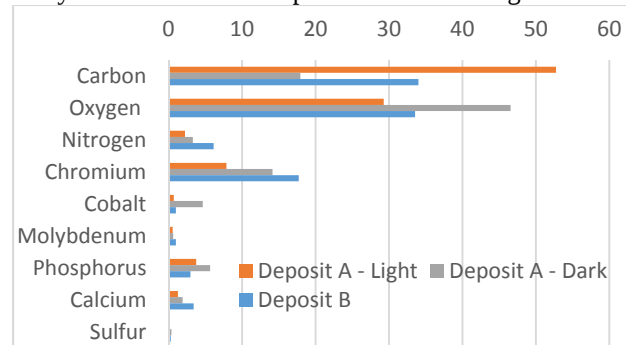


Figure 3. Atomic % of elements at 150 nm from the surface

For Deposit A, the main inorganic materials were $\text{Cr}_2\text{O}_3 \cdot x(\text{CrPO}_4 \cdot 2\text{H}_2\text{O})$, where x varied from 0.245 in the darker areas of the deposit to 0.807 in the lighter areas. This is in good agreement with the identification of an amorphous chromium orthophosphate hydrate-rich material in the vicinity of taper junctions in the early 1990s [2]. Additionally, it was also found that the lighter areas of the deposit had more calcium hydroxyapatite and the darker areas had more aged bone mineral. The environment seems to be basic, since a number of the cobalt and molybdenum compounds are hydroxides and oxyhydroxides. This is consistent with the higher pH values produced by the oxygen reduction processes at the cathodic sites. There was more cobalt in the darker areas of the deposit. At the greatest depth examined, the composition appeared to be characteristic of that at a metal-oxide interface. Overall, Deposit A appeared to be a mixture of coagulated corrosion product deposits, metallic wear debris, and particles of biological origin.

For Deposit B, the main inorganic material in the sub-surface was $\text{Cr}_2\text{O}_3 \cdot 0.339(\text{CrPO}_4 \cdot 2\text{H}_2\text{O})$. Lower concentrations of Mo and Co oxides – but more sulfur – were found. Cr and Mo carbides were also identified along with graphitic carbon. This finding is of particular interest since evidence for graphitic material in the tribological layer in metal-on-metal hip replacements retrieved from patients has been reported [6]. The graphitic carbon may have originated from that layer.

Conclusions: This initial study indicates that important information on the origin of certain corrosion and wear products can be obtained by making detailed analyses of these complex systems. Future work should focus on identifying the sources of, and mechanisms that created the corrosion products.

References: [1] Kovacs et al., ASTM STP 1144 (1992) pp.160-176; [2] Urban et al., ASTM STP 1301 (1997) pp. 33-44; [3] Fricka et al., J. of Arthroplasty 27 (2012) 8 S 1 pp. 26-31; [4] Vesnovsky et al. *Trans. 23rd Ann. Meeting, SFB* (1997) p.393; [5] Vesnovsky et al. *Trans. 37th Ann. Meeting, SFB* (2013) p.856; [6] Liao et al., Science 334 (2011) pp. 1687-90