

Micro-abrasion–corrosion of a CoCrMo alloy in simulated artificial hip joint environments

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Abstract

This study aims to investigate the synergistic effects of corrosion and wear of artificial human joints made from a surgical grade cast F-75 cobalt–chromium–molybdenum (CoCrMo) alloy. Both electrochemical and gravimetric measurements have been used to determine the performance of CoCrMo samples in static environments and under predominantly three-body abrasive wear conditions using the micro-abrasion test method. Electrochemical measurements are presented from embedded corrosion cells within a micro-abrasion rig. Micro-abrasion–corrosion has been studied using an aggressive abrasive slurry (SiC/Ringer's) to identify depassivation and repassivation processes. These initial conditions are an attempt to simulate worst-case scenarios where wear, cement or bone debris are entrained into the contact. The in situ wear–corrosion measurements have been used to identify the implications of wear and corrosion on both the implant and tentative implications for the patient over the long term. Results show strong synergistic effects occur ranging from negative to positive (i.e. beneficial to accelerated surface removal rates). The synergistic levels appear to be dependent on the integrity of the passive films and the repassivation kinetics. Corrosion potentials are presented which corroborate depassivation within the scar.

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1. Introduction

As an alternative to metal-on-polyethylene (MoP) hip joint bearings metal-on-metal (MoM) bearings are increasingly gaining more acceptance [1,2]. MoM bearings have excellent wear resistance [3] for instance the Muller type (CoCr–CoCr) has lower wear rates ($3.0 \mu\text{m year}^{-1}$) than other material combinations such as CoCr/HDMWPE ($100\text{--}200 \mu\text{m year}^{-1}$) [4,5]. Recent developments also indicate that frictional torque is reduced by a factor of three during simulated gait when compared with MoP bearings [6]. It is generally accepted that wear particles from prosthetic implants induce inflammatory reactions that provoke the release of inflammatory mediators from macrophages. This inflammatory response induces periprosthetic bone loss

and subsequent loosening of the prosthesis. The presence of metal debris is an important factor in the failure of hip and knee prosthesis [7]. Debris can be generated from articulated surfaces and reverse surfaces if joint/cement/bone movement occurs. Cement and bone debris can also be entrained during the implantation on the artificial hip joint. It is well established that the cellular response to wear debris is dependent upon particle number, shape, size, surface area, and material chemistry, among other factors [8–11], with smaller and more irregular particles causing the most damage. Particles formed through wear are believed to induce tissue reactions such as osteolysis, macrophagic reactions, inflammation and granuloma [12–16]. Such reactions lead to the loosening of the implant and hence pain and discomfort for the patient [11,17]. In addition, metallic wear particles in the soft tissues paint the tissues black, this is known as metallosis. The release of metallic-ions from metal implants [18,19] can also cause ad-

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verse local effects like osteolysis [20] and systemic effects [21,22].

Corrosive wear is considered to be a form of third-body wear, where the corrosion debris acts as an abrasive third-body. The presence of articulating motion within an artificial joint damages the protective oxide layer and leads to the formation of the corrosion products more rapidly than if there was no motion at all. Active bare metal is then exposed to an electrochemical reaction with the tissue fluid and hence results in further material loss. In between successive contact events, it is generally assumed that a depassivation–repassivation event can occur only if the material has the ability to repassivate quickly enough. This means that only materials with the ability to rapidly form a protective oxide layer can be used as permanent implant materials. The combined effect depends on the type of contacting materials, the type of physiological environment, the applied load and the electrode potential [23–25].

To better understand the tribological performance of the CoCrMo implants a means of simulating debris entrainment, or debris generated within artificial joints would be beneficial. However, the corrosion–wear response of surface engineered bio-implant materials has received little, if any, investigation [26,27]. One method proposed is to investigate the tribological properties of CoCrMo using a micro-abrasion or ball cratering test [28–30]. The test requires a ball to be rotated against a specimen in the presence of a slurry of fine abrasive particles. This method offers good reproducibility and also allows continuous measurement of the wear scar during the test [28]. The response of materials to this test depends critically on the nature of the motion of the abrasive particles in the contact zone, whether they roll and produce multiple indentations, or slide causing grooving abrasion. Similar phenomena also occur when hard contaminant particles enter a lubricated contact.

2. Background and scientific context

2.1. Cobalt–chromium–molybdenum alloys

CoCrMo alloys have superior tribological properties than titanium alloys when used in articular applications [31–34]. CoCrMo alloys have two phases consisting of a cobalt alloy solid solution matrix and metal carbides. The material properties are related to the crystallographic nature of cobalt, the solid-solution-strengthening effect of chromium and molybdenum and the formation of extremely hard carbides, and the corrosion resistance is due to chromium [34]. The mechanical properties are enhanced by the microstructure being fine grained and homogeneous while the chemical composition is related to carbon content (and hence abrasive resistance is affected by percentage of carbides). The corrosion resistance of CoCrMo results from the formation of a thin passive oxide film on its surface. This oxide, consisting of a mixture of chromium and cobalt oxides, in effect acts as a physical

and charge transfer barrier [35,36] and, thus provides high corrosion resistance to the base alloy [37]. Molybdenum has only been found in air-formed films, however, it readily dissolves when exposed to an electrolyte [35]. The integrity of the oxide film has been strongly correlated to the chemical and mechanical stability of implants [38,39]. Being an extremely thin film, ~1–4 nm thick, it is susceptible to fracture owing to mechanical loading resulting in scratches, dents, and fretting [40]. Typically the load bearing areas of artificial implants such as the femoral head (hip) and femoral component (knee) have highly polished articulated surfaces. The manufacturing process history will influence both the bulk and surface properties, generating subtle differences in the microstructural and mechanical properties. CoCrMo is known to be susceptible to work hardening and the finishing processes, grinding and polishing, involved in the manufacture of these joints result in the near surface affected layers undergoing strain induced transformations [41]. CoCrMo alloys used for implants possess very low stacking fault energies. Plastic deformation by dislocation glide in the face centred cubic (fcc) metastable phase is severely restricted [42–44]. This behaviour has been attributed to the formation of strain-induced defects, e.g. intrinsic stacking faults, twins and regions of highly localised slip along pre-existing and strain-induced stacking faults, when these alloys are subjected to external stresses exceeding their yield strength. Thus, the ductility of these alloys, particularly in as-cast and solution treated conditions, is low compared with other fcc alloys. The interactions between dislocations of limited mobility and dissociations and/or twins lead to very rapid and highly localised hardening [45].

2.2. Biocompatibility

Biocompatibility is the mutual coexistence between the biomaterials and the physiological environment where neither has a damaging effect on the other [11]. Many trace elements are found in low concentrations in the human body. In high concentrations these elements have a potential to cause hypersensitivity, toxicity and/or carcinogenic reactions. The toxicity of an element depends on its concentration and nature of the compound. It is through corrosion of metallic implant alloys that ions are released into the body.

2.3. Wear-mode mapping

As described by Adachi and Hutchings [46] a wear-mode map defines the regimes for which two-body abrasion (grooving wear) or three-body abrasion (rolling wear) dominate in the micro-scale abrasion test. The wear-mode was determined empirically to be a function of two dimensionless groups. The group S_c which represents the severity of contact:

$$S_c = \frac{L}{AvH'}, \quad (1)$$

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