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Mechanical load assisted dissolution response of biomedical cobalt–chromium and titanium metallic alloys: Influence of in-plane stress and chemical environment

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ABSTRACT

Mechanical load-assisted dissolution is identified as one of the key mechanisms governing material removal in fretting and crevice corrosion of biomedical implants. In the current study, material removal on a stressed surface of cobalt–chromium–molybdenum (CoCr) and titanium (Ti-64) alloys subjected to single asperity contact is investigated in order to identify the influence of contact loads and in-plane stress state on surface damage mechanisms. The experiments were conducted in ambient as well as three different aqueous environments – phosphate buffered saline (PBS) at pH 7.4, PBS at pH 4.1 and high chloride solutions at pH 4.0. The tip of an atomic force microscope is used as a well-characterized "asperity" to apply controlled contact forces and mechanically stimulate the loaded specimen surface in different aqueous environments from passivating to corroding. The volume of the material removed is measured to determine the influence of contact loads, in-plane stresses and the environment on the material dissolution rate. Experimental results indicate that surface damage is initiated at all the contact loads studied and as expected in a wear situation, removal rate increases with increase in contact loads. For both alloys, removal rates display a complex dependence on residual stresses and the environment. In a passivating environment, the material removal rate is linearly dependent on the stress state such that surface damage is accelerated under compressive stresses and suppressed under tensile stresses. In a corrosive environment, the dissolution rate demonstrates a quadratic dependence on stress, with both compressive and tensile stresses accelerating material dissolution. The material removal rates are found to be consistently larger for CoCr in comparison to Ti64 surfaces under the same mechanical and electrochemical stimuli, despite the higher hardness of CoCr surfaces.

1. Introduction

Titanium alloys and cobalt–chrome alloys have gained widespread usage as orthopedic implant materials especially in total joint replacements [1–26]. Their outstanding structural integrity and chemical stability in corrosive environment have been used successfully to restore joint functions. The structural benefit (less weight/volume ratio) of titanium alloy makes its use suitable as a stem component of modular hip joints. The higher wear resistance of cobalt–chrome alloy is suitable for its application in bearing portion [16,24,27]. Therefore, total hip joint replacements commonly consist of titanium femoral stem and cobalt–chrome femoral head. The modular connection of two dissimilar materials is made by self-interlocking at the tapered stem end into the bored head [7,28,29]. This modular design causes inevitably micron size relative motions at the modular connection [27]. The contacting asperities from each component abrade the oxide film, crack the surface layer, and establish localized plastic deformations. These mechanical interactions take place in the corrosive physiological solutions that generate anodic reaction on the metal surface [11,30–33]. The anodic response of metal surface develops protective passive layer as well as releases metal ions in the surrounding liquid. The combining effect from mechanical and electrochemical interactions is known as fretting corrosion [34–36]. In many of retrieval investigations of hip joint replacements, it is evident that the major hip joint implant damage was from fretting corrosion on the modular interface and the fretting corrosion damage has limited the useful life of the implants [37–45]. The repeated contact at the interface damages the protective oxide layer and results in formation of particulate and soluble debris that can migrate locally or systemically [45–54].

The mechanical and electrochemical properties of the implant materials determine the degree of fretting corrosion damage on the implant surface [55–58]. Explant studies of total hip replacements have reported that cobalt–chromium surface undergo a greater

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surface damage than the titanium surface in mixed materials modular implants. This result is contrary to expectation based on the mechanical property of the implant materials because hardness and Young's modulus of cobalt–chrome alloys are greater than those of titanium [16]. It indicates the combined influence of the chemical and mechanical stimuli in hip replacements accelerates the wear damage of the harder cobalt–chrome surface.

The objective of this experimental study is to investigate the role of mechanical stimuli and chemical environment in damage initiation on cobalt–chrome and titanium surfaces. An atomic force microscope (AFM) was used to perform single asperity contact experiments on stressed material surfaces in four different environments: ambient, phosphate buffered saline at pH of 7.4, phosphate buffered saline at pH of 4.1 and $CaCl_2$ solutions at pH of 4.1. The tip of an atomic force microscope is used as a well-characterized "asperity" to apply controlled contact forces and mechanically stimulate the loaded specimen surface in different aqueous environments from passivating to corroding. The volume of the material removed is measured to determine the influence of contact loads, in-plane stresses and the environment on the surface damage.

2. Materials and experimental set-up

2.1. Materials

The materials used in this study are cobalt–chromium–molybdenum (CoCr) alloy as specified by ASTM F1537 and Titanium–Vandium–Aluminum (Ti-64) as specified by ASTM136. The samples were in form of rectangular bars with dimensions of 1 mm by 2 mm by 25 mm in the thickness, depth, and length respectively. The 1 mm thickness of the beam was then mechanically polished by 1200 grit, 3 μm diamond suspension, 1 μm diamond suspension, and finally with a 0.05 μm colloidal silica suspension to a mirror finish. AFM measurements on the polished side indicate that the initial surface follows a Gaussian distribution with skewness approximately zero (−0.1 to 0.08) and kurtosis of approximately 3 (2.8–3.2). The root mean square (RMS) roughness ranges from 0.5 nm to 2 nm on 10 μm scans, indicating a smooth initial surface.

2.2. Four point bending frame

The four-point bending frame (c-frame) is designed to apply varying levels of stress states throughout the sample and is schematically represented in Fig. 1. The sample along with four rollers are placed in-between the c-clamp and the extrusion on the base. The rollers, which are modified pin gages (Meyer's Gage Company, South Windsor, CT), force the c-clamp to open against the base. The amount of force is measured by monitoring the free end

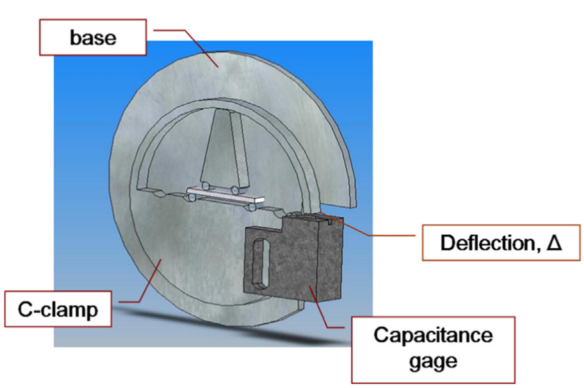

Fig. 1. The four point bending setup. The main components are a c-clamp, base (B), capacitance probe, rollers, and a rectangular sample.

deflection of the clamp with a capacitance gage (Capacitec, Myer, MA). This deflection has been calibrated by a dead weight method and calibration curve is used to determine magnitude of applied force. The force applied to the clamp is disturbed over the four rollers creating a load control setup. The four-point bending configuration ensures that mid-span of the sample between the top rollers will experience a range of stresses from compressive stresses at the top to tensile stresses at the bottom (as schematically represented in the inset of Fig. 1). The stress state of any location of the sample surface may be determined from: the load on the rollers, sample dimensions and distance of the location from the edge.

2.3. Atomic force microscope (AFM) and tip characterization

A Dimension 3100 atomic force microscope (AFM) with a Nanoscope IV controller (VEECO Instruments, Woodbury, NY) was utilized for this experiment. A fluid cell and polymer protective skirt were employed in all testing to protect the piezoelectric scanner on the AFM. Silicon nitride (Si_3N_4) cantilevers with a reflective gold backside coating (DNP-S VEECO Instruments, Woodbury, NY) were used in the present study. Cantilever spring constant was experimentally determined prior to each study to ensure application of accurate contact loads. Each cantilever's spring constant was determined by monitoring the deflection of the cantilever against a hard substrate (SiC) as well as a reference cantilever with known spring constant (VEECO Instruments, Woodbury, NY). The two cantilevers act as two springs in series from which the spring constant of the experimental cantilever can be determined [59]. In addition, the radius of curvature of the probe was characterized before and after each set of experiments by a commercially available characterizer (TGT01 Micromasch, Wilsonville, OR) in order to determine the probe wear during mechanical stimulation.

3. Nanoscale wear test and data analysis

3.1. Experimental procedure

Surface damage response of specimens was investigated over a range of contact forces and five different pre-stress states. The metallic implant materials were loaded into the four-point bending frame and free end deflection of the c-clamp was monitored with the capacitance gage as schematically presented in Fig. 2. An optical camera and step-motor driving motion control were utilized to identify locations that correspond to desired stress states across the specimen surface. The loaded sample was then placed underneath the AFM head and all the tests were performed in each environment, *i.e.* ambient and aqueous environment of varying pH levels.

A group of specimens was subjected to the fatigue sliding contact (fretting) with AFM probe in ambient (humidity < 35%) to observe the sole effect from mechanical stimulus. Fretting contact experiment was performed on the second group of specimens in phosphate buffered saline solution (PBS) (Invitrogen, Carlsbad, CA) with varying pH ranges. The pH level was adjusted by adding hydrogen chloride (HCl). The third group of specimens was tested in calcium chloride solution (concentration 0.35 g/L) with desired pH levels. Three pH values were chosen to simulate the crevice environment. A pH value of 7 was used for the normal joint and the lower values of pH 4 and pH 2 targeted the corrosive modular crevice.

For each test, an initial 5 μm × 5 μm AFM image was taken at a low contact force of 1–2 nN. Fretting contact was then preformed at the center of the 5 μm × 5 μm scan on an area of 2 μm × 500 nm. The tip was rastered across this area at 5 Hz for 15 min at the desired contact force. Under these AFM setup, each 500 nm-long sliding contact repeats approximately 70 times within the test area for 15 min. After 15 min-long fretting contact, the final surface