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Tribocorrosion response of the Ti6Al4V alloys commonly used in femoral stems

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ABSTRACT

In prosthesis, tribochemical reactions occur at the stem/bone interface. When coupled with micro-motions it can lead to the loosening of the implant, osteolysis, release of metal ion and wear particles. The effect of these movements and the underlying mechanisms are quite unknown. This work investigates the tribocorrosion behavior of etched Ti6Al4V alloys under reciprocating sliding. Tests were performed in a phosphate buffer solution (PBS) containing proteins. A normal load of 1 N and anodic potentials of −0.1 and +0.5 V/SCE were applied. The destruction pathways of the top surface layers (adsorbed proteins, passive film) were studied. The results showed that the favorable/undesired effect of proteins in solution depends on the characteristics of the passive film under a mechanical stress.

1. Introduction

Titanium alloys used in orthopedic implants are susceptible to mechanical and chemical degradation. Despite having excellent corrosion resistance, biocompatibility, and low Young modulus (E), in the human body these alloys are exposed to body fluids that induce corrosion damage on the material. Additionally, and at the same time, tribological contacts created due to locomotion, contributes to the accelerated degradation of the material [1–3]. This can lead to crack initiation or early fracture of the implant, as well as serious inflammatory reactions, osteolysis or allergies, which can significantly shorten its life span [2,4–6]. Bio-tribocorrosion describes the irreversible material degradation process resulting from the synergistic interaction of wear and corrosion phenomena on surfaces subjected to a relative contact movement in biological environments [7]. The combination of the chemical and mechanical events usually leads to local damage or removal of the passive film accelerating the material loss in passive metals, in both sliding and fretting tribological conditions [8–10]. Metallic femoral stems are a common component in a hip reconstruction system, irrespective of the type of hip implants, such as Metal-on-Metal (MoM), Metal-on-Polymer (MoP) and Metal-on-Ceramic (MoC). At the stem-bone interface, micro-movements are expected to happen at the distal point of fixation, accounting for a fretting-corrosion mechanism, which involves small amplitude relative displacement between surfaces in contact with a harsh biological/chemical environment [2,11–14].

The main concern about metallic implants is the generation and release of wear particles and metallic ions in toxic concentrations, when the passive film destruction induces wear-accelerated corrosion. Several studies have described the evidences of surface damage due to corrosion and wear on metallic implants in physiological solutions [15–16]. Such studies also reported the effect of proteins that are adsorbed at the implant surface immediately after insertion into the body on the surface degradations process [17]. However, some doubts still persist on the way these organic molecules might interact with the surface under a mechanical articulation, and on the role of the nature of the passive film that might be formed on the same substrate material, under different mechanical/environmental conditions. Generally, proteins are negatively charged and they were found to interact with positively charged metal ions in the body, enhancing the corrosion rate and metal dissolution of the materials [17]. Their interaction with the active metal surfaces is endorsed by their beneficial lubricating properties [6].

In this study the tribocorrosion behavior of Ti6Al4V alloys in a simulated body fluid containing albumin is investigated, as a function of relevant electrochemical potentials. The passivation kinetics and its influence on the tribocorrosion mechanistic transition and overall synergistic interactions of wear and corrosion were studied under reciprocating sliding conditions.

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2. Experimental

2.1. Materials

The specimens used were Ti6Al4V alloys discs (Goodfellow, USA) with 24.8 mm diameter, 5.5 mm thickness, and nominal chemical composition (in wt%) of 89.0% Ti; 5.88% Al; 4.34% V; 0.208% Fe; 0.015% Ni; 0.459% Cr and 0.064% Si. The samples were prepared using a standard metallographic preparation procedure. These were then chemically etched with Kroll's reagent (H_2O:HNO_3:HF/88:10:2, in mL) for 10 min, washed in warm water and dried in hot air, based in previous protocols [1,18]. Prior to the experiments, the samples were stored in a desiccator. An alumina ball of 10 mm diameter (model Biolox Forte, CeramTec, Plochingen, Germany) with a highly polished surface ($Ra=0.002$ μm) was used as a counterbody for reciprocating sliding tests.

2.2. Electrolytes

All tests were carried out in a phosphate buffer solution (PBS), a simulated body fluid commonly used in biomedical research for implant materials applications [1,11,17,19–20], at 37 °C (±2 °C), composed by 8.18 g/L NaCl; 0.14 g/L KH_2PO_4; 0.22 g/L KCl and 1.42 g/L Na_2HPO_4, and maintained at pH 7.5 (room temperature). To reproduce the biological environment another solution was also used by adding albumin fraction V (Merck, Germany) to the initial composition of the previous electrolyte (PBS). A small concentration of 2 g/L of albumin was used based on previous successful studies reported in literature using this electrolyte on Ti6Al4V alloys, for orthopedic applications [6,11,17,21].

2.3. Electrochemical corrosion tests

Electrochemical tests were performed in a three-electrode electrochemical cell, using a saturated calomel electrode (SCE) with KCl saturated solution ($E_{SCE}=+240$ mV/SHE) as reference electrode (RE), a platinum (Pt) electrode as counter electrode (CE), and the Ti6Al4V alloy as working electrode (WE). The corrosion behavior was evaluated by measuring the open circuit potential (OCP) with a sample period of 0.6 s, during 1200 s, followed by the electrochemical impedance spectroscopy (EIS) in a frequency range from 10 kHz to 1 mHz with a ±10 mV sinusoidal amplitude at a rate of 10 frequency/decades, in E_{ocp} vs. SCE. The active exposed area to the electrolyte solutions used was 0.385 cm^2. The potentiodynamic polarization test (PD) was also performed in the range −1 V to 1.5 V, at a scan rate of 1 mV/s. For data acquisition, a potentiostat Gamry Reference 600 was used with the software Gamry Framework 5.5 (Gamry Instruments, Warminster, PA, USA) and analyzed in OriginPro 8 SR0 software (OriginLab Corporation, Northampton, MA, USA).

2.4. Tribocorrosion tests

Tribocorrosion tests were carried out in a CETR tribometer (Model UMT-2, Campbell, California, USA), in reciprocating sliding conditions (ball-on-plate). The oscillation frequency of the counterbody pin was controlled at 1 Hz under a normal applied load of 1 N (415 MPa Hertzian initial contact pressure) and a stroke length of 2 mm, during 1800 cycles. Each test started with a fresh alumina ball surface. The active area of the alloy was 4.71 cm^2. A three-electrode electrochemical cell configuration was also used with the same electrodes used for corrosion tests (Section 2.3). The potentiostatic tests were carried out at potentials of −0.1 V/SCE and 0.5 V/SCE, corresponding to the anodic region of the alloy, based on the polarization curves obtained in corrosion tests. Current and friction coefficient evolution were monitored during sliding at potentiostatic conditions. Friction coefficient data were analyzed using UMT-2 software (Campbell, California, USA). Impedance results were performed before and after sliding tests, in a frequency range from 100 kHz to 1 mHz with a ±10 mV sinusoidal amplitude, at a rate of 10 frequency/decades, and at the applied potentials referred before.

The topographical measurements of the wear scar were made using a scanning white light interferometry microscope (Zygo Corporation, Middlefield, CT, USA), from which the wear volume was calculated using the MetroPro 8 software (Zygo Corporation).

All tests were performed a minimum of three times ($n=3$) for all conditions.

2.5. Wear volume loss estimation

The weight loss distribution in terms of total wear-corrosion loss (K_{wc}) during tribocorrosion test, estimated from the wear scar dimension, is the sum of wear loss due to corrosion (K_c), using Faraday's law, and wear loss due to sliding wear (K_w) [22–25], so that

$$K_{wc}=K_w+K_c \tag{1}$$

The total mass loss K_{wc} is obtained from a direct calculation using the software MetroPro 8 (Zygo Corporation), and from the surface profile of the wear scar. The results were then multiplied by the equivalent density of the Ti6Al4V alloy, 4.51 g/cm^3.

The wear loss due to corrosion (K_c) is calculated using Faraday's law:

$$K_c=\frac{Q\times M}{n\times F} \tag{2}$$

where ‘Q’ is the anodic charge in coulombs passed through the working electrode, ‘M’ (g/mol) is the equivalent weight of the elements dissolved, ‘n’ is the dissolution valence, and ‘F’ is the Faraday's constant (96490 mol^{-1}).

Finally, the weight loss due to wear (K_w) is obtained by modifying Eq. (1) as follows:

$$K_w=K_{wc}-K_c \tag{3}$$

2.6. Surface characterization

Morphological characterization techniques were used to analyze the surface of etched and corroded samples, and the wear scar after mechanical tests, with different techniques: scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) (Model-JEOL JSM-6490 LV, Oxford Instruments, England), and white light interferometry (Zygo Corporation, Middlefield, CT, USA).

2.7. Statistical analysis

The values of wear volume loss and impedance were statistically analyzed for presence/absence of proteins in both potentials applied. Independent t-tests were performed to compare the effect of proteins in each potential and the differences between each potential in the same solution. A significance level of 0.05 was used for all tests (Statistical Package for the Social Sciences, version 17.0, SPSS Inc, Chicago, IL, USA).

3. Results and discussion

3.1. Surface characterization of Ti6Al4V alloy prior to testing

Different stem surfaces are presently available in the market: polished, matte, or with surface treatments ranging from plasma