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A TRIBO-ELECTROCHEMICAL APPROACH FOR THE CHARACTERIZATION OF ARTIFICIAL IMPLANT BIOMATERIALS[1]

Nitin S. More [2]
Nikitas Diomidis [3]
Stefano Mischler [3]
Manish Roy [4]
S.N. Paul [2]

Abstract

β Titanium alloys are potential biomaterials for joint prostheses due to their biocompatibility and increased compatibility with the mechanical properties of bone. Knee and hip joints involve a sliding contact between the femoral head and the accetabular cup thus making the metallic components susceptible to tribocorrosion. Micro-motions occur at the fixation between the implant stem and the bone leading to debris and ion release by fretting-corrosion. Ti-29Nb-13Ta-4.6Zr was tested in Hank's balanced salt solution at open circuit potential and at an applied potential in the passive region at 37^0C. Reciprocating tribocorrosion tests were carried out against technical grade ultra high molecular weight polyethylene (UHMWPE), while fretting-corrosion tests were carried out against alumina. Under tribocorrosion conditions, the wear of the alloy is insignificant when sliding against polyethylene. Additionally, the tested alloy showed the ability to recover its passive state during sliding. The abrasivity of the alloy depends on the electrochemical conditions in the contact, while the wear of polyethylene proceeds through 3rd body formation and material transfer. Under fretting-corrosion conditions no recovery of passive state was possible due to the increased contact pressure. The wear resistance of the alloy was found to be dependent on the electrochemical conditions in the contact.
Keywords: Tribocorrosion; Fretting-corrosion; Biomaterials; Artificial Implants.

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1 INTRODUCTION

Human joints operate by low-friction articular cartilage bearing surfaces, which are conforming and self-regenerating.[1-3] When natural joints are severely damaged, they are often replaced by artificial implants. In total joint replacement, femoral components are generally made of metal-metal, ceramic-polymer or metal-polymer couples. The use of metallic alloys and polymers has increased considerably in total joint replacement in recent years.[4]

Titanium alloys are potential materials for biomedical applications such as joint prostheses due to their excellent corrosion resistance, high specific strength and biocompatibility.[5] The release of aluminium and vanadium ions from the commonly used Ti-6Al-4V alloy was found to be toxic and their accumulation in the surrounding tissues was a cause of great concern.[6] Consequently, effort was diverted towards the development of Ti based biomaterials free from Al and V. Furthermore, it was noted that these α or α+β alloys have an elastic modulus significantly higher than the elastic modulus of implant and bone. In order to overcome this drawback, β Ti alloys were developed with the aid of β stabilising elements such as Nb, Mo, Zr and Ta. β Ti alloys were found to have enhanced biocompatibility and increased compatibility with the mechanical properties of bone and implants.[7]

Knee and hip joints involve a sliding contact between the femoral head and the accetabular cup during the motion of the human body, and thus making the metallic components of the artificial joint susceptible to tribocorrosion. Tribocorrosion is an irreversible transformation of a material due to the simultaneous action of corrosion and wear taking place in a tribological contact.[8] It involves numerous synergy effects between mechanical and chemical or electrochemical phenomena.[9] The release of metallic ions due to corrosion and wear is of vital importance, since it can adversely affect the biocompatibility and mechanical integrity of implants.[10] Therefore, the assessment of biomaterials to corrosion and corrosive wear is required to ensure their safe application in the corrosive environment of the human body.[11]

Fretting-corrosion is a surface degradation process occurring between contacting bodies due to the simultaneous action of a displacement with an amplitude which is small compared to the size of the contact area, and a corrosive attack by the environment.[12] In the particular case of orthopedic implants, a micro-motion is known to occur at points of fixation between the different components,[13] while corrosion is caused by the body fluid which contains various inorganic and organic ions and molecules.[14] Fretting-corrosion has been identified at the neck/head contact and at the stem/bone interface of modular hip joints and at the screw head/plate junction of fixation plates.[15] Fretting corrosion results in the potential disruption of the passive oxide surface film which protects the metal, thereby reducing the metal's resistance to further corrosion.[16] The repeated removal of oxide films produces wear and corrosion products, i.e. debris and ions, which can result in adverse biological reactions and can lead to mechanical failure of the device.[17-20] A high wear resistance and an ability to repassivate at a high rate can minimize an alloys' susceptibility to fretting-corrosion. Therefore, an approach combining both electrochemistry and tribology is the necessary means to study these complex phenomena and to screen candidate biomaterials.[21]

By performing a tribological experiment under well defined electrochemical conditions it is possible to obtain information on the removal of surface films due to the imposed mechanical perturbation and on their possible regrowth as a result of interactions with the environment. Different tribo-electrochemical techniques have

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been applied[22] and methodologies have been developed that allow an identification and quantification of the mechanical and electrochemical components of wear in a tribo-electrochemical system.[23] In general, tribo-electrochemical experiments performed at open circuit potential can provide information on the performance of the test material at conditions that are similar to a real life application. On the other hand, tribo-electorchemical experiments done at an imposed potential can provide information on the properties of passive layers.

In the present investigation, the tribocorrosion and fretting-corrosion behavior of a newly developed β titanium alloy, Ti-29Nb-13Ta-4.6Zr, is studied in physiological solution. The changes in open circuit potential, anodic current and friction coefficient are measured in-situ as a function of time, and the electrochemical and wear response of the test material is analyzed. The prevalent wear mechanisms are revealed, assisting in the screening of candidate biomaterials and providing insight on the phenomena governing material degradation in-vivo.

2 MATERIALS AND METHODS

The titanium alloy with β microstructure, Ti-29Nb-13Ta-4.6Zr (wt%), used in the present study has a hardness of 249 MPa and an elastic modulus of 55 GPa. More detailed studies on this material have been published previously.[24,25] Specimens were cut at dimensions of 20 mm diameter and 5 mm thickness. Sample preparation was done by progressively polishing with emery papers of 240, 400, and 500 grit, followed by fine polishing with diamond paste (6 μm) and final polishing with alumina powder (3 μm). The specimens were then washed in deionised water and ultrasonically cleaned in acetone and ethanol for 10 min respectively. The tests were done in Hank's balanced salt solution (HBSS), consisting of NaCl (8.00 g/l), KCl (0.40 g/l), $CaCl_2$ (0.18 g/l), $NaHCO_3$ (0.35 g/l), $NaHPO_4.2H_2O$ (0.48 g/l), and $MgCl_2.6H_2O$ (0.10 g/l) at 37±1 ^oC.

Reciprocating sliding wear tests were carried out with a tribo-electrochemical apparatus, details of which are given in a separate publication.[26] The applied load was 6.5 N, at a frequency of 1 Hz, with a stroke length of 5 mm. A Wenking LB 95 L Auto Range Laboratory Potentiostat served to control the potential of the titanium specimen disk (working electrode). A platinum wire and a mercury sulfate electrode (MSE) were connected to the potentiostat as counter and reference electrodes, respectively. The pins having 12 mm diameter and 38 mm length were made up of technical grade UHMWPE and were used as counterbodies for sliding wear tests. Experiments were performed at open circuit potential and at an applied potential of +2 V vs. MSE corresponding to the passive region. All sliding tests were carried out for 3600 s. For tests at open circuit potential the samples were immersed in the electrolyte 1800 s before the initiation of the sliding. For tests at applied potential, the samples were immersed in the solution at rest potential for 300 s, and then the anodic potential was applied for 1800 s prior to the initiation of sliding. The wear of the hemispherical polymer pin was determined by measuring on optical micrographs the flat end formed during rubbing and geometrically calculating the corresponding volume of the worn spherical cup.

Fretting-corrosion tests were carried out with a fretting tribo-electrochemical apparatus described in detail elsewhere.[27] A three-electrode set-up identical to the one used for tribocorrosion experiments was used as well as the same experimental procedure. Alumina balls of 5 mm radius (SWIP AGBrügg, G10 AFBMA finish) were used as counterbodies. Fretting-corrosion experiments were done at an applied

normal load of 10 N, with a displacement of 100 µm and a frequency of 1 Hz was applied for 3600 s. The mean frictional coefficient was calculated by dividing the tangential force by the normal force when the ball was in the middle of the stroke. Laser profilometer surface scans were performed at a resolution of 300 points per mm and the wear volumes were calculated according to Fouvry et al.[28] Scanning electron microscopy (Philips XL30-FEG SEM) and optical microscopy were used to characterize the morphology of the wear tracks.

3   RESULTS AND DISCUSSION

3.1 Tribocorrosion

The evolution of the coefficient of friction and the potential and anodic current with time during tribocorrosion experiments on Ti-29Nb-13Ta-4.6Zr at open circuit potential (E_{oc}) and at a passive applied potential (E_{pass}) respectively is shown in Fig. 1. Before the initiation of sliding the measured open circuit potential is high due to the spontaneous formation of a passive film on the alloy surface in contact with the electrolyte [24]. Upon the initiation of sliding, the open circuit potential decreases indicating a depassivation of the surface induced by the mechanical removal of the passive film. During sliding, the open circuit potential gradually increases until it reaches a value similar to the one measured before the initiation of sliding. This indicates that the alloy has the ability to recover its passive state while a mechanical perturbation is taking place. Similarly, when sliding at an imposed passive potential, the measured anodic current increases at the onset of sliding. The increased anodic current is due to the depassivation of the sample surface. The mechanical removal of the passive surface layer induces an increase in the rate of oxidation of the uncovered substrate alloy which is reflected in the increased anodic current. During the course of the experiment, the anodic current decreases again, indicating that the material as the ability to regain its passive state during sliding. On the other hand, no important effect of potential on the coefficient of friction is noticed. In both cases a value of 0.35-0.4 is measured after 3600 cycles.

The ability of the alloy to regain its passive state while sliding is a critical point in biomedical prosthetics applications since it indicates that the release of ions due to corrosion will be limited during the lifetime of the artificial joint. The critical parameters in this case appear to be the contact pressure and the thickness of the passive layer. Indeed, for tests at E_{oc} where a thin passive layer is expected, depassivation takes place immediately upon the initiation of sliding. On the other hand, for tests at E_{pass} where a thicker passive film is expected, apart from an initial current peak, the anodic current does not start to increase until a few hundred cycles have been done. This indicates that the thicker passive film at E_{pass}, takes longer time to wear through compared to the passive film at E_{oc}.

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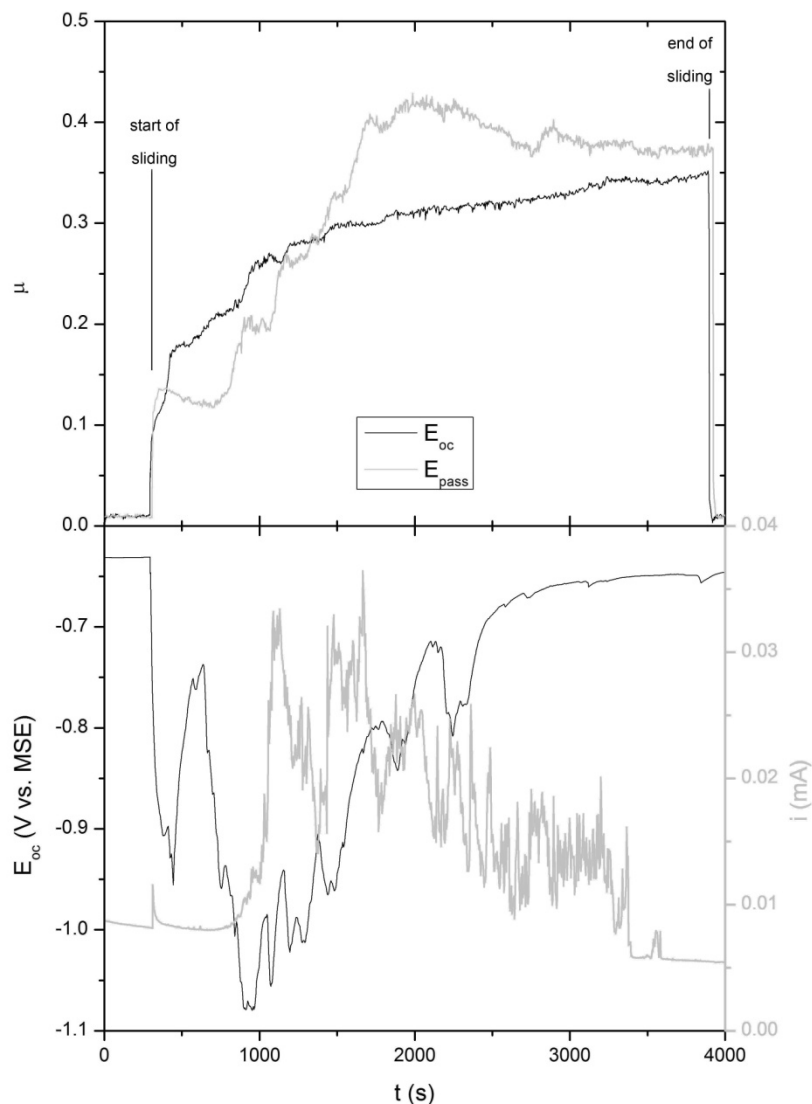

Figure 1: Evolution of the coefficient of friction (top) and the potential and anodic current (bottom) during tribocorrosion experiments at open circuit potential and at a passive applied potential respectively.

After the tribocorrosion experiments both the alloy and the UHMWPE counterbody were examined for wear. No measureable wear was found on the metallic alloy samples. On the other hand, transfer of polyethylene to the alloy is taking place at both open circuit potential and at a potential in the passive region. The wear of the UHMWPE pin after tribocorrosion tests at different potentials is shown in Figure 2.
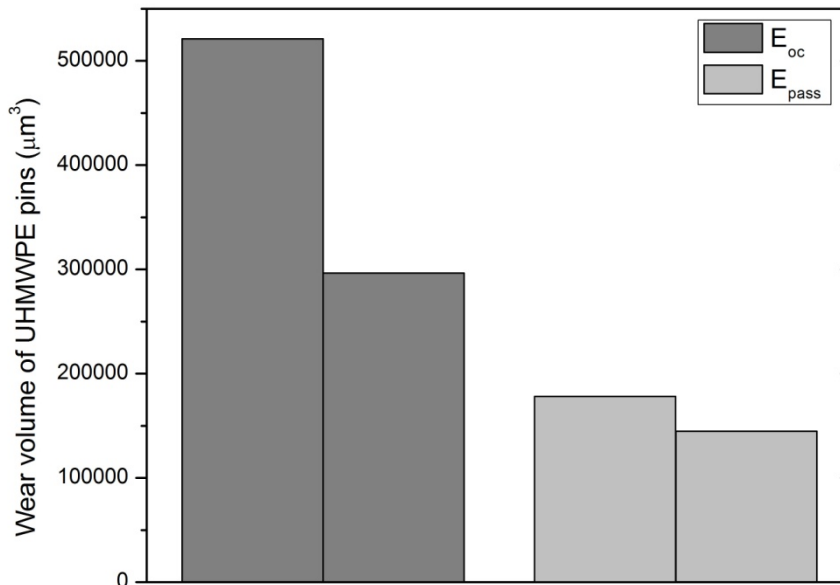
Figure 2: The wear volume of UHMWPE pins after tribocorrosion experiments against Ti-29Nb-13Ta-4.6Zr at open circuit potential and at an applied potential in the passive region. The results of two independent measurements are shown for each potential.

For the material do be able to recover its passive state after depassivation has taken place, it is necessary that the contact pressure is lower than the critical pressure required for passive film removal. In the present case where the metallic alloy practically does not wear, the evolution of the contact pressure depends on the wear of polyethylene. An initial maximum Hertzian contact pressure of around 30 MPa is calculated before the initiation of sliding, and it is expected to decrease during the course of the experiment due to the continuous increase of the contact area as the UHMWPE pin wears. The results of Fig. 2 indicate that the abrasivity of the alloy depends on the electrochemical conditions. A lower wear of polyethylene is found when tribocorrosion tests are performed at a passive potential. As a result, the contact pressure at the end of the test is expected to be higher for tests at E_{pass}. The lower contact pressure at E_{oc} is reflected on the fact that the alloy is able to recover its passive state earlier compared to the experiment at E_{pass}.

3.2 Fretting-corrosion

The evolution of the coefficient of friction, and the potential and anodic current with time during fretting-corrosion experiments on Ti-29Nb-13Ta-4.6Zr at open circuit potential and at a passive applied potential respectively is shown in Figure 3. Similarly to sliding tests, the open circuit potential decreases upon the initiation of fretting. After a few hundred cycles it reaches a steady state value around -0.65 V vs. MSE. At the end of fretting the potential rises again to reach values similar to the ones measure before fretting. For fretting-corrosion tests at E_{pass}, the anodic current rises with the initiation of fretting indicating a depassivation in the wear track, reaches a steady state value of 1 μA after a few hundred cycles, and decreases upon the end of fretting indicating a passive state recovery in the wear track. No recovery of passive state is noticed during fretting-corrosion irrespective of potential. This indicates that when fretting against alumina, the initial maximum Hertzian contact pressure of 590 MPa does not decrease due to wear below the critical pressure required for passive layer removal, and thus the depassivated state remains in the

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wear track during the course of the experiment. The coefficient of friction reaches a stedy state value of around 0.55 at E_{pass}, and around 0.65 at E_{oc}.
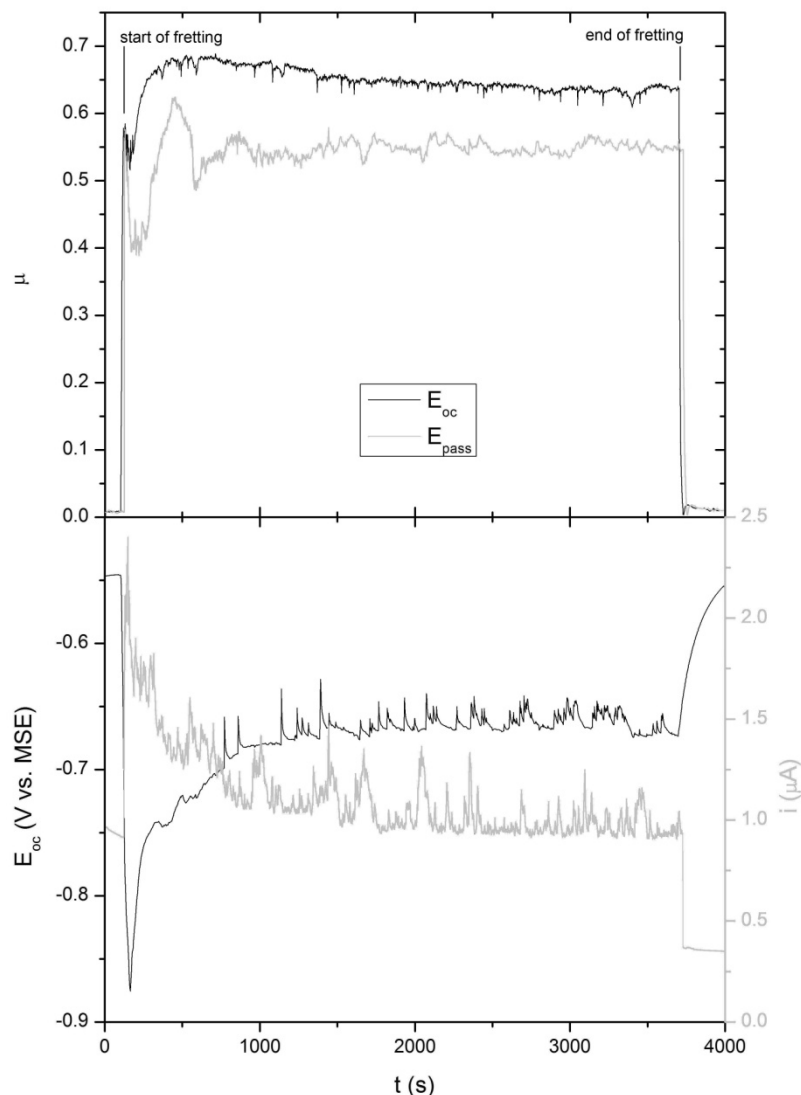

Figure 3: Evolution of the coefficient of friction (top) and the potential and anodic current (bottom) during fretting-corrosion experiments at open circuit potential and at a passive applied potential respectively.

After the fretting-corrosion experiments both the alloy and the alumina counterbody were examined for wear. No measureable wear was found on the alumina sphere. On the contrary, wear does take place on the titanium alloy samples at both open circuit potential and at a potential in the passive region. A large amount of debris particles are found surrounding the wear track. Additionally, metallic material transfer to the alumina counterbody was noticed. The wear of the alloy after fretting-corrosion tests at different potentials is shown in Figure 4. The wear volume at E_{pass} is lower than the one measured at E_{oc}. This indicates that the thicker surface layer expected at E_{pass} protects the alloy from fretting wear.

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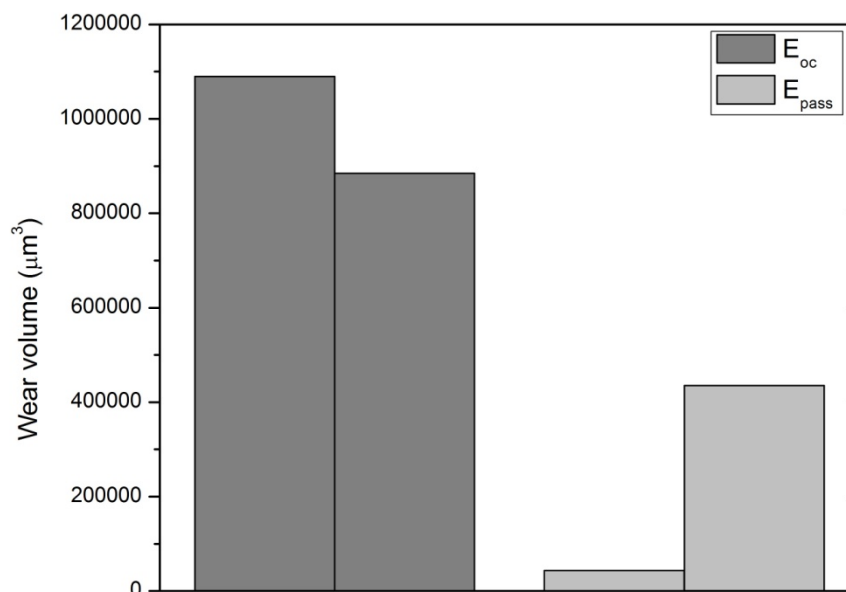ITS - IFToMM 2010 - 2nd International Tribology Symposium of IFToMM

Figure 4: The wear volume of the Ti-29Nb-13Ta-4.6Zr samples after fretting-corrosion experiments at open circuit potential and at a passive applied potential. The results of two independent measurements are shown for each potential.

4   CONCLUSIONS

A tribo-electrochemical approach has been applied successfully to the study of the behavior of a newly developed β titanium alloy for biomedical applications in simulated body fluid in a fretting and a sliding contact. The removal due to mechanical perturbation and the regrowth of passive surface films was monitored in real time, and the wear of the alloy and the counterbodies was examined. Under tribocorrosion conditions against polyethylene, it was found that the alloy has the ability to recover its passive state during sliding probably because the contact pressure decreases below the critical value required for depassivation. The wear of polyethylene depends on the electrochemical conditions in the contact zone. Under fretting-corrosion conditions against alumina, recovery of the passive state during fretting was not possible likely due to the high value of the contact pressure. The wear resistance of the alloy during fretting depends on the electrochemical conditions.

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