Importance of applied normal loads on the tribocorrosion behaviour of Ti-6Al-4V alloy in bio-simulated environment

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The tribocorrosion behaviour of untreated Ti-6Al-4V alloy in artificial saliva solution was evaluated based on the change in open circuit potential (OCP) measured as a function of time. The experiments were performed using a unidirectional reciprocating fretting experimental set-up which was mechanically and electrochemically instrumented, under various solicitation conditions. The effect of applied normal force on corrosion-wear of the tested material was determined. Before the onset of fretting a large increase of the OCP in the noble direction for the Ti-6Al-4V alloy was observed. With the onset of fretting it was observed a cathodic shift in OCP, shift which decreases linearly with increasing normal load. The restoration ability of Ti-6Al-4V alloy after the passive films damaged during fretting was observed when the fretting motion has ceased. A decrease in friction coefficient with gradually increasing load was observed.

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1. Introduction

Pure Ti and Ti-6Al-4V alloy are mainly used for biomedical applications and satisfy most of the demands for implant materials in the medical and dental fields [1-2]. The increasing use of Ti-based metals for implant is due to high strength, low density, good resistance to corrosion, enhanced biocompatibility, moderate elastic modulus compared to other metallic biomaterials [2].

Titanium based metals derives theirs resistance to corrosion by the formation of an adhesive TiO_2 oxide layer at the surface to a depth of approximately 5 nm [3-5]. The spontaneous formation of a titanium oxide film on their surface as long as oxygen is present, leads to extremely stable film and gives a passivating effect on the metal. Passivation effect does not by itself mean that the metal will not corrode but the percentage of corrosion is much lower in the presence of a stable oxide layer [6]. This high corrosion resistance of titanium alloys can be strongly decreased by damage of the passive film when a mechanical stress is loaded on the sample [3].

There are very few studies on the literature which use as test solution in fretting corrosion behaviour of Ti-6Al-4V artificial saliva compared with other simulated body fluids (Hank solution, Ringer solution, sodium chloride solution) [7-11]. As well, the combination of mechanical parameters used in the present research such as load, motion frequency, displacement amplitude and number of cycles, is different compared to the studies mentioned above [7-11].

The aim of this research is to investigate the wear and corrosion behaviour as a function of normal load of Ti-6Al-4V alloy in artificial saliva.

2. Experimental

2.1. Materials

Annealed grade 5 Ti-6Al-4V alloy according to the international standard ISO 5832-3, with mechanical properties in accordance with ASTM B265 and whose chemical composition and mechanical properties are presented in Table 1 was used as a base material.

Table 1. Chemical composition and mechanical properties of Ti-6Al-4V alloy.

Chemical composition									
Specification	8-12-05832-1	N	Al	C	V	H	Fe	O	Ti
Ti-6Al-4V	Max. [%]	0.003	6.01	0.008	3.83	0.002	0.083	0.088	89.976
Grade 5	Min. [%]	0.003	5.86	0.008	3.73	0.002	0.068	0.084	90.245

Mechanical properties		
Resistance to flow [MPa]	Tensile strength [MPa]	Elongation [%]
865	937	11

The samples of Ti-6Al-4V used, in the form of plates, were cut to dimensions of 25×25×2 mm and then successively polished with waterproof abrasive paper with grit (320 – 4,000) µm, diamond paste (1 and 3 µm size) and colloidal silica solution (0.04 µm size of particles), finally achieving a mirror surface. Samples were cleaned in an ultrasonic ethanol bath during 5 minutes and dried using dry, cold air. Then the samples have been stored for about 24 hours in a desiccator to allow the formation of a stable surface film on the test samples.

Al_2O_3 (corundum) balls (G 10 grade) with 10 mm diameter (Ceratec Technical Ceramics BV) were used as counterpart in the sliding tests. The electrolyte utilized in fretting corrosion tests was the Fusayama - Mayer artificial saliva [12], with the chemical composition presented in Table 2 and having a pH equal to 5.

Table 2. Chemical composition of test electrolyte.

Compounds	[g/L]
NaCl	0.40
KCl	0.40
$CaCl_2*2H_2O$	0.80
NaH_2PO_4	0.69
Urea	1.00

2.2. Fretting-corrosion tests

Fretting-corrosion tests were performed using a uni-directional reciprocating tribometer shown schematically in Fig. 1.

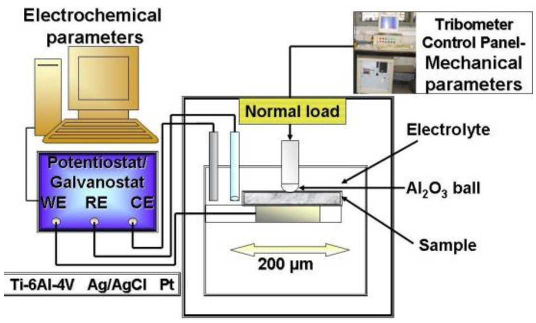

Fig. 1. Schematic view of the experimental set up for fretting-corrosion tests.

Ti-6Al-4V alloy samples serve as working electrode and its potential was controlled using Solartron Instruments 1287 Electrochemical Interface potentiostat/galvanostat provided with a frequency response analyzer SI 1255. The counter electrode was made of platinum wire and the reference electrode was Ag/AgCl (saturated KCl solution, E = 200 mV vs. NHE). These electrodes were placed in the fretting corrosion cell in such a way that only 1 cm^2 area of working electrode was exposed to electrolyte. During the tribocorrosion test, the normal force, tangential force, coefficient of friction, number of cycles as well as the electrochemical parameter, were monitored. The wear tests were performed at room temperature (23 ^oC) and carried out with 1, 2 and 5 N normal forces, at 1 Hz reciprocating frequency, with a displacement amplitude of 200 µm during 1,000 cycles.

The protocol used for the tribocorrosion tests consisted of two steps: (1) measuring the open circuit potential (OCP) of the sample immersed for 1 h to allow stabilization of potential and (2) fretting test during which OCP was measured.

2.3. Characterization techniques

The surface topography and mass loss of the volume removed from the wear track was determined from measurements using non contact Wyco NT3300 optical profilometer with white light interferometry and Vision (version 2.210) software. Philips scanning electron microscope, XL 30 FEG, was used to describe the morphological features of fretted zone.

3. Results and discussions

3.1. Evolution of open circuit potential under static conditions

Prior starting the fretting-corrosion tests, the Ti-6Al-4V alloy was allowed to stabilize in artificial saliva for 1 h. In this interval, a large increase of the OCP in the noble direction for the Ti-6Al-4V samples was observed, fact which indicates that a stable passive film grows on the surface (Fig. 2).

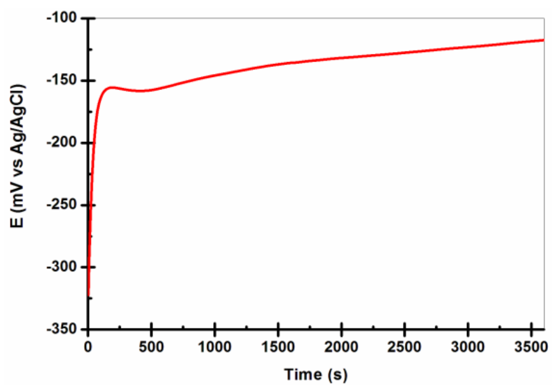

Fig. 2. Evolution of OCP of Ti-6Al-4V alloy measured as a function of time (1 h).

3.2. Effect of normal force on open circuit potential measurement

After the period of 1 h when OCP exhibits an anodic shift (from -322 to -117 mV vs. Ag/AgCl) were monitored the effects of normal force on OCP evolution before, during and after sliding wear test, tracked on Ti-6Al-4V samples.

In Fig. 3 there are shown the variations on OCP of Ti-6Al-4V alloy immersed in artificial saliva before (3 min.), during (1,000 cycles) and after (10 min.) fretting tests at frequency of 1 Hz, with a displacement amplitude of 200 µm, for 1,000 cycles, by applying normal forces mentioned above.

For all tests performed it was observed that with the onset of fretting a sudden decrease of the OCP occurs. This potential shift is associated with the damage of passive film by its partial or complete removal [8,13].

In the period of friction some oscillations in the OCP for Ti-6Al-4V alloy were reported, these being attributed to the periodic removal caused by the contact with counter body (depassivation) and growth caused by contact with the electrolyte (repassivation) of the passive film in the fretted zone [14-15].

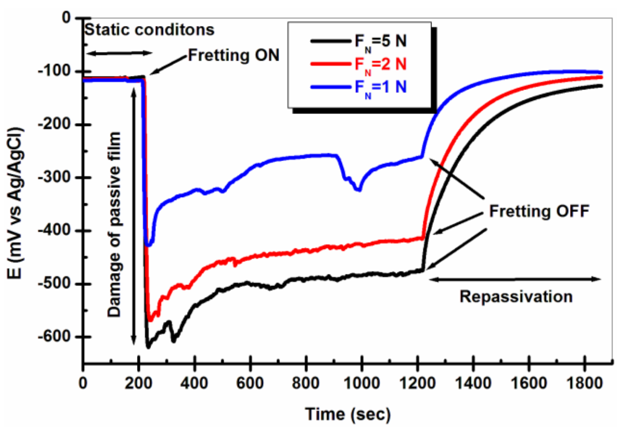

Fig. 3. Variation in OCP of Ti-6Al-4V alloy measured vs. time before, during and after loading at 1 N, 2 N and 5 N.

After unloading, the OCP of Ti-6Al-4V samples shows an anodic shift due to repassivation of Ti-6Al-4V substrate forming immediately a thin film of titanium oxide [8,13-15].

In conclusion, from Fig. 3 it is observed that the potential measured during the fretting-corrosion tests decreases linearly with increasing normal load.

3.3. Effect of normal force on the friction coefficient evolution

The effect of normal loads (1, 2 and 5 N) on the evolution of friction coefficient for Ti-6Al-4V alloy at fretting frequency of 1 Hz, with a displacement amplitude of 200 µm, for 1,000 cycles, in artificial saliva is observed in Fig. 4.

This figure reveals a decrease in the coefficient of friction with increasing normal force at constant frequency and constant number of cycles, due to smoothening of the surface under high load, similar to observations made also by Ahmad *et al*. for Aluminium Matrix Composite [16].

By correlation of potential values recorded during friction with friction coefficients it is noticed that the potential drop events are accompanied by a sudden decrease in these coefficients. This behaviour may be explained by the delamination of the tribolayers formed in the contact region, opinion also shared by Vieira *et al*. [17].

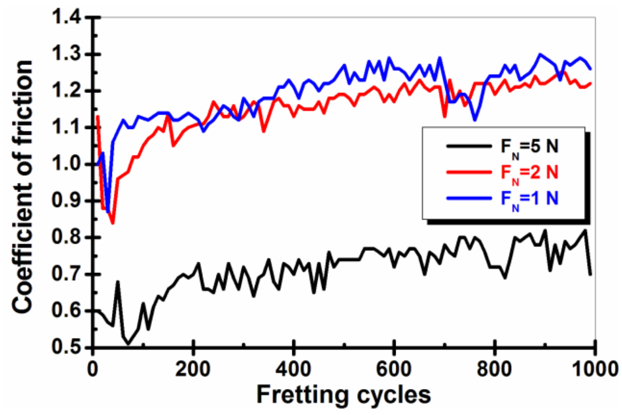

Fig. 4. The influence of normal loads (1 N, 2 N, 5 N) on the evolution of friction coefficient.

3.4. Characterization of the wear track

3.4.1. Scanning electron microscopy

The secondary electron images of the fretted zone of Ti-6Al-4V alloy, after subjecting it to fretting corrosion in artificial saliva at normal loads of 1, 2 and 5 N, fretting frequency of 1 Hz, with a displacement amplitude of 200 µm, for 1,000 cycles are shown in Fig. 5.

A first observation at investigation of the wear tracks from Fig. 5 is that with increasing normal load the dimensions of the wear track are increasing, too. Also, the damage suffered by the sample is directly proportional to increasing applied force.

3.4.2. Profilometric measurements

After the tribocorrosion experiments were finished, the total wear of the Ti-6Al-4V sample was evaluated by profilometry. Three dimensional surface profiles of the fretted zone of Ti-6Al-4V alloy are shown in Fig. 6.

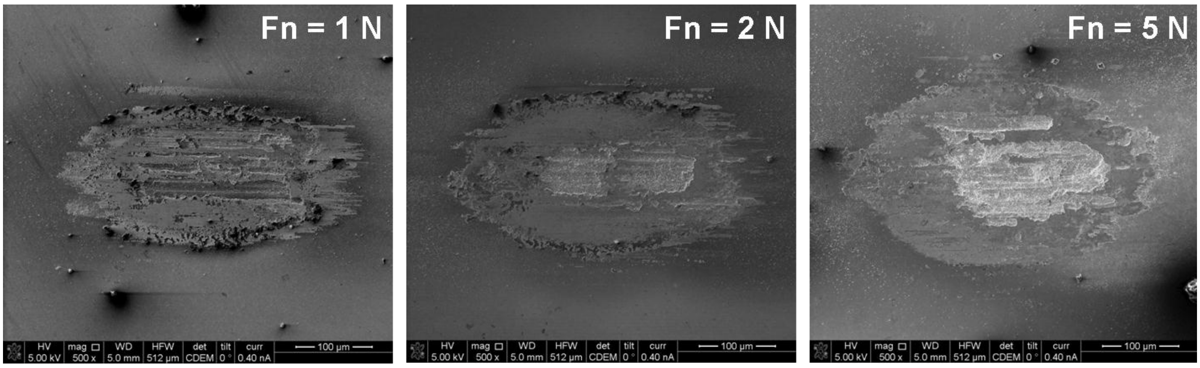

Fig. 5. SEM images of the fretted zone of Ti-6Al-4V after tribocorrosion tests under normal loads of 1, 2, 5 N.

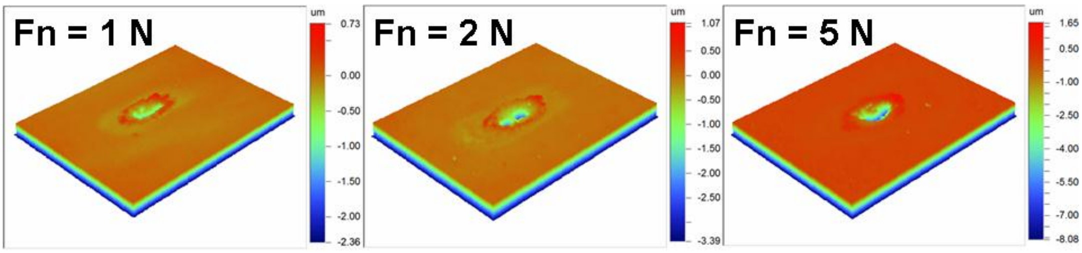

Fig. 6. 3-dimensional profiles of the fretted zone of Ti-6Al-4V alloy after tribocorrosion tests under normal loads of 1, 2, 5 N.

It can be seen clearly the same trend as for scanning electron micrographs of the entire fretted zone of Ti-6Al-4V, namely, with increasing normal load also the dimensions of the wear track increase. At the same time, the irregular surface profile of the wear track, in the case of higher normal loads, points towards the presence of adhered wear debris in the track indicating the abrasive wear mechanism (Fig. 6).

Once again the fretting-corrosion experiments made on Ti-6Al-4V alloy in artificial saliva have demonstrated that the wear is very pronounced if the applied normal loads are increasing.

4. Conclusions

The tribocorrosion behaviour of titanium alloy Ti-6Al-4V fretting against Al_2O_3 (corundum) in an artificial saliva solution was investigated in a ball-on-flat contact configuration combined with *in situ* electrochemical measurements (OCP).

According to evolution of OCP from immersion for a period of 60 minutes of Ti-6Al-4V alloy in artificial saliva it was observed an increase of the potential in the noble direction, fact which indicates that a stable passive film has grown on the surface. With the onset of fretting it was seized a drop in cathodic domain of OCP, decreases which is linearly with increasing normal load, due to the removal of the passive oxide layer induced by fretting and confirms its increase in susceptibility for corrosion.

Applied normal force was found to greatly affect the potential during fretting-corrosion, an increase in the normal force induces a decrease in potential accelerating the depassivation of the Ti-6Al-4V alloy.

According to the applied normal force a decrease in coefficient of friction with gradually load increase was confirmed, due to smoothening of the surface under high load.

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