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INFLUENCE OF NORMAL LOADS ON CORROSION BEHAVIOUR OF Ti-6Al-4V ALLOY DURING FRETTING IN ARTIFICIAL SALIVA

Eliza MARDARE[1], Lidia BENEA[1,*], Jean-Pierre CELIS[2]
[1]Dunarea de Jos University of Galati, Metallurgy, Materials Science and Environment Faculty, Competences Center: Interfaces-Tribocorrosion-Electrochemical Systems, Galati, Romania
[2]Katholieke Universiteit Leuven, Dept. MTM, B-3001 Leuven, Belgium
[*]Corresponding author: Lidia.Benea@ugal.ro

ABSTRACT

The fretting corrosion 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. Fretting corrosion 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 after the fretting motion ceased. It was confirmed a decrease in friction coefficient with gradually increasing load. The morphological features of the fretted zone and the wear mechanism were assessed using scanning electron microscopy and non-contact optical profilometer.

KEYWORDS: implant application, fretting corrosion, wear, electrochemistry, Ti-6Al-4V alloy

1. Introduction

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

Titanium based metals derive theirs resistance to corrosion from formation of an adhesive TiO_2 oxide layer at the surface to a depth of approximately 5 nm [3-7]. As long as oxygen is present, the spontaneous formation of a titanium oxide film on their surface leads to an extremely stable film and gives a passivating effect to the metal.

The 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 [8]. 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 in literature which use artificial saliva as test solution in the fretting corrosion behaviour of Ti-6Al-4V, compared with other simulated body fluids (Hank solution, Ringer solution, sodium chloride solution) [9-13].

Moreover the combination of mechanical parameters used in the present research such as load, frequency, displacement amplitude and number of cycles, is different compared to the same studies mentioned above [9-13].

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 solution.

2. Experimental procedure

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

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mechanical properties are presented in Table 1 was used as base material. The samples of Ti-6Al-4V used, in the form of plates, were cut to dimensions of 25 x 25 x 2 mm and then successively polished with waterproof abrasive paper with grit (320 - 4000 µm), diamond paste (3 and 1 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 were stored for about 24 hours in a desiccator to allow the formation of a stable surface film on the test samples.

Al_2O_3 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 Fusayama - Mayer artificial saliva [14-15], with the chemical composition presented in Table 2 and having a pH equal to 5. Tests were performed at room temperature (23^{o}C).

Table 2. *Chemical composition of test electrolyte*

Compounds	Saliva Fusayama - Mayer [g/L]
NaCl	0.4
KCl	0.4
$CaCl_2$*$2H_2O$	0.8
NaH_2PO_4	0.69
Urea	1

2.2. Fretting-corrosion tests

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

Ti-6Al-4V alloy samples serve as working electrode and their potential was controlled using Solartron Instruments 1287 Electrochemical Interface potentiostat/ galvanostat with a frequency response analyzer SI 1255. The counter electrode was made of platinum wire and the reference electrode was the Ag/AgCl (saturated KCl solution, E=200mV vs. NHE). These electrodes were placed in the fretting corrosion cell in such a way that only 1 cm^2 area of the working electrode was exposed to the 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 carried out with 1, 2 and 5 N normal forces, at 1 Hz reciprocating frequency, with a displacement amplitude 200 µm and 1000 cycles.

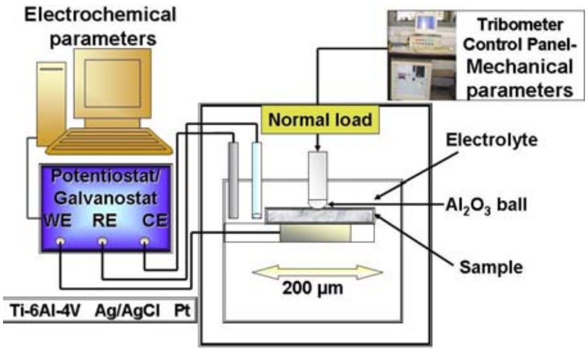

Fig. 1. *Schematic view of the experimental set up for fretting-corrosion tests*

The protocol used for the tribocorrosion tests consisted of two steps: (1) measuring the open circuit potential (OCP) of the sample by immersion for 60 minutes 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 surface in the wear track were determined by 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 characterize the morphological features of the fretted zone.

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	Tensile strength	Elongation
[MPa]		[%]
865	937	11

3. Results and discussions

3.1. Evolution of open circuit potential under static conditions

Prior to starting the fretting-corrosion tests, the Ti-6Al-4V alloy was allowed to stabilize in artificial saliva for 60 minutes. 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).

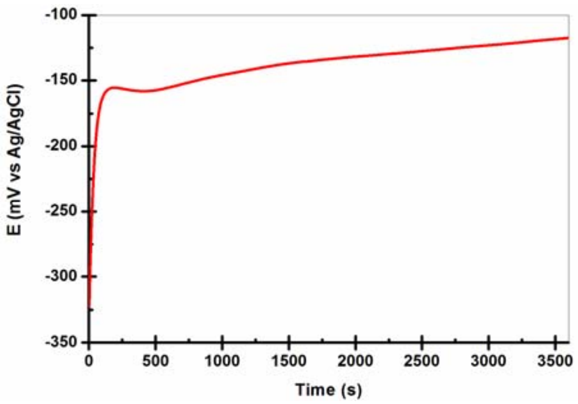

Fig. 2. *OCP evolution of Ti-6Al-4V alloy measured during 60 minutes of immersion*

3.2. Effect of normal force on open circuit potential measurement

After the period of 60 min. 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. These tests were performed at three different normal forces of 1, 2 and 5 N, fretting frequencies of 1 Hz, with a displacement amplitude of 200 µm and finally at 1000 number of cycles.

In Fig. 3 there are shown OCP variations of the Ti-6Al-4V alloy immersed in artificial saliva solutions before (3 min.), during (1000 cycles) and after (10 min.) fretting tests at a 1 Hz frequency with a displacement amplitude of 200 µm, for 1000 cycles, by applying the 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 partial or complete removal of its [10, 16]. In the period of friction were reported some oscillations in the OCP for Ti-6Al-4V alloy and this is 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 [17-18].

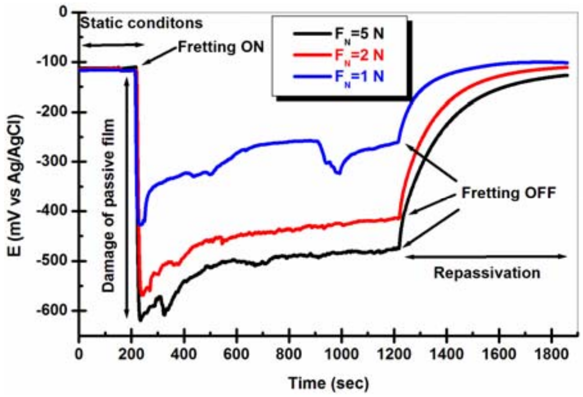

Fig. 3. *OCP variation of Ti-6Al-4V alloy measured vs. time before, during and after loading at 1 N, 2 N and 5 N.*

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 [10, 16-18].

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 imposed normal loads (1, 2 and 5 N) on the evolution of friction coefficient for the Ti-6Al-4V alloy at a 1 Hz fretting velocity at with a displacement amplitude of 200 µm, for 1000 cycles, in artificial saliva is observed in Fig. 4.

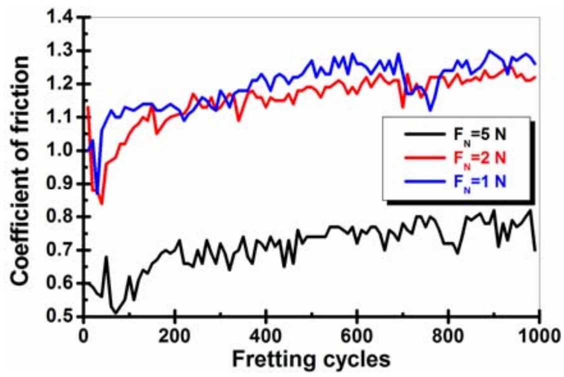

Fig. 4. *The influence of normal loads (1 N, 2 N, 5 N) on the evolution of friction coefficient*

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 observations which were made by F. Ahmad et al. for Aluminium Matrix Composite [19].

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By correlation of potential values recorded during friction with coefficient of friction values is observed that the potential drop events are accompanied by a sudden decrease in the coefficient of friction and this behaviour may explain by the delamination of the tribolayers formed in the contact region, similar observations being made by A.C. Vieira et al. [21].

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, at a 1 Hz fretting velocity of with a displacement amplitude of 200 µm, for 1000 cycles are shown in Fig. 5.

A first observation that can be made at investigation of the wear tracks from Figure 5 is that with the increase of the normal load the dimensions of the wear track also increase. Also, the damage suffered by the sample is directly proportional with the increase of the 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.

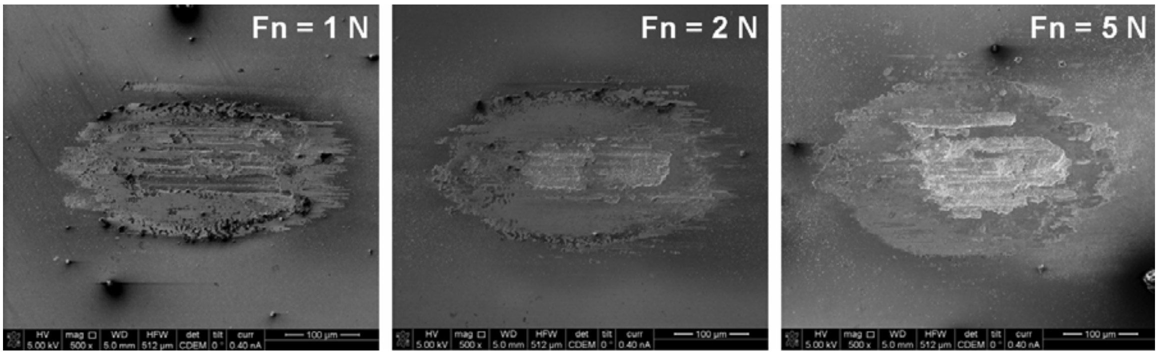

Fig. 5. *SEM images of the entire fretted zone of Ti-6Al-4V after tribocorrosion tests in artificial saliva solution under normal loads of 1, 2, 5 N*

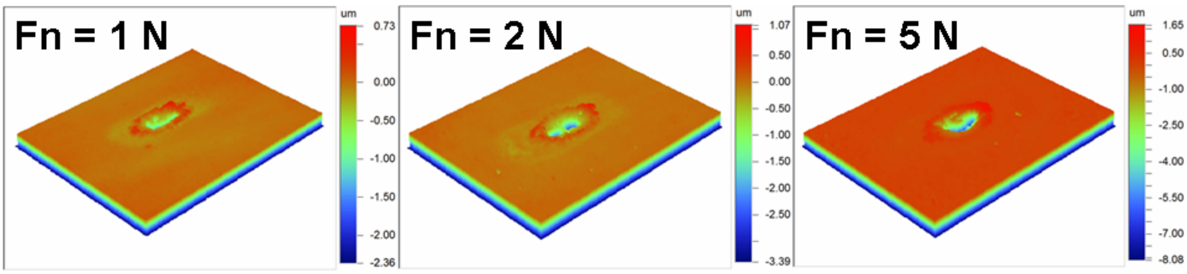

Fig. 6. *3-dimensional profiles of the fretted zone of Ti-6Al-4V alloy after tribocorrosion tests in artificial saliva solution under normal loads of 1, 2, 5 N*

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

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

4. Conclusions

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

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

The effect of normal force applied on corrosion-wear of the tested material was determined. The applied normal force was found to greatly affect the potential during fretting-corrosion, an increase in the normal force inducing a decrease in potential accelerating the depassivation of the Ti-6Al-4V alloy. Also, depending on the applied normal force, a decrease in coefficient of friction was confirmed, with gradual load increase, due to the smoothening of the surface under high load.

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