

Tribocorrosion behaviour of titanium in artificial saliva solutions

A.C. Vieira^{1,2*}, A.R. Ribeiro^{1,2}, L.A. Rocha^{2,3}, J.P. Celis¹

¹*Katholieke Universiteit Leuven, Dept. of Metallurgy and Materials Engineering, B-3030 Leuven, Belgium*

²*Research Centre on Interfaces and Surfaces Performance, Campus Azurém, 4800-058 Guimarães, Portugal*

³*University of Minho, Dept. of Mechanical Engineering, Campus Azurém, 4800-05 Guimarães, Portugal*

Abstract

Dental implants are used to replace teeth lost due to decay, trauma or periodontal disease. In last years, the demand for such implants has increased exponentially due mostly to the ageing of the population and/or increased reliability of implant therapy. To choose a material for a particular rehabilitation treatment different characteristics must be considered such as mechanical strength, elastic properties, machinability, chemical resistance, etc. There is, however, one aspect that is always of prime importance; namely how the tissue at the implant site responds to the chemical disturbance imposed by the presence of a foreign material. In this work, commercially pure titanium (grade 2) was selected mainly due to its excellent corrosion behaviour and biocompatibility, that make this material one of the most used in dentistry. The tribocorrosion behaviour of the material in conditions simulating mastication, when in contact with artificial saliva solutions was investigated. Corundum was used as counterface material. The tests were performed, at MTM- KULeuven (Belgium), in a fretting machine specially adapted for tribocorrosion experiments. A normal load of 2 N was applied to the specimens and a displacement amplitude of 200µm at a frequency of 1 Hz. The number of cycles was varied between 5.000 and 10.000. In order to simulate different environmental conditions, simple artificial saliva (0.7%KCl + 1,2%NaCl; pH =6), artificial saliva with corrosion catalyst (citric acid), and artificial saliva with anodic, cathodic and organic corrosion inhibitors (sodium nitrite, calcium carbonate or benzotriazole, respectively), was used. The tribocorrosion degradation mechanisms were investigated by Electrochemical Noise technique (TEN), which combines Electrochemical Emission Spectroscopy with fretting tests^[1]. After being tested, the surface of the samples was investigated by SEM and EDX. Roughness measurements and wear volume measurements were also performed. The depassivation/repassivation phenomena occurring during the tests were clearly detected, and are discussed. Considering the influence of the corrosion inhibitors, it was possible to observe that the degree of protection varies with the nature of the inhibitor.

Keywords: Tribocorrosion; Dental Implants; Titanium Grade 2; Different Types of saliva.

1. Introduction

The demand for metallic materials in medical and dental devices is large. Metals and alloys are widely used as biomedical materials and are indispensable in medical field. In particular, toughness, elasticity, rigidity, and electrical conductivity are essential properties in medical devices, as well as the biological properties (biocompatibility and bioadhesion), which are influenced by the physical, chemical and physicochemical behaviour of the material. Among metallic materials, titanium and its alloys have become increasingly established as biomaterial, essentially due to its excellent biocompatibility and good corrosion resistance of Ti grade 2. The stability under corrosion conditions of titanium is essentially due to a n-semiconducting passive layer ($Ti_{1+\delta}O_2$) which is formed on the surface. This passive film appears to be biologically inert not inducing toxic or inflammatory reactions in connective or epithelial tissues. Additionally it is bacteriostatic and does not significantly activate or inhibit different enzymatic systems specific for toxic reactions^[2]. It has been shown that the very good *in vivo* corrosion stability of titanium and its alloys can be further improved by increasing the thickness of the passive layer^[2].

Up to now, no cases have been reported for titanium and its alloys in which biodegradation without mechanical damage or fretting corrosion would have caused implant failure. Considering dental implants, particularly endosseous implants, degradation may be a consequence of mechanical stresses, resulting in small relative displacements (fretting) between implants and the surrounding bone tissues. The corrosive nature of the physiological environments (saliva) exacerbates material degradation leading to fretting-corrosion. Thus, this is a situation where materials are exposed to the combined attack by corrosion and fretting (tribocorrosion). The two mechanisms of degradation do not proceed separately, but will depend on each other in a complex way, and normally the corrosion is accelerated by wear and, similarly wear may be affected by corrosion phenomena^[3]. By other words, tribocorrosion may be considered as an irreversible transformation of a material resulting from simultaneous physicochemical and mechanical surface interactions taking place in a tribological contact. Therefore, fretting may lead to local removal of the passive film resulting on the exposure of the metal surface to the aggressive environment. Consequently, the corrosion rate will increase (wear accelerated corrosion) leading to a rapid degradation of a contact.

The contact conditions in fretting change with increasing displacement amplitude. Thus, fretting wear is often divided into the three following fretting regimes: the stick regime, in which the displacement is accommodated by elastic deformation of the asperities and no energy is dissipated; the stick-slip regime, or partial slip regime, in which there is a central stick region, where the corresponding asperities elastically deform, and an outer annular region where microslip occurs; and the gross slip regime, in which slip occurs through the entire contact region and the work done by sliding is irreversibly dispersed via friction.

In this work the tribocorrosion behaviour of commercially pure titanium in contact with artificial saliva solutions was studied in fretting conditions, considering a gross-slip regime^[4,5].

2. Experimental

Samples of Ti grade 2 (all from the same ingot) were cut in 2.5cm × 2.5cm size and mechanically polished up to 0.25µm SiO₂ particles. The nominal chemical composition of Ti grade 2 was O (0.25wt.%), N (0.03wt.%), C (0.08wt.%), H (0.015wt.%), Fe(0.3wt.%) and residuals (0.4wt.%). All the samples were ultrasonically cleaned with ethanol and

finally dried. The initial sample roughness was 0.43 μm (R_a). All the samples were polished only one day before the tribocorrosion test, to control the formation of the oxide passive layer.

Fretting behaviour was investigated using a triboelectrochemical technique^[6]. Integrating a fretting wear and corrosion tests, the Electrochemical Noise Technique (ENT) was used to determine tribocorrosion mechanisms, and to investigate the depassivation and repassivation kinetics of surface area activated by tribocorrosion processes. In this work, the counterbody used in the fretting test, consisted in a stationary alumina ball (corundum). Corundum balls (ϕ 10mm) were selected as counterbody material because of the high wear resistance, the chemical inertness, and the electric insulating properties of corundum^[1]. The fretting conditions correspond to a fretting (gross slip regime) test performed at an oscillating frequency of 1 Hz, a normal load of 10 N and linear displacement amplitude of 200 μm . These fretting tests were performed at 5000 and 10000 cycles for each sample. All experiments were performed in artificial saliva (AS) solutions at room temperature (23 °C) and with one relative humidity of 50%. The chemical composition of the AS solutions is presented in Table 1.

Table 1: Chemical composition of the different saliva solutions.

Components	Artificial saliva (AS)	AS with citric acid	AS with anodic inhibitor	AS with cathodic inhibitor	AS with organic inhibitor
Sodium Chloride, NaCl	0.70	0.70	0.70	0.70	0.70
Potassium Chloride, KCl	1.20	1.20	1.20	1.20	1.20
Citric Acid, C ₆ H ₈ O ₇ .H ₂ O		0.025			
Sodium Nitrite, NaNO ₂			0.16		
Calcium Carbonate, CaCO ₃				0.5	
Benzotriazole, C ₆ H ₅ N ₃					1.5

The corrosion potential was measured using a microelectrode (Pt), a reference electrode (SCE) and the working electrode (Ti grade 2). The different solutions used as electrolyte were pure AS, AS acidified with citric acid, AS with sodium nitrite (anodic inhibitor), AS with calcium carbonate (cathodic inhibitor), and AS with benzotriazole (organic inhibitor).

After the tribocorrosion test, the samples were cleaned with distilled water and ultrasonically cleaned with ethanol during 10 minutes. The topography of the wear tracks was evaluated using a Philips XL 30 ESEM FEG microscope equipped with energy-dispersive X-ray spectrometer (EDX). A profilometer was used to measure the volume of removed material.

3. Results and Discussion

3.1 Tribological Parameters

Fig. 1 shows SEM micrographs of the samples surfaces after the tribocorrosion test. Under the imposed conditions, two regions of the wear track can be identified. The central

part is characterized by the relative severe material damage and the presence of wear debris. The surrounding external part of the wear scar is smoothest and exhibits some material smearing^[7]. Also, it can be observed that the wear scar is characterized by sliding wear marks aligned in the fretting direction. By the high magnification of the fig. 1b) it can be seen the extensive plastic surface shear results in a structure of scales, which eventually, will delaminate and detach from the surface. Additionally, during fretting wear (gross slip regime) under oxidizing conditions, cracking and delamination of wear particles will be accelerated by their oxidation. This oxidation attack varies with the material and experimental conditions, but also with the wear scar. In all the different solutions used, the SEM and EDX results are very similar. EDX results show that continuous layers of titanium oxide are frequently found in the centre of the wear scar.

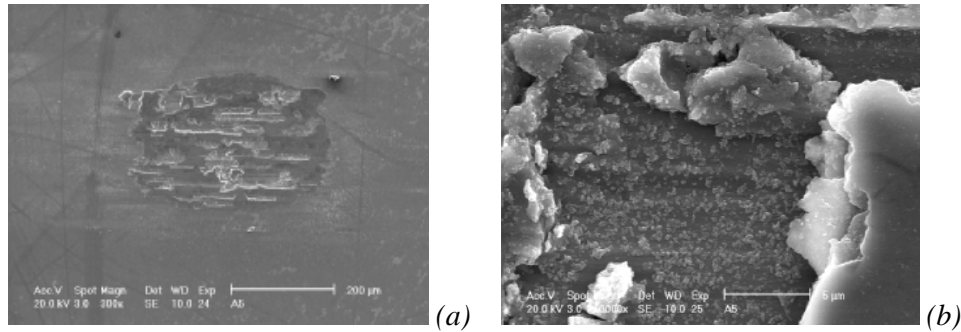


Fig. 1: SEM micrographs of the wear zone: overview (a) and centre part (b) of the wear scar.

Fig. 2, provided by wear measurements, gives precise information of the material removal, assuming that all the debris has been eliminated before the measurements (with the ultrasonic cleaning). In all cases, it is possible to detect transference of debris and its consequent aggregation in the borders of the wear scar. The lost of material is higher in the centre and minimum in the borders. This can be explained by the higher amount of time during which the centre was exposed to the fretting action when compared to the borders. This means that while the borders are only subject to the fretting action during an amount of time consistent with the frequency of the test (1 Hz), the centre of the wear scar is subjected to this action all over the entire test.

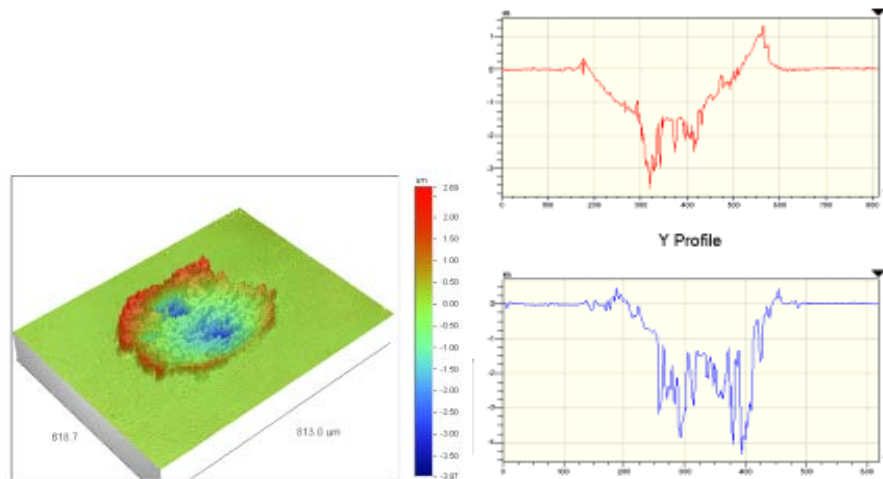


Fig. 2: Surface data form the wear scar, with 3D picture.

Fig. 3 shows the wear volume lost (a) and the coefficient of friction (b) obtained for each one of the solutions tested. The sample tested with AS solution with cathodic inhibitor is the one showing a higher increase in the amount of the wear volume within the 10000 sec tested in this investigation. However it should be referred that the sample tested in the AS solution with organic inhibitor is the one presenting a higher material lost after the test. Also, this sample is characterised by a high coefficient of friction (see fig. 3 b).

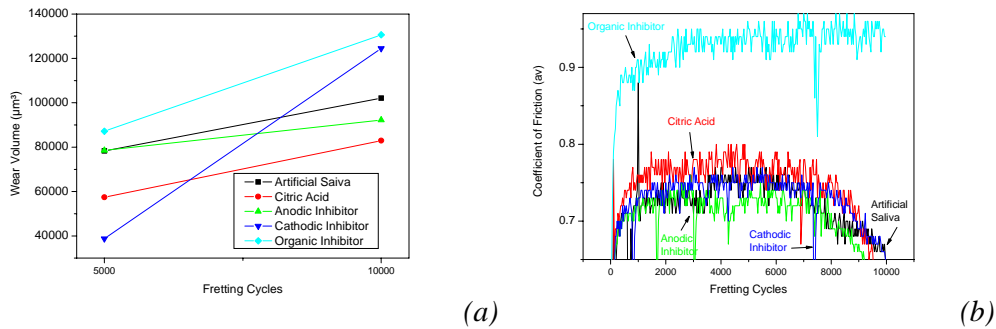


Fig. 3: (a) Representation of missing wear values for the different solutions presented. (b) Representation of medium coefficient of friction values for the different solutions presented, for 10000 fretting cycles.

The observation of the evolution of the coefficient of friction presented in Fig. 3b, reveals the presence of some peaks that can be attributed to the momentaneous formation of wear particles and their ejection from the contact area^[4]. With the exception of the test performed with the addition of the organic inhibitor, for all the other samples, the coefficient of friction tend to be attenuated after 5000 seconds. This behaviour may be explained by the build-up and accommodation of the debris after the adjustment of the two surfaces in contact^[3]. The fact that the sample tested with the solution with the organic inhibitor is the one presenting a higher wear loss and the higher coefficient of friction can be connected with the fact that the passive film that is expected to form, is quickly degraded when the fretting process is initiated. This can be caused by an inadequate concentration of organic inhibitor in AS.

During the fretting tests, the tangential force varies with the displacement and this variation corresponds to a closed cycle as presented in fig. 4a. The area A from these cycles represents the work made from the tangential force, and it can be expressed by $A = \oint F(s)ds$, where $F(s)$ represents the tangential force as a function of the displacement s . Thus, the area A will be the dissipated energy by the tangential force in each cycle. In the presented loops (fig. 4a) the first vertical line corresponds to the applied force. When this force is bigger than the attrite force, the loop change the direction and the sliding starts (horizontal line)^[8]. For all the tests, the tangential force presents an almost constant value of approximately ± 1.5 N or ± 2 N during the almost complete imposed displacement.

In fig. 4b, dissipated energy from the different solutions, at different fretting cycles, are presented. For 5000 fretting cycles, the sample tested with artificial saliva is the one that have more dissipated energy, i.e., the one who need more energy to start the sliding. The samples tested with the others solutions have similar values of dissipated energy.

However, at the end of the fretting test (10000 fretting cycles), there are no significant differences between the values of dissipated energy for the different solutions. The sample tested in the AS+citric acid solution appears to exhibit a lower global dissipated energy which might be in accordance with the lower quantity of lost material (see fig.3a).

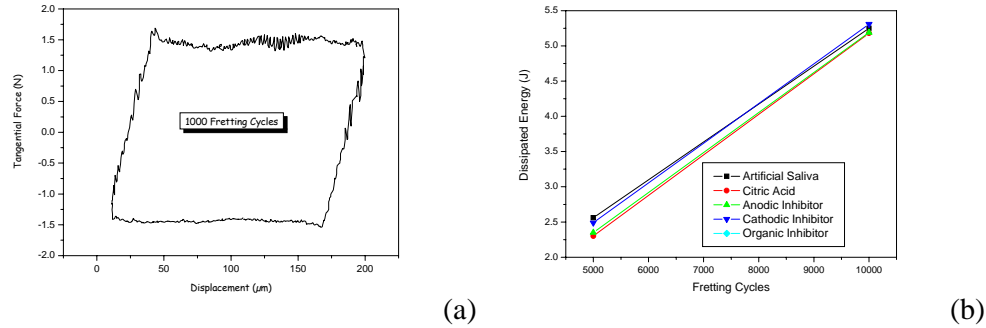


Fig.4: (a) Tangential Force versus the displacement. (b) Representation of the total dissipated energy values for the different solutions presented.

3.2 Electrochemical measurements

Fig.5 displays the evolution of the corrosion potential with time, recorded during the fretting test. As it can be observed, the potential of all samples significantly drops at the start of the fretting test, indicating that the mechanical action causes the destruction of the passive layer of the material (depassivation). However, a repassivation phenomenon appears to happen in all samples, as indicated by the increase in potential observed a short period of time after the start of the rubbing. As it can be observed, depassivation events, indicated by an abrupt decrease in potential occurs in some samples, probably due to the action of mechanical damage of the film, due to the failure and ejection of wear particles/debris from the wear track, according to the mechanism already referred above. This behaviour appears to be characteristic of the samples presenting a monotonically increase of the potential during the fretting test.

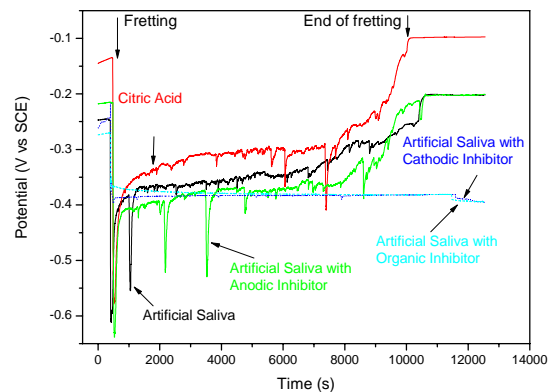


Fig. 5: Representation of potential values for the different solutions presented.

It should be referred that the sample tested with AS with citric acid is the one exhibiting higher electrochemical potential before, during and after the test. Remarkable is the fact that the evolution of this curve during the fretting test indicates the formation of a stable passive film, which appears to have a higher protective character at the end of the test than in the beginning. This behaviour indicates a beneficial influence of the citric acid on the characteristics of the passive film. It is known that, when formulated correctly, citric acid produces excellent results in passivation of almost any metals product [10].

The samples tested with AS solution and the AS solution with anodic inhibitor shows a similar behaviour, in terms of evolution of corrosion potential with the time, although they achieve a lower potential, just slightly above the initial potential (before fretting). In fact, for all these three samples, the characteristics of the newly formed passive film, after mechanical damage, i.e. partial or even total removal of the atmosphere naturally formed passive film by the fretting action, appears to be superior, indicating that the corrosion behaviour of the material may be improved due to the contact with this kind of solutions. In contrast, in the samples tested in the AS solutions with addition of the cathodic and the organic inhibitor, the potential remain at a relatively constant potential throughout the test, this behaviour being indicative of the establishment of a steady-state condition of the system. No depassivation/repassivation events were observed in these samples. However, it can be observed that at the end of the test the electrochemical potential is lower than that found before the fretting. As a consequence, the passive film formed under these conditions appears to have a less protective character than that formed under atmospheric conditions.

In Fig. 6, the corrosion current monitored during the fretting test by the electrochemical noise technique is presented. As it can be observed, the de-passivation of the materials caused by the initial stage of fretting is accompanied by a sudden increase in corrosion current. As shown in fig. 6a) the corrosion current then tends to slowly decrease during the fretting test, in accordance with the evolution of the potential shown in Fig. 5, achieving very low values at the end of the test. Again, the peaks of the current are also in accordance to the peaks in the coefficient of friction (see fig 3b), and this can be associated with the particles accumulation in the contact area and their ejection to out of this area. This suggests that debris formation contributes to the effect of a local repassivation of the metal, which is depassivated by the suddem loosening and ejection of the formed tribolayer[9].

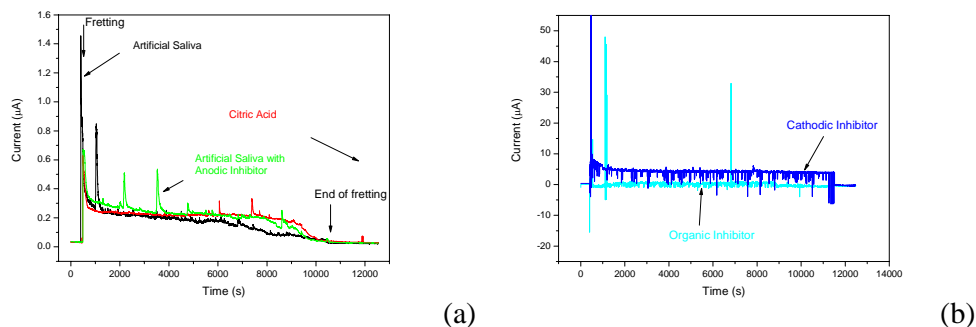


Fig. 6: Representation of current values for the different studied solutions.

As expected from the electrochemical potential results presented in Fig. 5, the efficiency of both the organic and cathodic inhibitors, in the concentrations used in this work, is very low. In fact, as shown in fig. 6 b) the corrosion current monitored during

the fretting test in the samples immersed in those solutions is much higher than that found in the other samples. Nevertheless, a slight better behaviour of the organic inhibitor may be inferred from the corrosion current results. As referred above, the detrimental effect of the addition of both inhibitors to the AS solution caused a higher mass loss of the materials (see fig. 3 a), this being a clear indication of the synergism between fretting and corrosion solicitations.

A cathodic inhibitor is used to slow the cathodic reaction or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. So, when the solution with cathodic inhibitor is used, the corrosion current should decrease. The organic inhibitor was expected to have the same influence on the corrosion current. In fact, these inhibitors, are usually designated as 'film-forming', because they protect the metal by forming a hydrophobic film on the metal surface.

4. Conclusions

In this work the tribocorrosion behaviour of pure Ti in artificial saliva solutions was studied by electrochemical noise technique performed during fretting tests.

The results obtained with the AS show that this solution don't affect negatively the surface of the Ti samples. This solution provides the formation of a passive film in the sample surface, with better characteristics than the naturally air-formed film. As a consequence, the combined effect of fretting and corrosion produce a surface that is electrochemically more passive with respect to the non-worn surface.

The addition of citric acid to the AS solution improves the protective character of the film. Consequently samples tested in this solution presents a higher corrosion potential and lower wear volume, as compared with the film formed over the Ti in the pure AS solution.

The addition of a anodic inhibitor to the AS solution does not influence significantly the behaviour of the samples in fretting-corrosion conditions. In contrast, the addition of a cathodic or a organic inhibitor to the AS solution, in the concentrations tested in this work, has a deleterious effect on the fretting-corrosion behaviour of the material, resulting in a surface that is electrochemically more active with respect to the non-worn surface, originating, at the same time, higher wear rates.

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