



Influence of pH and corrosion inhibitors on the tribocorrosion of titanium in artificial saliva

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Abstract

Dental implants are used to replace teeth lost due to decay, trauma, or periodontal diseases. Dental implants are most of the times subjected to micro-movements at the implant/bone interface or implant/porcelain interface (due to the transmitted mastication loads) and chemical solicitations (oral environment). Such implant becomes part of a tribocorrosion system, which may undergo a complex degradation process that can lead to implant failure. In this work, the fretting–corrosion behaviour of titanium grade 2 in contact with artificial saliva was investigated under fretting test conditions. Citric acid was added to artificial saliva to investigate a pH variation on the tribocorrosion behaviour of the material. Additionally, three different inhibitors were added to investigate cathodic and anodic reactions on the electrochemical response. Also, the influence of inhibitors included in the formulation of tooth cleaning agents or medicines was investigated. Degradation mechanisms were investigated by electrochemical noise technique that provided information on the evolution of corrosion potential and corrosion current during fretting tests. Depassivation and repassivation phenomena occurring during the tests were detected and discussed. Considering the influence of corrosion inhibitors, it was observed that the degree of protection varies with the nature of the inhibitors.

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1. Introduction

In dentistry, metallic materials are used as implants in reconstructive oral surgery to replace a single teeth or an array of teeth, or in the fabrication of dental prosthesis such as metal plates for complete and partial dentures, crowns, and bridges, essentially in patients requiring hypoallergenic materials [1,2]. Due to its mechanical properties, good resistance to corrosion in biological fluids and very low toxicity, titanium is the most commonly material selected for dental implants and prosthesis [1–4]. Corrosion of metallic implants is of vital importance, because it can adversely affect the biocompatibility and mechanical integrity of implants [3–5]. The stability of titanium under corrosion conditions is essentially due to the formation of a stable and tightly adherent thin protective oxide layer on its surface [5–7]. The passive film stability depends on its structure and

composition, which in turn are dependent on the conditions in which it was formed [5–7]. For instance pH is known to have a strong influence on the corrosion resistance of Ti and Ti alloys [8]. Ion release to the surroundings takes place when the dissolution of the surface passive film is accompanied by corrosion of the underlying base material. Extensive release of ions from implants can result in adverse biological reactions, and can lead to mechanical failure of the device [4–6]. It should be referred that an accumulation of Ti ions in tissues adjacent to implants has been reported in conditions not totally attributed to wear [6,9].

Despite their attractive corrosion and toxicological properties, titanium and titanium alloys generally exhibit poor fretting and wear resistance [4,10,11]. In fact, when used as implants or prosthesis, cyclic micro-movements at the implant/bone interface or implant/abutment interface may occur, inducing wear [1,4]. The low fretting and wear resistance of Ti and Ti alloys is attributed to the poor integrity of the TiO₂ surface passive layer, or to the plastic deformation of surface and subsurface layers [11]. Additionally, under sliding wear conditions Ti alloys have

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a strong tendency for transferring material to their counter faces, and tribochemical reactions at the contact surface are likely to occur [10]. Also, the release of wear debris may lead to cellular damage, inducing inflammation or encapsulation of the implant by fibrous tissue [4]. These environmental alterations may also alter the corrosion behaviour of the material.

Therefore, Ti dental implants and prostheses exposed to the combined degradation by corrosion and fretting, constitute a tribocorrosion system. It should be stressed that the two mechanisms of degradation do not proceed separately, but depend on each other in a complex way. Normally corrosion is accelerated by wear and, similarly wear may be affected by corrosion phenomena [12,13]. In fact, wear 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. Eventually, corrosion products will accumulate in the mechanical contact region, influencing the wear regime [12,13].

Several recent studies have focused on the fretting–corrosion behaviour of Ti alloys. Barril et al. [14] investigated the effect of the displacement amplitude, normal force, and tribometer stiffness on the tribocorrosion behaviour of Ti6Al4V/Al₂O₃ pairs, in contact with a 0.9 wt% NaCl solution. They concluded that wear accelerated corrosion would only occur, if the amplitude of the displacement was enough for causing slip between the materials. They proposed a model describing the influence of mechanical parameters (normal force, elasticity, and speed) on the wear-accelerated corrosion of materials. Duisabeau et al. [15], studied the tribocorrosion behaviour of Ti6Al4V/316L stainless steel pairs in a Ringer's solution, under gross slip conditions. They concluded that the dissipated mechanical energy and fretting regimes are strongly affected by the presence of a corrosive lubricant, because of the electrochemical phenomena caused by the electrolyte. The effect of the electrochemical conditions on the tribocorrosion behaviour of Ti6Al4V/Al₂O₃ contacts was investigated by Barril et al. [13,16]. They observed that under gross slip conditions, friction and wear are critically dependent on the applied potential, affecting the thickness, composition, and stoichiometry of the passive film. They concluded that the degree of oxidation of the plastically deformed metallic material would influence the extent of wear.

In this work, the tribocorrosion of titanium grade 2, under fretting regime, in contact with artificial saliva solutions, is investigated. The influence of pH and corrosion inhibitors in the artificial solution are considered.

2. Experimental

Samples made of Ti grade 2 (all from the same sheet) were cut in size as 2.5 cm × 2.5 cm, and mechanically polished down to 0.25 μm. The initial sample roughness was $R_a = 0.03 \mu\text{m} \pm 0.004 \mu\text{m}$. All the samples were polished 1 day before the experiments in order to allow the formation of an oxide surface layer. After polishing they were ultrasonically cleaned with ethanol and distilled water and finally dried. The nominal chemical composition of Ti grade 2 was 0.25 wt% O,

0.03 wt% N, 0.08 wt% C, 0.015 wt% H, 0.3 wt% Fe, and residuals (0.4 wt%).

Fretting–corrosion behaviour was investigated using a triboelectrochemical approach, in which the electrochemical noise technique was used to monitor the fluctuations of corrosion potential and corrosion current during the fretting tests. Corundum balls (Ø 10 mm) were selected as counter body material (Ceratec, The Netherlands) because of high wear resistance, chemical inertness, and electrical insulating properties. Titanium grade 2 specimens used as working electrode (WE) were covered with an adhesive tape to leave an area of 1 cm² exposed to the test solutions. A Ag/AgCl reference electrode and a microelectrode consisting in a Pt electrode with a diameter of 0.25 mm and a tip length of 1.2 mm were used. The experimental set-up used for electrochemical noise measurements during corrosion–wear tests on immersed samples is schematically shown in Fig. 1. As described elsewhere [17], the configuration of the experimental set-up was optimised to improve accuracy and minimize external noise. A potentiostat (Solartron electrochemical interface model 1287) was used, which allows voltage and current measurements at a resolution of 1 μV and 1 pA, respectively. The microelectrode coupled to the working electrode was used to sense the current flowing between them. The counter body was lifted away from the WE at the end of fretting tests. The electrochemical noise data are reported according to ASTM conventions [18]. The bidirectional sliding (fretting) test equipment was described elsewhere [19]. The sliding conditions correspond to a fretting test performed at a normal load of 2 N, an oscillating frequency of 1 Hz, and a linear displacement amplitude of 200 μm. These fretting tests were performed for 5000 and 10,000 cycles at an ambient temperature of 23 °C. The number of cycles, the tangential force, the normal force, the displacement amplitude, and the coefficient of friction were recorded at equally spaced time increments during the whole test duration.

The solutions used during the experiments were artificial saliva (AS), with different chemical compositions (Table 1). Citric acid was added in order to investigate the influence of a pH variation on the tribocorrosion behaviour of the contact. Three different kinds of inhibitors were added in order to investigate the action of the cathodic and anodic reactions on the electrochemi-

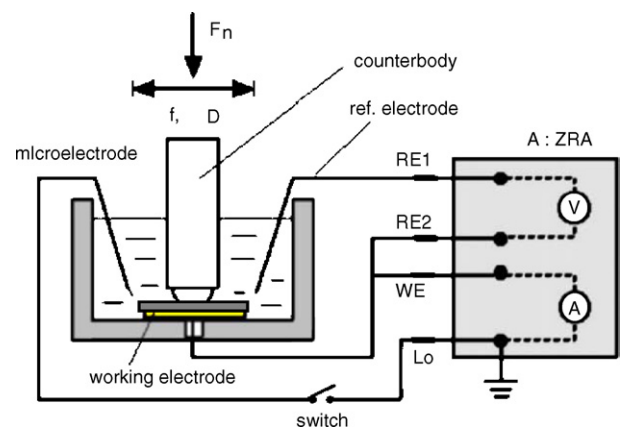


Fig. 1. Schematic representation of the experimental set up used for the tribo-corrosion experiments.

Table 1
Chemical composition of the artificial saliva solutions used (wt%)

Solution compound	Artificial saliva (AS)	AS + citric acid	AS + anodic inhibitor	AS + cathodic inhibitor	AS + 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 ($C_6H_8O_7 \cdot H_2O$)		0.025			
Sodium nitrite ($NaNO_2$)			0.16		
Calcium carbonate ($CaCO_3$)				0.5	
Benzotriazole ($C_6H_5N_3$)					1.5
pH	5.5	3.8	5.5	5.5	5.5

cal response. Also, it was found useful to analyse the influence of corrosion inhibitors, which may be included in the formulation of tooth cleaning agents or medicines.

After the tribocorrosion tests, the samples were ultrasonically cleaned with ethanol and distilled water during 10 min. The wear scars were investigated by reflected light microscopy with Nomarski contrast, laser profilometry (Rodestock RM 600), and SEM-EDX (Philips XL 30 ESEM FEG). The wear volume was determined by a profilometric method as described earlier [19].

3. Results and discussion

3.1. Tribological measurements

The evolution of the mechanical contact behaviour was investigated by acquiring force–displacement hysteresis loops at certain time intervals during the fretting tests. For tests performed during 5000 fretting cycles, loops at 20, 1000, and 5000 cycles were obtained. As these tests were performed at a frequency of 1 Hz, the number of cycles corresponds to the testing time in seconds. Moreover, during tests performed for 10,000 fretting cycles tests, the loop at 10,000 fretting cycles was also recorded. In Fig. 2 representative fretting log diagrams (AS and AS + citric acid) are presented. The shape of the tangential force–displacement (F_t – D) cycles is, in all cases, a parallelogram, indicating that the accommodation of displacement occurs under a gross-slip regime [15,19,20]. In fact, under the imposed fretting conditions, the elastic deformation of the material and the stiffness of the apparatus do not accommodate the imposed displacement, and an effective relative motion between the two contacting materials takes place. Consequently, friction occurs between the two materials, resulting in a measurable tangential force. F_t increases during the test, and reaches a steady state after 5000 cycles. This behaviour was observed under all test conditions.

In Fig. 3 the average coefficient of friction monitored in the AS and artificial saliva plus organic inhibitor (AS + organic) is presented. In the other solutions, the evolution of the coefficient of friction with fretting cycles is similar to the one noticed in the AS solution. In the AS solution three regions can be identified during the fretting tests. A first region extends up to ca. 2000 cycles where an increase of the coefficient of friction is observed. This region corresponds to the running-in period in which an adjustment of the two contacting surfaces occurs by crushing

and smearing of the asperities [14]. A second region expands up to ca. 6000 cycles, during which the coefficient of friction remains fairly stable. Finally, after ca. 7000 cycles, a monotonic decrease of the coefficient of friction is observed.

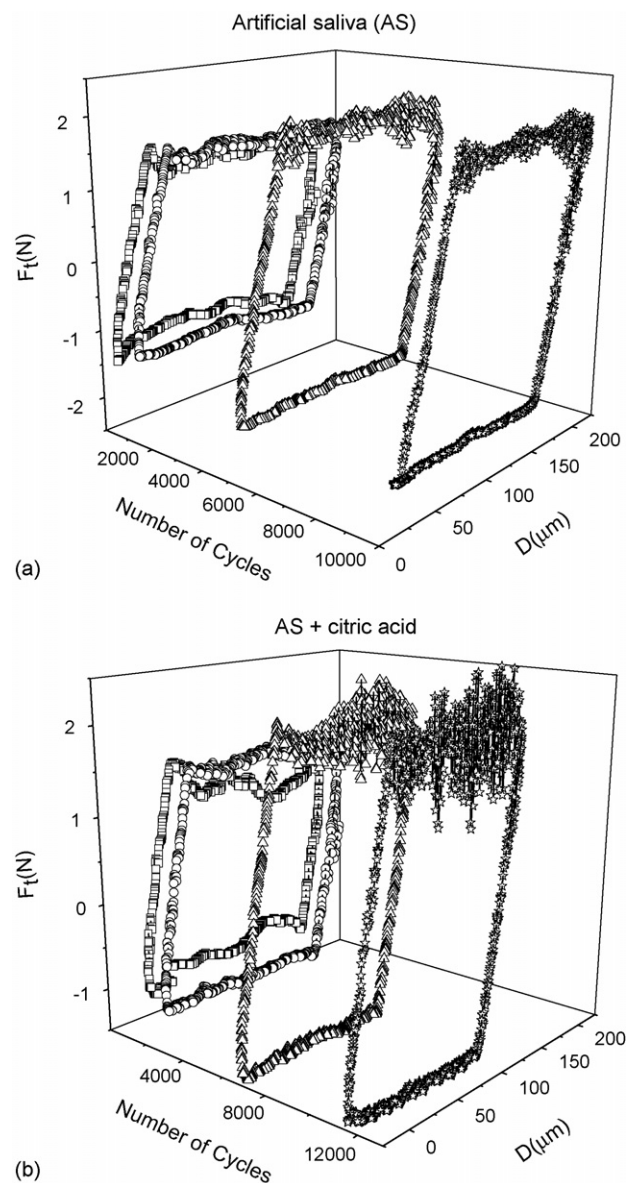


Fig. 2. Fretting logs recorded during tests conducted for 10,000 cycles in (a) AS and (b) AS + citric acid solution. Fretting test parameters: 2 N, 1 Hz, 200 μ m, and 10,000 cycles.

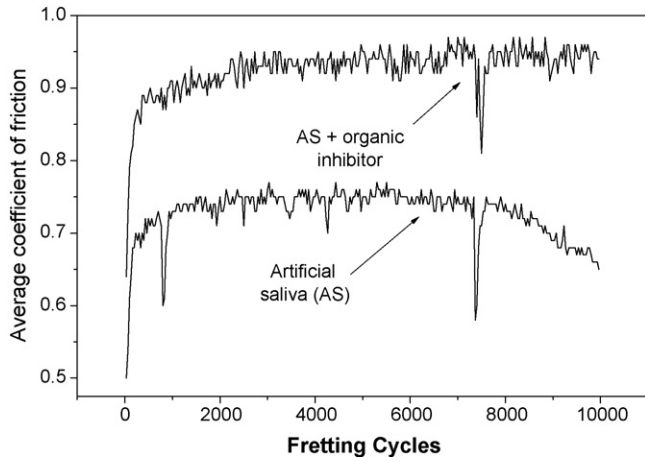


Fig. 3. Evolution of the average coefficient of friction during fretting tests performed for 10,000 fretting cycles in AS and AS+organic inhibitor solutions. Fretting test parameters: 2 N, 1 Hz, 200 μm , and 10,000 cycles.

The coefficient of friction exhibits strong oscillations during the fretting test. After the running-in period, these oscillations may be attributed to the build-up and accumulation of third-body particles in the contact region. After the accommodation of the two surfaces debris are ejected out of the contact as rubbing keeps on [13]. Micrographs of the wear scars of Ti samples are presented in Fig. 4. No significant differences were observed between samples tested in the different solutions. Under the imposed wear test conditions, two regions can be identified in the wear track. The central part is characterized by a relative severe material damage and the presence of wear debris. The surrounding external part of the wear scar is smooth and exhibits some material smearing [21]. The wear scar is characterized by sliding wear marks aligned in the fretting direction. The central area of the wear scar reveals scales, most probably formed by an extensive plastic surface shear. These scales are likely to delaminate and detach from the surface, inducing the oscillations in F_t . Additionally, it is expected that during fretting under gross slip regime and oxidizing conditions, cracking, and delamination of wear particles will be accelerated by their oxidation [13,16].

As shown in Fig. 2, the real displacement is inferior to the imposed displacement 200 μm , because a part of the displacement was accommodated by the elastic deformation of the fretting contact and the limited stiffness of the test equipment [20]. The area (A) in the fretting logs shown in Fig. 2 can be expressed as [15]:

$$A = \oint F_t(D) ds \quad (1)$$

with F_t the tangential force and D is the displacement. Thus, area A represents the dissipated friction energy in the contact during each fretting cycle [16,17]. In Fig. 5a the evolution of the dissipated energy as a function of the number of friction cycles is presented. In all test solutions, the dissipated energy increases with fretting duration. In the artificial saliva with organic inhibitor (AS+organic) the dissipated energy is substantially higher than in the other solutions, attending a value of ca. 6.7 J, after 10,000 cycles due to the higher coefficient of fric-

tion (Fig. 2). Also, as observed in Fig. 5a, the dissipated energy tends to reach a steady state as the number of fretting cycles increases.

The evolution of the wear volume, calculated from profilometric measurements after 5000 and 10,000 cycles, is plotted in Fig. 5b as a function of the dissipated energy. These wear volumes account for the material removed from the contact region both by wear and corrosion. When the fretting contact is under gross slip regime, a linear relation between the wear volume and the cumulated dissipated energy is commonly observed [15,16]. In Fig. 5b the existence of a linear relationship is assumed. The slope of the wear volume/dissipated energy curves expresses the wear rate per unit of dissipated energy. Some differences are observed among the different solutions although these distinctions are dependent on the extent of the fretting tests. Regarding the test performed during 5000 cycles, it can be observed that the Ti sample tested in the AS + organic solution suffers a lower weight volume loss that is ca. 2 times lower than that the one noticed in the AS + cathodic inhibitor solution. However, after 10,000 fretting cycles, Ti has a lower wear volume loss in the AS + citric acid solution, indicating that some protection is provided by the addition of citric acid to the solution.

Regarding the wear rate per unit of dissipated energy, values between 7.2×10^4 and $7.8 \times 10^4 \mu\text{m}^3 \text{J}^{-1}$ have been reported in the literature for the Ti6Al4V alloy in contact with saline solutions [15,16]. However, such data for pure titanium are not yet available in literature. In this work, depending on the nature of the solution, values between 8.9×10^3 and $8.6 \times 10^4 \mu\text{m}^3 \text{J}^{-1}$ were derived. The nature of the solution appears to influence this behaviour. The AS+cathodic inhibitor and AS+anodic inhibitor solutions induce a higher wear rate of Ti per unit of dissipated energy than the other solutions. No significant differences in this behaviour were observed between the AS and the AS+citric acid solutions, while a rather slow evolution of the wear volume loss with dissipated energy was observed in the AS+anodic solution.

3.2. Electrochemical measurements

The evolution of the corrosion potential with fretting testing time is shown in Fig. 6. Before the start of the fretting tests, the test samples were immersed in the different electrolytes to reach stabilization. Once stabilization was achieved, fretting tests were started. A significant drop in potential is observed immediately after the start of the mechanical action, indicating the destruction of the passive film (depassivation), and the exposure of fresh active titanium to the test solutions [12–17].

The evolution of the corrosion potential at the start of the fretting test is shown in Fig. 7. In the AS (Fig. 7a), AS+citric acid and AS+anodic inhibitor (Fig. 7b), the potential reaches very low values within a short period of ca. 100 s, before it evolves to more noble values. Concerning the behaviour of Ti in the AS+organic inhibitor (Fig. 7a) and in the AS+cathodic inhibitor (Fig. 7b) solutions, it can be observed that the drop in potential is significantly lower attending, after some time, a steady state value that remains almost unchanged during the remaining fretting test cycles (Fig. 6a and b). In all the other

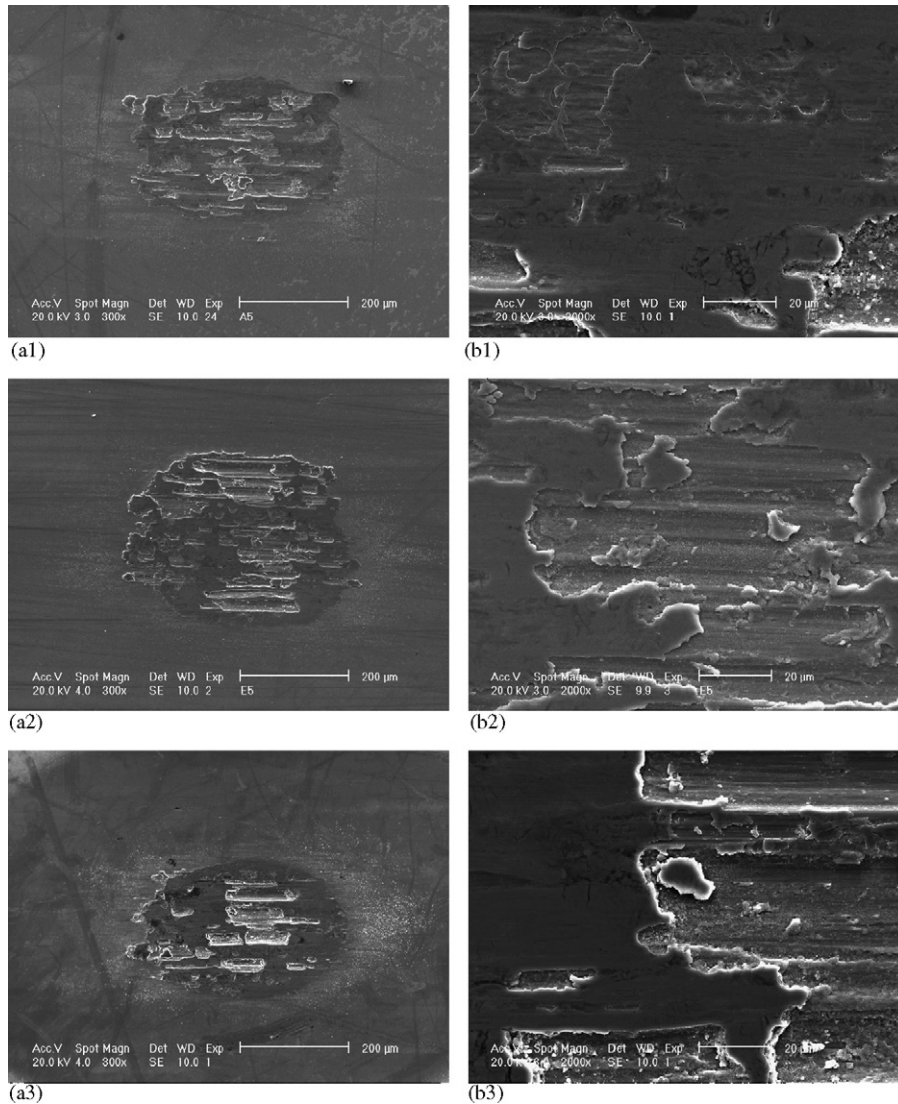


Fig. 4. Micrographs of (a) the wear scar, and (b) of the interior of the scar: (1) AS; (2) AS + organic inhibitor; (3) AS + citric acid. Fretting test parameters used were: 2 N, 1 Hz, 200 μm , and 5000 fretting cycles.

solutions, an abrupt increase in potential occurs after the first stage. Then, the corrosion potential slowly evolves to more noble values, indicating a decrease in corrosion susceptibility as the fretting tests go on. As shown in Fig. 4, this behaviour may be attributed to the build-up of a tribolayer in the contact region that creates a barrier between the Ti surface and the test solution. As observed in Fig. 6a and b, the slow increase in potential is sometimes interrupted by abrupt potential drop events, probably due to the sudden partial delamination of the tribolayers. The sample tested in the AS + citric acid solution is the one exhibiting the highest electrochemical potential before, at the beginning, during, and after the fretting test (see Figs. 6b and 7b).

A representative evolution of the coefficient of friction and of the corrosion potential as a function of the fretting time is plotted in Fig. 8 for Ti in AS + anodic solution. The potential drop events are accompanied by a sudden decrease of the coefficient of friction. As explained above, the delamination of the tribolayers formed in the contact region may explain this behaviour.

Remarkable is the evolution of the corrosion potential towards higher potential values, observed after ca. 7000 cycles in the AS solution and in the AS + citric acid or AS + anodic inhibitor (Fig. 6). As shown in Fig. 8, this variation in potential is accompanied by a decrease of the coefficient of friction. This new regime might be attributed to the stabilization of the three body contact area, after 7000 cycles. In other words, as the mechanical action proceeds in the contact area, wear debris become smeared out and entrapped into the surface. Consequently, a delamination of the tribolayers at the contact area becomes less probable, and the formed mechanical mixed layer acts as a protective film both in terms of wear and corrosion.

Finally, it should be noticed that at the end of the fretting test, the corrosion potential recovers its original value of before the test or becomes even slightly higher. This behaviour indicates that the newly formed passive film, after a total removal of the naturally formed passive film by the fretting action, together

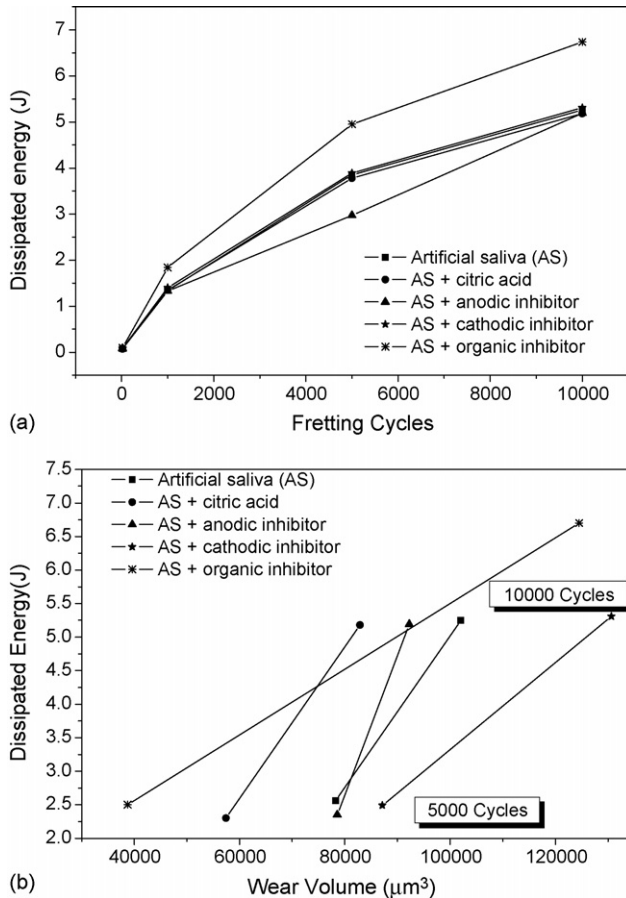


Fig. 5. (a) Evolution of the contact dissipated energy with testing time; (b) evolution of the wear volume as a function of contact dissipated energy. Fretting test parameters used were: 2 N, 1 Hz, 200 μm , and 10,000 cycles.

with the mechanical mixed layer has quite similar characteristics as the naturally formed film present on titanium before mechanical loading. The exception to this behaviour are the Ti samples tested in the AS + cathodic inhibitor and AS + organic inhibitor, in which such a recovery of the corrosion potential is not observed after the fretting tests. These solutions by inhibiting the cathodic reaction(s), probably hinder the formation of a new passive film on the surface of worn Ti.

The evolution of the corrosion current monitored by the electrochemical noise technique during the fretting tests is presented in Figs. 9–13. The behaviour of Ti in the AS, AS + citric acid, and AS + anodic inhibitor solutions (Figs. 9–11) differs from that observed in the AS + cathodic inhibitor and AS + organic inhibitor solutions (Figs. 12 and 13). Nevertheless, as it can be observed, in all samples the depassivation of the materials during the initial stage of fretting is accompanied by a sudden increase in corrosion current density. This increase is much higher in the AS + cathodic inhibitor and AS + organic inhibitor solutions than in the other solutions (see current scale in the graphs), indicating that these solutions have a much stronger corrosive action on fresh (depassivated) titanium surfaces than the other ones. In fact, the presence of organic and cathodic inhibitors, at concentrations used in this work, significantly affects the corrosion rate of titanium. Actually, as shown in Figs. 12 and 13, the cor-

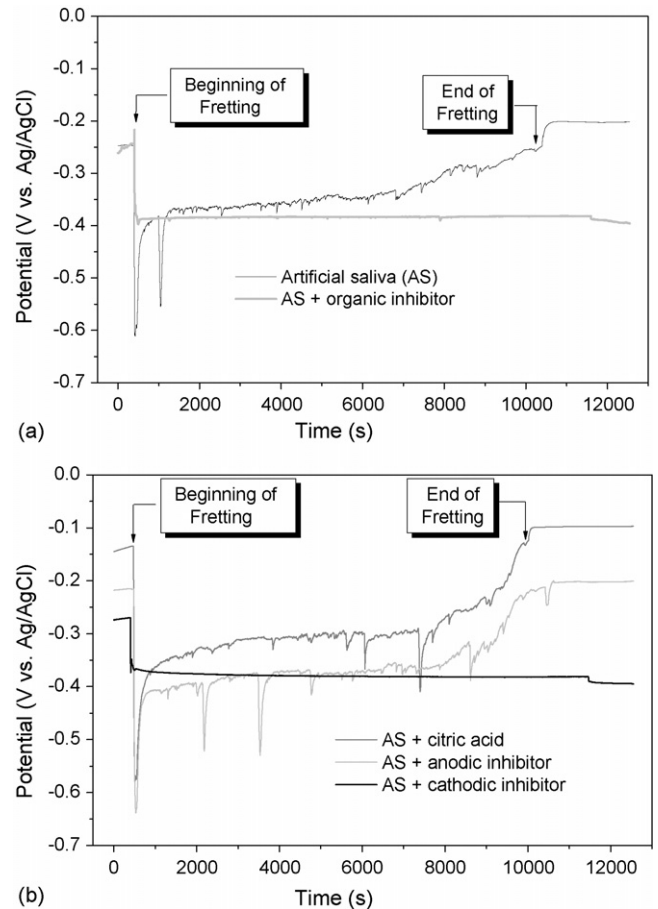


Fig. 6. Evolution of open-circuit potential: (a) AS and AS + organic inhibitor solutions; (b) AS + citric acid and AS + anodic and cathodic inhibitor solutions. Fretting test parameters: 2 N, 1 Hz, 200 μm , and 10,000 cycles.

rosion current monitored during the fretting tests on samples immersed in these solutions, is much higher than the one found in other solutions. Also, after the first increase in current, arising from the removal of the passive film in the contact region when sliding starts, no significant variation in the corrosion current is observed during the fretting tests. Nevertheless, the organic inhibitor seems to be somewhat more effective based on the corrosion current results. That is in accordance with the slightly lower wear volume loss noticed on Ti in this solution (Fig. 5b), in comparison with the AS + cathodic inhibitor solution, notwithstanding the higher coefficient of friction (Fig. 3).

In all the other samples (Figs. 9–11), after the initial increase in corrosion rate caused by the destruction of the passive film, the corrosion current monotonically decreases during the fretting test. Again, as the corrosion potential evolution revealed (Fig. 6a and b), some current peaks are observed, which are in good agreement with the oscillation in the coefficient of friction, as appears from Fig. 14. The delamination of the tribolayers formed at the contact surface, by exposing or facilitating the access of the solution to the metallic Ti, may explain this behaviour.

A decrease in the corrosion current is observed after ca. 7000 cycles, in the AS, AS + citric acid, and AS + anodic inhibitor solutions indicating the formation of a third-body protective layer in the contact region, as already referred. However,

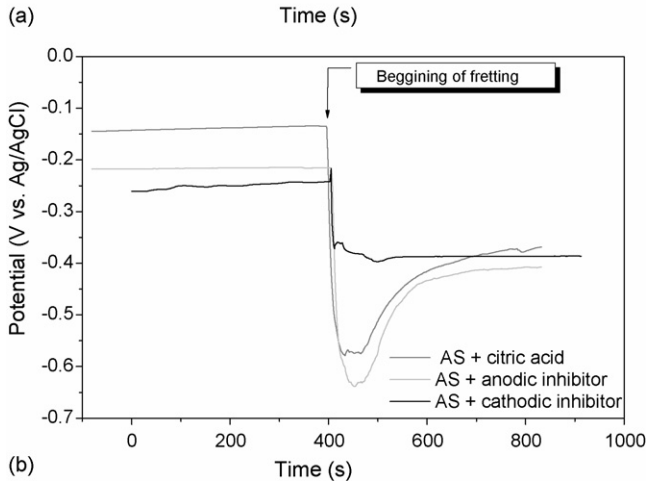
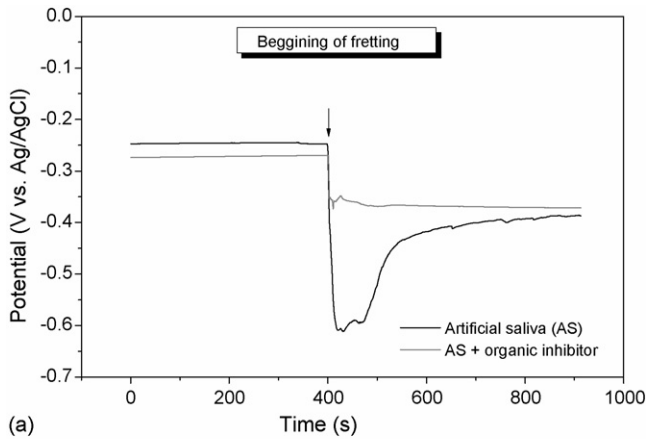


Fig. 7. Evolution of open-circuit potential values during the running-in of the fretting tests: (a) AS and AS + organic inhibitor solutions; (b) AS + citric acid and AS + anodic and cathodic inhibitor solutions. Fretting test parameters: 2 N, 1 Hz, 200 μ m, and 10,000 cycles.

the decrease in corrosion current is more pronounced in the AS + citric acid and AS + anodic inhibitor solutions, indicating that these additives provide some protection to titanium. The slightly lower wear volume loss of Ti in these solutions, in comparison to the AS solution (Fig. 5b), may be attributed to the corrosion protection afforded by the presence of the citric acid or the anodic inhibitor. In other words, the wear

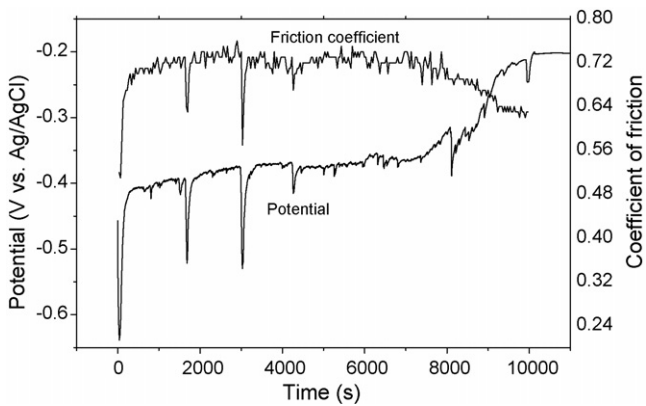


Fig. 8. Evolution of the open-circuit potential and of the coefficient of friction during the fretting test. AS + anodic inhibitor. Fretting test parameters: 2 N, 1 Hz, 200 μ m, and 10,000 cycles.

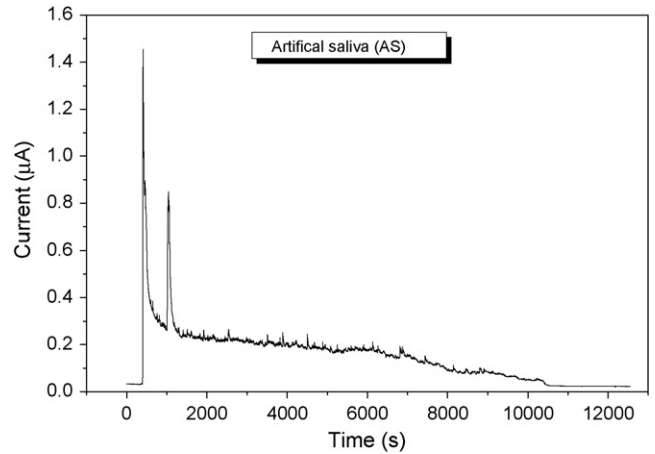


Fig. 9. Evolution of the corrosion current during the fretting tests in AS solution. Fretting test parameters: 2 N, 1 Hz, 200 μ m, and 10,000 cycles.

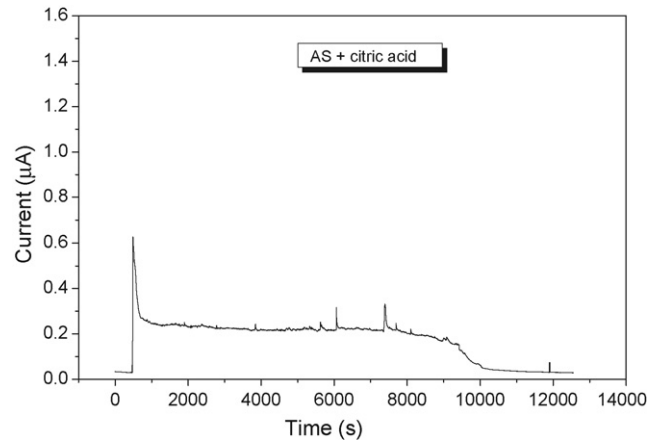


Fig. 10. Evolution of the corrosion current during the fretting tests in AS + citric acid. Fretting test parameters: 2 N, 1 Hz, 200 μ m, and 10,000 cycles.

and corrosion behaviour of Ti is influenced by the oxidation and reduction reactions occurring in the contact area during fretting, depending on the chemical composition of the test solutions.

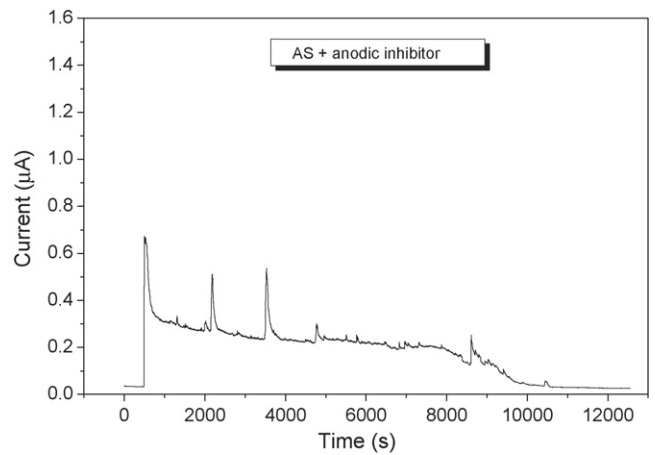


Fig. 11. Evolution of the corrosion current during the fretting tests in AS + anodic inhibitor. Fretting test parameters: 2 N, 1 Hz, 200 μ m, and 10,000 cycles.

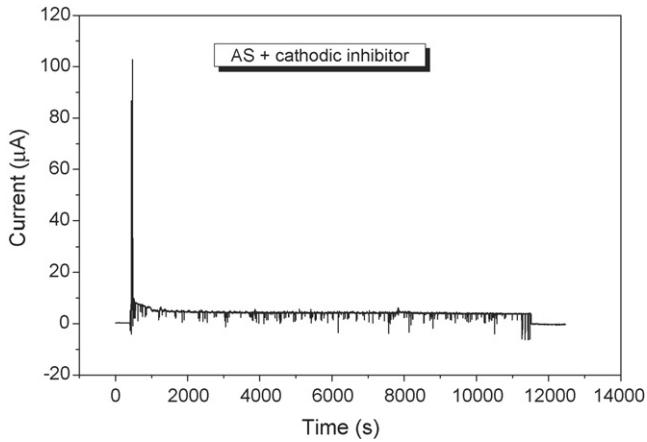


Fig. 12. Evolution of the corrosion current during the fretting tests in AS + cathodic inhibitor. Fretting test parameters: 2 N, 1 Hz, 200 μm , and 10,000 cycles.

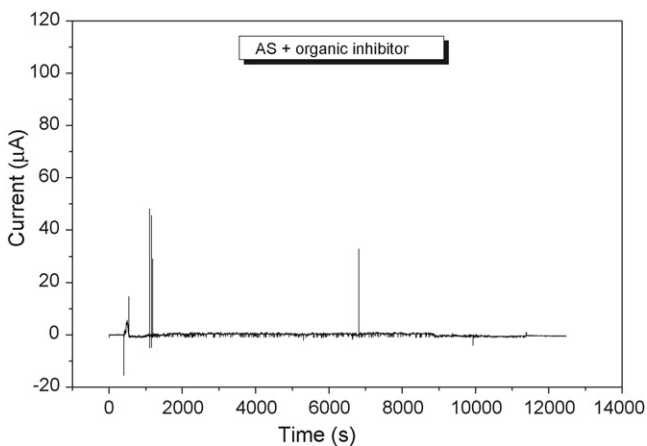


Fig. 13. Evolution of the corrosion current during the fretting tests in AS + organic inhibitor. Fretting test parameters: 2 N, 1 Hz, 200 μm , and 10,000 cycles.

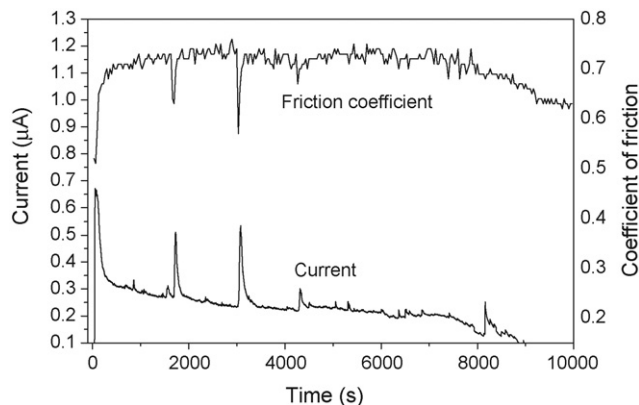


Fig. 14. Evolution of the corrosion current and of the coefficient of friction during the fretting tests in AS + anodic inhibitor. Fretting test parameters: 2 N, 1 Hz, 200 μm , and 10,000 cycles.

4. Conclusions

In this work, the influence of pH and corrosion inhibitors in artificial saliva on the tribocorrosion behaviour of pure Ti under fretting was investigated.

The addition of citric acid or anodic inhibitor to artificial saliva results in a slight improvement of the tribocorrosion behaviour of Ti. No significant differences were observed in the wear rate per dissipated energy, but a lower wear volume loss was obtained that can be attributed to the slightly lower corrosion rate observed in these solutions during the fretting tests.

The protection noticed by the addition of citric acid or an anodic inhibitor to artificial saliva is probably due to the nature of the oxidation and reduction reactions occurring in the contact area during fretting. Tribolayers are formed in the contact region during the tribocorrosion test. These tribolayers become more stable after ca. 7000 cycles in solutions containing citric acid or anodic inhibitor, as revealed by a lower coefficient of friction and a lower corrosion current.

The addition of a cathodic or an organic inhibitor to artificial saliva at concentrations tested in this work, has a hazardous effect on the fretting–corrosion behaviour of titanium. Both an increase in the wear volume loss per unit-dissipated energy and a significant higher corrosion rate during fretting tests, were observed in these solutions.

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