Simultaneous degradation by corrosion and wear of titanium in artificial saliva containing fluorides

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Abstract

The degradation of titanium-based oral rehabilitation systems can occur by corrosion and wear processes taking place simultaneously (tribocorrosion) and influenced by the presence of fluorides. In this study, the tribocorrosion behavior of titanium in artificial saliva solutions containing fluorides is investigated. Before sliding tests were started up, electrochemical measurements such as open circuit potential (OCP) and impedance spectroscopy (EIS) were performed to get information on the corrosion behavior of titanium in artificial saliva solutions. Then, sliding wear tests were carried out at the OCP taken by the test sample. Scanning electron microscopy and weight loss measurements were performed after the tribocorrosion tests.

The presence of a compact passive surface film on titanium immersed was demonstrated in artificial saliva free of fluorides and in presence of up to 227 ppm F^-. However, a progressive degradation of titanium was observed at a F^- concentration of 12,300 ppm. Additionally, the corrosion and wear resistance of the titanium oxide film formed at a F^- concentration of 12,300 ppm differ from the ones obtained up to 227 ppm F^- reflected by a decrease of the coefficient of friction although the material loss increased. The synergism between wear and corrosion processes on titanium needs thus to be further investigated to reach a reliable prediction of the long-term behavior of titanium-based prostheses and implants in the oral cavity.

Highlights

► Wear and corrosion of titanium. ► Material loss in fluorides. ► Failures in prostheses and implants.

Keywords

Titanium; Fluorides; Degradation; Corrosion; Wear; Tribocorrosion

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1. Introduction

The good corrosion resistance of titanium in different environments allows its use in several engineering and medical applications [1-7]. For medical applications, the stable oxide surface film on titanium is biologically acceptable, but once must be aware that the stability of the oxide film depends on the corrosivity of the environment in contact with the titanium [8-10]. *In-vitro* tests in artificial saliva are used to simulate the degradation of prostheses and implants exposed to an oral environment [1-7, 11]. Passive films on titanium behave like a compact oxide film in artificial saliva at pH 3.0-3.8 [8,9]. However, in presence of fluorides titanium may corrode [1,2,5,12]. In solutions containing a considerable F$^-$ concentration or in acidic fluoride solutions, hydrofluoric acid (HF) may form above 30 ppm HF$^-$ and may promote the localized corrosion of titanium [2].

The elastic modulus of titanium is only 120 GPa which is a great advantage compared to other titanium alloys, although it is still much higher than the one of the bone which is 10 to 30 GPa [8,9]. The absence of a periodontal ligament between titanium implants and bone, amplifies the stress at the artificial joint surfaces due to the higher rigidity of their structural materials compared to their natural counterparts [9]. On the contrary, titanium has a poor wear resistance in comparison to ceramics and alloys used as implant abutments [8,9]. In fact, one should be aware that micro-movements take place at joints between dental implant and abutment as well as between abutment and crown, as a result of torque application, mastication or effortless occlusion [13, 14-16]. For instance, titanium-based implant and abutment are connected by applying a torque ranging from 15 to 32 N.cm on abutment screws generating sliding of contacting materials. After, occlusal loads during mastication are distributed through the materials down to the bone, promoting fretting micro-movements at crown-abutment and

implant-abutment joints under variable displacement. That leads to fatigue and wear of contacting materials and detorque of abutment screws depending on the direction and magnitude of loads [13-16]. The wear rate of structural materials can be higher when there is a large difference in hardness between abutment and implant fixture or between abutment and crown joints. Friction on titanium due to micro-movements taking place at those joints can detach the protective TiO_2-film that leads to a material loss, and possible mechanical failures in dental implant, abutment and prostheses [13-16]. Also, wear sliding can occur due to abrasion by hard particles from food intake or tooth brushing [27]. Furthermore, corrosive substances from dietary pattern, human saliva, and oral biofilms, can accumulate at the peri-implant areas promoting corrosion at the metallic surfaces [17-19]. This combined wear and corrosion process known as tribocorrosion, results from interactions between mechanical, chemical, and electrochemical processes taking place on contacting surfaces that undergo a relative motion, and may cause an irreversible transformation of materials [20-22]. As a consequence, a release of metallic ions and oxide particles may induce chronic peri-implant inflammations since they act as foreign bodies on periodontal tissues, and stimulate the attraction of macrophages and T lymphocytes from immune system [9,22,23]. The chronic inflammation of peri-implant tissues leads to osteolysis and subsequently a loss of bone that supports implant-supported prostheses [9,24,25]. This can be considered as a self-sustained system because corrosion may be accentuated by oxidative species released by the immune system. The accumulation of corrosive substances in such areas moreover increases the corrosion of titanium [9,18,19] while loads due to mastication intensify osteolysis [9,25].

Electrochemical methods as e.g. open circuit potential (OCP) monitoring, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization, allow the

evaluation of the electrochemical behavior of materials during sliding tests. The correlation between corrosion, wear, and friction taking place in a given system can be clarified based on such measurements, but their interpretation is complex [26-29]. Even though the oral environment cannot be adequately replicated due to its biological, chemical, and physical variables, *in vitro* tribocorrosion tests are useful to investigate the relative importance of these variables like roughness, sample geometry, or chemical surface state, and of tribocorrosion test parameters like equipment, load applied, chemical composition and pH of the solution, temperature, type and velocity of motion, geometry and area of contact on the corrosion and tribological behavior of metallic materials [26-29]. A good control of the test variables is important in order to be able to unravel the phenomena occurring at material surfaces in sliding contacts, and to develop materials and/or systems guaranteeing a good performance in aggressive environments.

Even though the tribocorrosion behavior of titanium was recently evaluated in artificial saliva [8] and in physiologic solutions [26], the influence of corrosive elements present in saliva like fluorides has still to be investigated. That is the objective of this study.

2. Materials and methods

CP titanium grade II (VSMPO TIRUS, US, CP titanium, ASTM B 348, Grade 2) samples were wet ground down to 1200 mesh. After that, the samples were cleaned in isopropyl alcohol for 10 min, and subsequently in distilled water for 5 min using an ultrasonic bath. Following that, the samples were stored in a desiccator before performing tribocorrosion tests.

A modified Fusayama's artificial saliva (see Table 1) was formulated for the tribocorrosion tests. This solution was chosen on one side since it is frequently used in previous

research work [1,5,30,31], but also because it generates a similar electrochemical behavior of metallic materials as observed in human saliva [32].

Table 1. Composition of the stock Fusayama's artificial saliva solution used in this work.

Compounds	(g/l)
NaCl	0.4
KCl	0.4
$CaCl_2.2H_2O$	0.795
$Na_2S.9H_2O$	0.005
$NaH_2PO_4.2H_2O$	0.69
Urea	1

NaF was added to the Fusayama's stock solution to reproduce F^- concentrations found in the oral cavity. The fluoride concentrations selected from literature and commercial data [33-35] were 20, 30, and 227 ppm F^- in a solution of pH 5.5; and 12,300 ppm F^- in a solution of pH 6.5. Concentrations ranging from 20 to 227 ppm F^- were found in oral biofilms after use of toothpastes containing 1,000 to 1,500 ppm F^- [33,36]. Additionally, concentrations of 227 and 12,300 ppm F^- are present in commercial solutions and gels, respectively [34,35].

Before starting up tribocorrosion tests, the solutions were stirred for 24 hours and the pH was measured. The open circuit potential (OCP) was recorded on titanium immersed in the solutions versus a standard calomel reference electrode (SCE, Radiometer Analytical, XR110 model) and by using a potentiostat PGZ100 model coupled to a Voltamaster 4 software. The

OCP corresponds to the corrosion potential (E_{corr}) of an electron conductive material immersed in an ion conductive electrolyte.

For EIS tests, a Pt-electrode (Radiometer Analytical, M231PT) was used as counter electrode. After stabilization of E_{corr}, EIS tests were carried out at a potential of 50 mV above OCP and over a frequency range from 100 KHz down to 10 mHz. Also, an AC sine wave peak-to-peak amplitude of 10 mV was superimposed. ZView software was used to analyze the experimental data, and to evaluate the capacitance and the polarization resistance of titanium by a non-linear square fitting procedure. After the EIS measurements, the OCP was measured for another 10 min, and then the reciprocating sliding test was performed during 20 min which the OCP was further recorded. The sliding tests were performed against an alumina ball (10 mm diameter) at a normal load of 3 N, a sliding frequency of 1 Hz, and a linear displacement amplitude of 2 mm using a tribometer (CETR UMT2 Multi specimen Test system) coupled to the UMT test viewer software (CETR, 1997) to monitor the tangential force (F_t) from which the coefficient of friction was calculated. After the end of the sliding tests, the OCP was recorded for another 10 min, and then EIS tests were carried out once again over the same frequency range as before. The exposed area of titanium to the solutions was of 2.62 cm^2. The experimental set up is shown in Fig. 1.
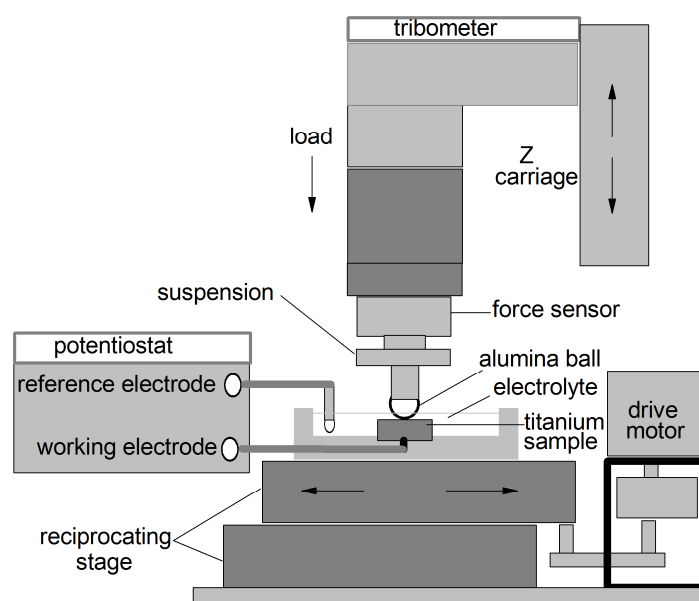
Fig. 1. Schematics of the experimental set up used for tribocorrosion tests.

The surfaces were inspected before and after tribocorrosion tests by scanning electron microscopy (LEICA CAMBRIDGE SEM-S360). Moreover, the weight loss of the samples was measured by gravimetric analysis. Duplicated tests were done on different samples produced at the same time, and one set of the test was repeated five times. The results were statistically analyzed following ANOVA at a significance level of $p < 0.05$.

3. Results and discussion

3.1 Electrochemical measurements

The open circuit potential curves *vs*. time of immersion are shown in Fig. 2 for titanium immersed in artificial saliva solutions with different F concentrations.
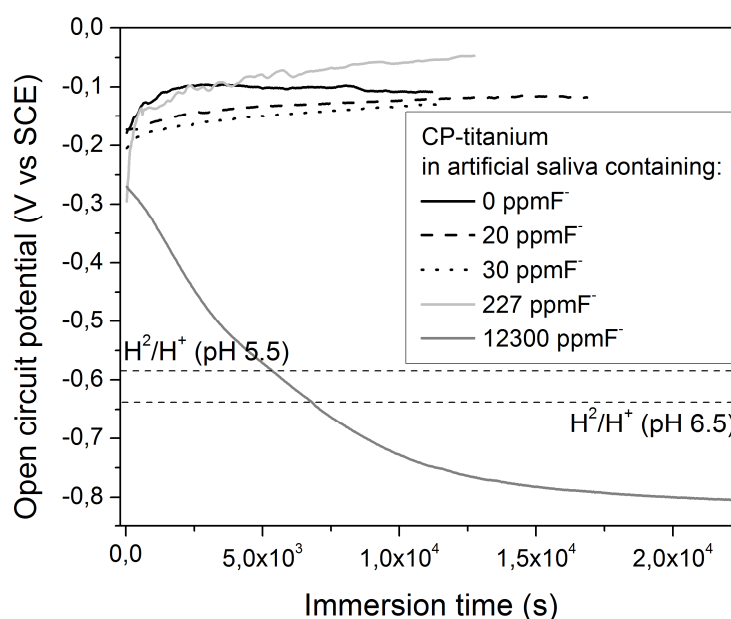
Fig. 2. Open circuit potential (OCP) vs. time of immersion for CP titanium in artificial saliva containing different amounts of fluoride ions. Broken horizontal lines indicate the equilibrium potential of the hydrogen evolution reaction (H^2/H^+) related to pH.

After 3 h of immersion, the OCP of titanium in artificial saliva is at about -0.1 V vs. SCE in solutions containing 0 up to 227 ppm F⁻ (Fig. 2). However on immersion in such solutions, the OCP increases to more noble values. That suggests the growth of a passive film with improved dielectric properties. Thus, the reduction of oxygen dissolved in the solutions takes place [3,31,37].On the contrary, a decrease of the OCP is noticed on immersion in artificial saliva containing 12,300 ppm F⁻. On immersion in such a solution, the OCP decreases and stabilizes after 6 hrs of immersion at about -0.8 V vs. SCE. Such a decrease in potential at high F⁻ concentration was also reported earlier [1-5], and it indicates a significant increase of the chemical reactivity of titanium [2,12,38]. In this last case, the global electrochemical reaction is

cathodically controlled by the reduction of hydrogen dissolved in the solution, and the material corrodes.

OCP curves recorded in this study (Fig.2) indicate a noticeable increase of the chemical reactivity of titanium at high F^- concentrations with a probable change of the properties of the titanium oxide surface film. Therefore, a high F^- concentration combined with a low pH, can amplify the chemical reactivity of titanium [2, 12]. In fact, the corrosion in fluoride solutions depends on the pH and the formation of HF^- produced by the dissociation of NaF when it is present at high concentrations, or in low pH solutions due to the bonding between H^+ and F^- ions [2,5]. Based on literature, it can be stated that there is a large formation of HF that reacts with the titanium surface [1,2,5,31].

Thus, the relation between pH and F^- concentration might be expressed by the following equation proposed by Nagakawa et al. [2]:

$$pH = 1.49 \log F + 0.422 \quad (1)$$

The threshold fluoride concentration to promote localized corrosion was reported to be about 30 ppm HF^- dependent on the associated pH [2,5]. A concentration of 227 ppm F^- in a solution at pH 4.0 was reported to promote localized corrosion [2]. In our study the pH of solutions containing between 0 and 227 ppm F^-, was 5.5, and it appears that such a concentration of HF was not high enough to degrade the passive film on titanium. The OCP value recorded in this work in a solution containing 12,300 ppm F^- at pH 6.5, was similar to the one reported for titanium tested in a solution containing 554 ppm F^- at pH 2.5, by Schiff et al. [5].

Furthermore, differences in pH of fluoride solutions may cause a shift in the OCP recorded on titanium. The correlation between pH and equilibrium potential (*E*) of the hydrogen evolution reaction (H_2/H^+) is given [39]:

$$E_{H_2/H^+} = 0.000 - 0.0591pH \quad (2)$$

The OCP measurement is an important source of information on the chemical reactivity of materials immersed in liquids, but it just denotes a pre-disposition to corrosion or not. For a better understanding of the state of the oxide film formed on the surface of a test sample, electrochemical impedance tests are informative. Bode spectra obtained from EIS data recorded on titanium immersed in artificial saliva and before reciprocating sliding tests, are shown in Fig. 3A. The Bode spectra (Fig. 3A) for titanium immersed in artificial saliva solutions containing 0 up to 227 ppm F⁻ reveal values of the phase angle approach from -90 °and a higher inclination of the total impedance slopes ($|Z|$ vs. Frequency) when compared to those recorded on titanium immersed in artificial saliva containing 12,300 ppm F⁻. That indicates higher values of the total impedance for titanium immersed in artificial saliva solutions containing 0 up to 227 ppm F⁻ than immersed in artificial saliva containing 12,300 ppm F⁻.
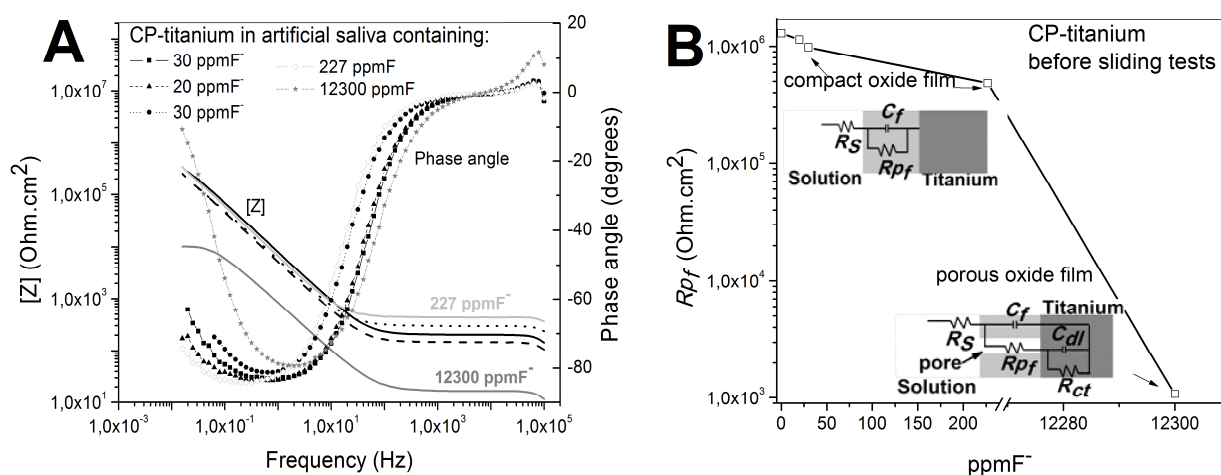

Fig 3. (A) EIS spectra (Bode representation) and (B) polarization resistance of the Cp-titanium oxide films (Rp_f) recorded on titanium immersed in artificial saliva solutions containing different amount of fluorides.

Also, a compact or a porous oxide film on titanium can be represented by two different equivalent electrical circuits from non-linear square fitting of EIS spectra (Fig. 3B). Based on such equivalent circuits, the polarization resistance of titanium oxide film (Rp_f) was derived (Fig. 3B). The equivalent electrical circuits as well as experimental and theoretical values showed an adequate fitting in agreement to chi-square values (x^2) between 10^{-4} and 10^{-5}. The equivalent circuit fitting at best with the experimental EIS spectra in artificial saliva containing 0 to 227 ppm F$^-$, consists of a constant phase element (CPE), that represents the capacitance of the titanium oxide film (*Cf*) in parallel with a polarization resistance of the passive film (Rp_f). This circuit, also known as Randle's circuit, is valid in presence of a compact passive film on titanium (Fig. 3B). Nevertheless, there was a decrease of Rp_f at increasing F$^-$ concentration, as noticed at 227 and 12,300 ppm F$^-$ (see Fig. 3B). That decrease of Rp_f indicates a decrease of the corrosion resistance of titanium in these solutions.

On the other hand, the equivalent electrochemical circuit that gives the best fitting of EIS spectra recorded on titanium immersed in 12,300 ppm F$^-$, consists of two CPE that represent a C_f and a double layer capacitance (C_{dl}) in the circuit. Such a circuit is typical for a system consisting of a porous oxide film on a dense substrate since the Rp_f values are quite low (see Fig. 3B). A decrease of the electrolyte resistance (R_s) containing 12,300 ppm F$^-$ appeared also from non-linear square fitting analyses. Thus, there is a large electrical current distribution along the surfaces and in current line distribution in the solutions containing high concentrations of fluorides denoting the corrosive effect of these solutions. A non-linear fitting procedure was applied in line to the chi-square values (x^2) between 10^{-4} and 10^{-5} to adjust experimental and theoretical values of Rp_f.

EIS results were also correlated with OCP data shown in Fig. 2, whereas the lowering of OCP in solutions containing 12,300 ppm F⁻ is associated to a high chemical reactivity, and consequently to a localized corrosion of titanium. Such a decrease of the corrosion resistance in fluoride solutions with increasing F⁻ concentration, is in agreement with EIS results reported earlier [6,40].

3.2. Tribocorrosion measurements

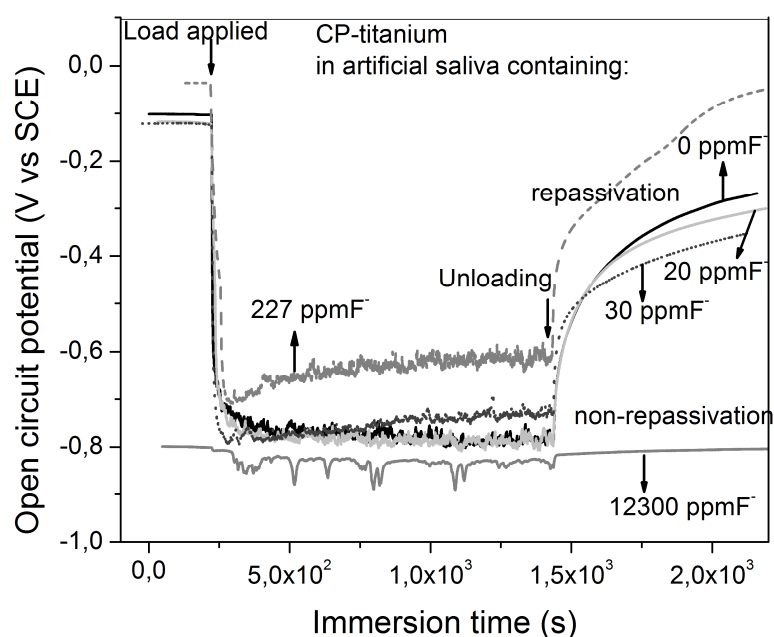The evolution of the OCP of Cp-titanium during reciprocating sliding tests is shown in Fig. 4.

Fig. 4. Evolution of OCP recorded on Cp-titanium immersed in artificial saliva containing fluorides during reciprocating sliding tests (F_n = 3N, displacement amplitude 2 mm, 1 Hz, 20 min of sliding).

The OCP for titanium immersed in artificial saliva either free of fluorides or containing 20 up to 30 ppm F⁻, stabilized at a quite similar value before sliding tests. EIS results indicated that a passive oxide film is present before sliding tests on titanium immersed in artificial saliva containing between 0 and 227 ppm F⁻. Once stabilization was achieved, sliding tests were started. When an alumina ball was loaded onto that passive titanium and sliding is started, a destruction of the titanium passive film (phenomenon known as depassivation) and the exposure of fresh active titanium take place. That results in an abrupt drop in the OCP curve [8, 20 ,21]. In fact, a galvanic couple is established between worn and unworn areas in contact with the test solutions [8, 20,21]. The OCP measured during sliding test is a mixed potential which value depends on the state of undamaged and damaged materials in the wear track [20]. That mixed potential is maintained during sliding due to the exposure of fresh active titanium (in the wear track) and removal of the passive surface film. The active titanium reacts with the surrounding solution as indicates by anodic peaks in the OCP curves [8, 20,21].

At the start of sliding, the OCP decreased to value that was maintained during the entire sliding test. The OCP recorded on titanium during sliding tests in a 227 ppm F⁻ solution, was higher than the one recorded at 0 up to 30 ppm F⁻. Nevertheless, a slightly increasing OCP was noticed during sliding test performed in a 227 ppm F⁻ solution what was not be observed in the other conditions except at 30 ppm F⁻. The slight increase of OCP recorded during sliding on titanium immersed in 30 and 227 ppm F⁻ solution (Fig. 4), can be associated with a higher chemical reactivity of titanium in these solutions. As a result, the chemical reaction between titanium and fluorides can change the chemical and mechanical properties of the new titanium oxide surface film.

In solutions containing 12,300 ppm F$^-$, a significantly lower OCP is noticed before sliding that was slightly affected by sliding. The EIS results and OCP measurements performed before sliding indicate that the unworn area is either an active one before and during sliding or that there is a complex and thick oxide layer decreasing the friction on titanium. However in that last case, a large drop in the OCP should occur after a certain time of sliding due to the wear of that oxide film. Once that is not noticed, it may be stated that in a12,300 ppm F$^-$ solution the unworn and worn areas are active before and during sliding.

Once sliding was stopped, an immediate increase of the OCP to noble values is noticed. It was noticed that after sliding in a 227 ppm F$^-$ solution, the OCP recovers its original value much faster than in the solutions containing 0 up to 30 ppm F$^-$.On unloading, the increase of the OCP follows from the re-growth of a passive film on titanium (repassivation process) in the wear track area. That repassivation process seems to be faster in the 227 ppm F$^-$ solution than in the other ones. The environmental parameters (in our study, pH and fluoride concentration) affect the repassivation of titanium. The depassivation and repassivation of titanium in artificial saliva solutions during tribocorrosion was also reported by Vieira *et al*. (2006). They reported on an improvement of the tribocorrosion behavior of titanium in artificial saliva at pH 3.8 compared to pH 5.5 during fretting tests [8].

It is also important to notice the non-repassivation of titanium in 12,300 ppm F$^-$ solution after the end of the sliding tests. That non-repassivation of titanium may be linked to the high aggressiveness of hydrofluoric acid (HF$^-$) at that concentration present in that solution. In fact, the reduction of hydrogen dissolved in the 12,300 ppm F$^-$ solution leads to a continuous dissolution of the passive film resulting in an active state of the titanium surface. The dissolution

of both worn and unworn titanium areas starts on immersion in artificial saliva containing a high

F⁻ concentration ending up in a severe material loss.

The morphology of wear scars produced in our study under tribocorrosion conditions, are
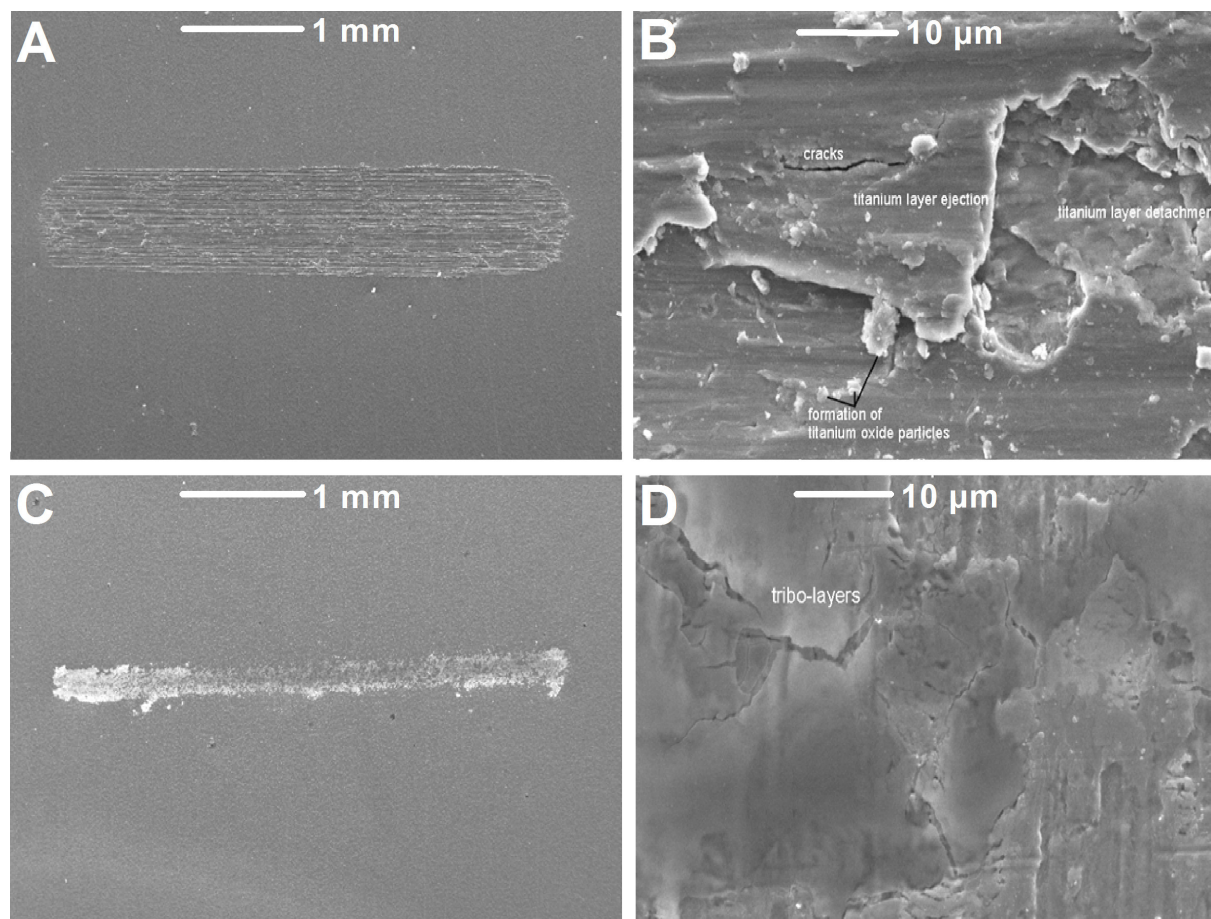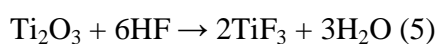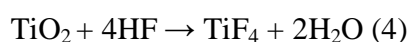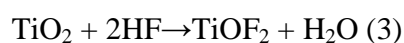
shown in Fig. 5:

Fig. 5. Topography of Cp-titanium after reciprocating sliding tests (F_n = 3N, displacement amplitude 2 mm, 1 Hz and 20 min of sliding) performed in artificial saliva containing (A, B) 0 and (C, D) 12,300 ppm F⁻.

Wear scars exhibiting marks aligned along the reciprocating sliding direction on titanium

immersed in artificial saliva appear in Fig. 5A. The topographic appearance of Cp-titanium

tested in artificial saliva solutions containing 0, 20, 30, and 227 ppm F$^-$ is the same. Surfaces of such wear tracks show areas where either ejection of material or detachment of surface layers took place (Fig. 5B), as well as the ejection of debris. That wear noticed on titanium in artificial saliva containing up to 227 ppm F$^-$ as tested in our study, is in accordance with the model proposed by Landolt *et al*. (2004). Nevertheless, the morphology of the wear scar differs at high F$^-$ concentration.

In a solution containing 12,300 ppm F$^-$, the width of the wear scars is smaller than when lower fluoride concentration solutions were tested. That reveals a smaller contact area (Fig. 5C). Such a smaller contact area results from a lower mechanical wear. Indeed, abrasion marks aligned in the wear track were not noticed, but a surface film is noticed (Fig. 5D). The smooth surface morphology can result from the formation of reaction product layers that can decrease the friction on titanium. The impedance spectra curves performed in this work (Fig. 3b), revealed a growth and dissolution of titanium oxide passive film forming reaction product layers on titanium in artificial saliva containing 12,300 ppm F$^-$. The degradation of titanium in fluoride solutions was found in this work to be consistent with previous reports revealing the occurrence of a localized corrosion process, namely pitting corrosion [9, 18, 24, 37]. The occurrence of pitting corrosion was described as resulting from the formation of Ti oxides layers as $Ti(OH)_2F^+$, and salts as $TiOF_2$ $[TiF_6]^{2-}$, TiH_2, $Na_3Ti_3F_{14}$, TiF_4 $[TiF_6]^{3-}$ in presence of HF according the following reactions [24, 54]:

$$TiO_2 + 2HF \rightarrow TiOF_2 + H_2O \quad (3)$$

$$TiO_2 + 4HF \rightarrow TiF_4 + 2H_2O \quad (4)$$

$$Ti_2O_3 + 6HF \rightarrow 2TiF_3 + 3H_2O \quad (5)$$

Despite the return of OCP once sliding is stopped towards its original value, one must be aware that the surface of the materials is not as the one before sliding. Wear scars as well as pores resulting from pitting corrosion, can be formed and are susceptible areas for accumulation of biofilms. Such areas can accumulate acidic substances from oral and microbial fluids enhancing the corrosion of metallic surfaces. In addition, the material loss can cause a misfit of prosthetic joints such as crown-to-abutment and abutment-to-implant fixtures. Such a dimensional misfit creates microgaps where the accumulation of biofilms and acidic substances can take place [18]. Concerning the biomechanics of dental implant systems, that misfit can generate a distribution of undesirable oblique loads through the structural materials of dental implant systems [41,42].

The evolution of the coefficient of friction recorded on Cp-titanium during reciprocating sliding tests in artificial saliva containing between 0 and 12,300 ppm F⁻, is shown in Fig. 6A. Furthermore, a clear correlation appears between variations of OCP and coefficient of friction during reciprocating sliding tests (Fig. 6B).
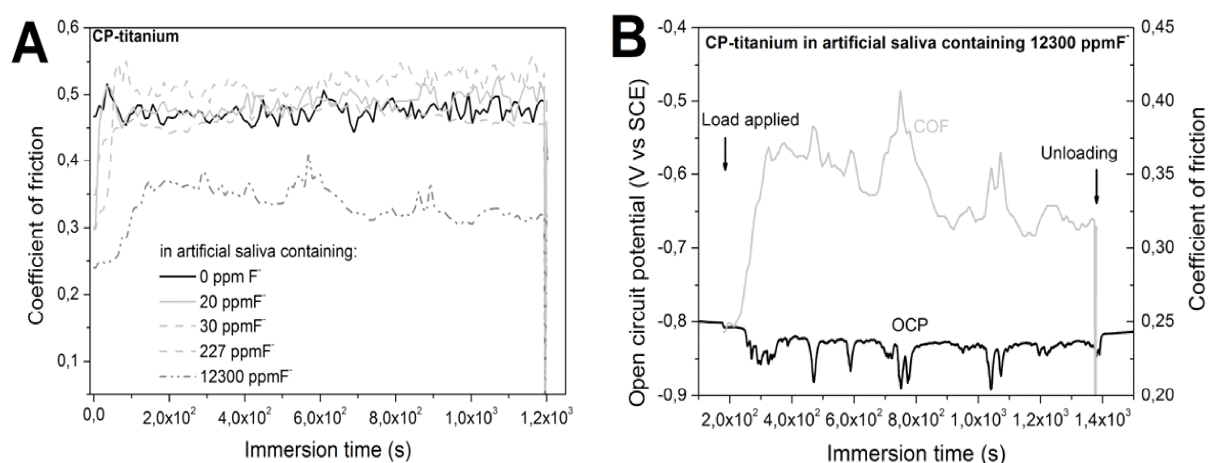

Fig. 6. (A) Evolution of the coefficient of friction recorded on titanium during reciprocating sliding test performed in artificial saliva free of and containing different fluoride concentrations

(F_n = 3N, displacement amplitude 2 mm, 1 Hz, 20 min of sliding). (B) Correlation between coefficient of friction and OCP during reciprocating sliding.

There were not significant difference between the coefficient of friction recorded on titanium in artificial saliva solutions free of fluorides and those containing up to 227 ppm F^-. As shown in Fig. 6A, the coefficient of friction recorded on titanium in a 12,300 ppm F^- solution was lower than that at lower fluoride content. The variations noticed in the OCP during sliding tests can be induced by the abrasive effect of wear debris destroying periodically the passive film on the wear track surface [20,21].

A lower number of variations of coefficient of friction and OCP were observed for titanium tested in a 12,300 ppm F^- solution than in solutions containing up to 227 ppm F^-. In artificial saliva containing up to 227 ppm F^-, the detachment of titanium layers in sliding tracks underneath alumina balls, and third-body particles inside the sliding tracks, may promote oscillations of the coefficient of friction as reported previously [8,26]. The formation and transformation of third-body particles are important phenomena to understand the oscillations of coefficient of friction during tribocorrosion tests [26,29,43]. The oxidation of metallic debris may lead to the formation of solid oxides or dissolved ions [26,28,43] that can accelerate or slow down the mechanical wear rate of first bodies [26, 43]. A study on the tribocorrosion of Ti6Al4V alloys performed at applied anodic potential (> - 0.2 Vs Ag/AgCl) in 0.9% NaCl solution, revealed that the oxidation of debris significantly decreased the mechanical energy required for wear [28]. The upsurge of hard debris increases the destruction of detaching surface layers and particles of titanium [26,28]. Thus, hard third-body particles originating between surfaces at

relative contact motion, and in prosthetic gaps can increase the rate and the extent of corrosion and wear of implants systems.

In 12,300 ppm F⁻ solutions, the adsorption of fluorides on titanium and the formation of reaction product layers could decrease the coefficient of friction recorded on titanium, and also its wear rate. During sliding relative motion, a plastic deformation followed by a rupture and compaction of the reaction product layers takes place between contacting materials. Thus, the reaction products layers remain in the sliding track like a smooth layer decreasing the wear of the fresh active titanium. However, wear particles originating from titanium or its oxide layer can be formed in the sliding track acting as abrasive third-bodies or ejected out of the sliding track [26]Harder debris might be smeared out and entrapped in the surface. Then, the lowest coefficient of friction values can be associated to the sliding on reaction product layers smeared out onto titanium surfaces while the highest coefficient of friction can be attributed to sliding on blank titanium, in analogy to what was found on TiN [44].

In order to evaluate the synergism between corrosion and wear, the weight loss of titanium was measured after tribocorrosion tests (Fig. 7):
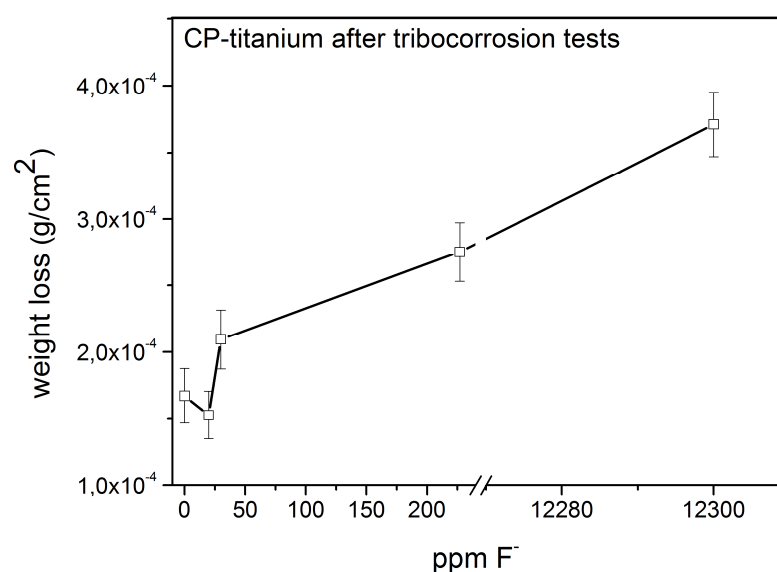
Fig. 7. Weight loss recorded on Cp-titanium after tribocorrosion tests in artificial saliva free of and containing different fluoride concentrations (F_n = 3N, displacement amplitude 2 mm, 1 Hz, 20 min of sliding).

The weight loss noticed in solutions free of fluorides or containing up to 30 ppm F⁻ ($p <$ 0.05) does not differ. However, a significant increase of the weight loss was noticed at 227 and 12,300 ppm F⁻, notwithstanding that in this last case, the coefficient of friction is the lowest one recorded in this study. From the SEM and wear analyses, the volume of the wear track at 12300 is smaller than at low F concentrations. Thus, the large material loss at 12,300 ppm F⁻ is probably due to corrosion of the entire surface area exposed to that high F⁻ concentration. A synergism between corrosion and wear can result in either corrosion that increases wear or a wear that increases corrosion. On the other hand, depassivation and repassivation processes may be affected by environmental, mechanical, and material parameters [20,21,26,28]. Friction conditions might hence be altered by the formation of tribo-reactive surface layers with unique sliding properties. Such friction conditions can also promote the formation of surface reaction layers that affect the corrosion sensitivity of materials [20,28]. Thus, such a material loss on titanium used in the oral cavity, may lead to a gradual loosening of structural materials of dental implant fixture, abutment, and prostheses frameworks.

Wear debris may also cause chronic inflammations of peri-implant tissues due to the stimulation of macrophages and T lymphocytes [9,22,23]. There are evidences that the size of debris is more important than their chemical composition, revealing that small particles at nanometer scale are more dangerous than large ones at micrometer scale [22,23,45]. In literature, titanium wear debris has been reported with granular, needle-like, filamentous or plate-like

morphology and diameter ranging from 0,01 µm up to 50 µm [22,46]. Studies reveal that nano-scale (<100 nm in diameter) TiO_2-particles (UF-TiO_2) may cause inflammations, fibrosis, pulmonary damage, and DNA [23, 47,48] in rats. It seems that UF-particles can be trans-located to the sub-epithelium, and may interact with immune systems to a greater extent than fine particles [49]. An investigation of UF-TiO_2 particles using the methyl tetrazolium cytotoxicity (MTT) assay, revealed cytotoxicity and genotoxicity in cultured human cells although the precise process of apoptosis formation, mutagenic, and inhibition of cell division by UF-TiO_2 particles were not totally explained [23].

4. Conclusions

A compact passive film forms on titanium surfaces immersed in artificial saliva solutions free of or containing fluoride concentrations up to 227 ppm F^-. However, the corrosion resistance of titanium decreases with increasing fluoride concentration as revealed by electrochemical impedance spectroscopy. The coefficient of friction recorded on titanium and subsequent wear induced in sliding tests performed in artificial saliva containing up to 227 ppm F^- is quite constant. On the contrary, coefficient of friction recorded on titanium revealed a significant decrease at a high fluoride concentration (12,300 ppm F^-) probably due to the presence of reaction product layers. Even though such low friction, an increase of material loss was noticed at high fluoride concentration as well as in 227 ppm F^- solution. That demonstrates a significant influence of the aggressive environment containing fluorides. As a result, the degradation of the protective titanium oxide layer may lead to failures in dental implants and prostheses. Also, the widespreading of wear debris close to the surrounding may induce peri-implant inflammations and toxic effects to the human body.

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