

How do titanium and Ti6Al4V corrode in fluoridated medium as found in the oral cavity? An *in vitro* study.

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## **Abstract**

The purpose of this work was to evaluate the corrosion of commercially pure (CP) titanium and Ti6Al4V *in vitro* at different F<sup>-</sup> concentrations regularly found in the oral cavity by using different electrochemical tests and surface analysis techniques. Electrochemical Impedance Spectroscopy (EIS), Open circuit potential (OCP) and potentiodynamic polarization tests were associated to advanced characterization techniques such as SEM, EDS, AFM, ICP-MS and XPS. OCP tests revealed a higher reactivity of both CP titanium and Ti6Al4V at 12300 ppm F<sup>-</sup> concentration than that recorded at 227 ppm F<sup>-</sup>. Also, a significant decrease of the corrosion resistance of both materials was noticed by EIS in fluoride solutions. Material loss caused by corrosion was noticed on titanium surfaces by SEM and AFM in the presence of high F<sup>-</sup> concentration. CP titanium degraded by pitting corrosion while Ti6Al4V suffered from general corrosion showing micro-cracks on surface. Furthermore, a high release of metallic ions from the test samples after immersion at high F<sup>-</sup> concentrations was detected by ICP-MS, that can be potentially toxic to oral tissues.

*Key words:* titanium, fluoride, Ti6Al4V, electrochemical tests, surface analysis

## Introduction

In dentistry, titanium and its alloys are the first choice for dental implant systems and for frameworks of implant-supported prostheses, due to their attractive corrosion resistance, high mechanical strength and biocompatibility [1,2]. In addition, low density and low thermal-electrical conductivity are essential for applications in oral rehabilitation [1-6]. Titanium has been classified as having a better corrosion resistance than other metals used for oral rehabilitation due to the formation of a protective compact oxide film on its surface when in contact with the surrounding environment [4-11]. However, titanium oxide films can be destroyed in certain acidic environments in the oral cavity resulting in a release of ions that can be toxic to oral tissues [10-16].

The oral environment may accumulate corrosive substances as lactic acid, hydrogen peroxide, citric acid, hydrochloric acid, and hydrofluoric acid at different concentrations. Ions as  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{H}^+$  in saliva are the main agents responsible for the corrosion of dental materials [13,14, 17-20]. That accumulation of corrosive substances depends on the oral hygiene, the dental treatments, and the patient dietary as well as on factors linked to the patient like patient health state, composition of oral biofilms as well as saliva flow and composition [5, 15,21, 22]. Furthermore, retentive areas at dental restorations, prostheses and dental implant systems are the main susceptible areas where substances responsible for corrosion can accumulate [5, 15,21]. Fluorides are frequently used to prevent caries or applied after bleaching treatment but may induce the degradation of titanium and its alloys [23, 24]. High concentrations of hydrofluoric acid [HF] can be generated by the dissolution of concentrated fluoridated agents in the saliva [21,23-27]. In solutions containing a considerable  $\text{F}^-$  concentration or in acidic fluoride solutions, hydrofluoric acid (HF) may form above 30 ppm HF and may promote the localized corrosion of

titanium. As a result, HF react with the protective titanium passive surface layer causing the release of Ti ions by a localized corrosion process [13, 15, 20]. Such a degradation may even be amplified when the medium has a low pH.

The corrosion of titanium can lead to poor aesthetics, compromise of physical properties, or increased inflammatory reactions [2, 29-31]. The effect of corrosion may be visible *in vivo* when it is severe and consequently a change of surface coloration or inflammations surrounding dental implants caused by ions release can take place [1, 29-31]. Moreover, metallic ions released into tissues can stimulate an initial inflammatory response, and a consequent toxic, mutagenic and/or carcinogenic reactions [28-35]. Additionally, some studies revealed a highly significant relationship between the amount of peri-implant inflammation and the magnitude of alveolar bone loss surrounding dental implants [29, 30]. Considering the systemic effect, coalescence of particles of all classes (including Ti particles) originating from prostheses was often seen in the vesicles of macrophage cytoplasm in the liver (0.1-10  $\mu\text{m}$  in diameter), spleen, and para-aortic lymph nodes [32-35].

The main aim of the present work was to study the electrochemical behavior of commercially pure titanium and Ti6Al4V immersed in artificial saliva solutions containing different  $\text{F}^-$  concentrations representative for oral cavity. Different electrochemical tests followed by chemical and topographic analyses were applied to clarify the degradation process of titanium and Ti6Al4V surfaces exposed to aggressive fluoridated solutions. The null hypothesis of this study was that there is no difference in corrosion behavior and surface degradation between CP titanium and Ti6Al4V in artificial saliva containing different fluoride contents.

## **Materials and Methods**

### *Preparation of the samples and medium*

Cylindrical samples (10 mm thick and 25 mm diameter) were cut from bars of Ti6Al4V (VSMPO TIRUS, US, ASTM B 348, Grade 5) and commercially pure titanium (VSMPO TIRUS, US, CP titanium, ASTM B 348, Grade 2). The samples were wet ground on SiC abrasive papers down to 1200 Mesh. After grinding, the samples were cleaned in isopropyl alcohol for 10 min and in distilled water for 5 min using an ultrasonic bath. Then, samples were stored in a desiccator for 24 h before performing electrochemical measurements.

A modified Fusayama's artificial saliva formulation was used as electrolyte solution in this in-vitro corrosion study [36]. The electrochemical behavior of metallic materials in that solution has been reported to be similar as in human saliva [36]. The composition of the Fusayama's artificial saliva solution used is given in Table 1.

NaF was added to the artificial saliva solution in order to simulate different fluoride media. Our selection of the fluoride concentration was dictated by the following literature data on fluoride concentrations in the oral cavity as well as on commercial formulations that can be used by dentists and patients [23, 24]. Different  $F^-$  concentrations are present in toothpastes up to 1500 ppm  $F^-$  and in prophylactic agents at concentrations ranging from 227 up to 22600 ppm  $F^-$  [23, 24]. Moreover,  $F^-$  can be present in food, and in tap water of some towns at about 0.7 ppm  $F^-$  [24]. For instance, high  $F^-$  concentrations are found in therapeutic gels ranging at 9000 or 12300 ppm  $F^-$  or in varnishes at 22600 ppm  $F^-$ . Fluoride gels are applied for 4 min after oral cleaning in dental practice; while  $SnF_2$  varnishes are applied only at specific areas of teeth surfaces that are thermal-electric sensible after dental bleaching or dentin exposure due to mechanical traumas [24].

The solutions were stirred for 24 h before starting up electrochemical tests, and at that time the pH was measured. In literature, it is mentioned that pH's between 3 and 7 have been used in commercial fluoride agents [23, 24]. In this work, it was decided not to alter the pH obtained after addition of NaF in order to avoid the addition of other substances. As a result, the pH of the different solutions used in this work are: 5.5 without fluorides, 5.5 at 20 ppm F<sup>-</sup>, 5.5 at 30 ppm F<sup>-</sup>, 5.5 at 227 ppm F<sup>-</sup>, and 6.5 at 12300 ppm F<sup>-</sup>.

### *Electrochemical measurements*

The samples were mounted in the acrylic electrochemical cell in contact with an electrical wiring. The volume of solution used was of 30 ml. The electrochemical tests ( $n = 5$ ) were carried out with a Voltalab PGZ100 potentiostat (Radiometer Analytical, France) coupled to the Voltmaster 4 software (Radiometer Analytical, France) used for electrochemical control and data analyses. The open circuit potential (OCP) is defined as the potential of an electron conductive material immersed in an ion conductive electrolyte and measured against a reference electrode. In this work, a standard calomel reference electrode (RE, SCE, XR110 model, Radiometer Analytical, France) was used (Figure 1). All potentials were recorded in respect to SCE. A Pt-electrode (M231PT model, Radiometer Analytical, France) was used as counter electrode (CE) in impedance and potentiodynamic polarization measurements (Fig. 1). The test samples were connected as working electrode (WE). Since on immersion of a test sample in the electrolyte, the OCP evolves with time, a waiting time was included till the OCP stabilized. In the case of both titanium and Ti6Al4V, a cathodic polarization was then performed at -0.9 V for 5 minutes in artificial saliva containing up to 227 ppmF<sup>-</sup>. Following, OCP was monitored for 1 hour. Then, potentiodynamic polarization was started up at -0.9 V, and performed till 2 V at a

scan rate of 0.5 mV/sec. In artificial saliva containing 12300 ppm F<sup>-</sup> that cathodic polarization was performed at -1.5 V for 5 minutes and the subsequent potentiodynamic polarization was started up at -1.5 V, and carried out till 2 V because of the low OCP value measured on Ti and TiAl6V4 in that solution. From these potentiodynamic polarization measurements, the potential,  $E_{(i=0)}$ , at which the anodic and the cathodic currents are equal but of opposite sign, was derived. Such potential does not necessarily coincide with the OCP value due to the effect of the cathodic polarization on the surface of the tested samples.

As the OCP measurements and their evolution with immersion time reveal only a tendency to corrosion or to passivation of the surface material, the evaluation of the corrosion rate requires the analysis of potentiodynamic polarization curves and impedance spectra. Electrochemical impedance spectroscopy (EIS) were carried out using a potentiostat PGZ100 model (Radiometer Analytical, France) coupled to the Voltmaster 4 software over a frequency range from 100 KHz down to 10 mHz (Fig. 1). The test samples were prepared as previously described. The impedance tests were carried out at 50 mV above OCP on which an AC sine wave peak to peak amplitude of 10 mV was superimposed. Such tests were performed after immersion times of 1, 24, 48, 120, and 168 h. In order to investigate the titanium oxide film behavior in the test solutions, a non-linear square fitting procedure was used to study the spectrum data by ZView software (Scribner Associates, Inc., USA) and to evaluate both the capacitance and polarization resistance. The experimental and theoretical data were in agreement with chi-square values ( $\chi^2$ ) between  $10^{-4}$  and  $10^{-5}$ .

Five specimens of each material were tested under each set of test conditions ( $n = 5$ ). The surface area of the test samples exposed to the test solutions was 0.64 cm<sup>2</sup>. The tests were carried out at 37 °C in a thermostatic water bath, simulating the normal temperature of an oral

cavity. The numerical results were statistically analyzed by a nonparametric method at a significance level of a  $p < 0.05$  using statistic software (SPSS 10.1 for Windows, SPSS, Chicago, USA). The Mann-Whitney  $U$  test was used to compare differences of different values per groups while Kruskal-Wallis test was used to compare the differences between groups.

### *Chemical and topographic analysis*

After electrochemical tests, the samples were cleaned in isopropyl alcohol for 10 min and in distilled water for 5 min using an ultrasonic bath. The topography of the samples was analyzed by scanning electron microscopy (LEICA SEM-S360, Cambridge, UK) coupled to energy dispersive spectroscopy (EDS), at 15 kV by secondary electron (SE) mode. Atomic force microscopy was carried out using a atomic force microscope (AFM Multimode digital Instruments, Veeco, USA) controlled by Nanoscope III software. AFM images and roughness analysis were obtained from  $10 \times 10 \mu\text{m}$  areas on the sample surfaces.

The chemical composition of the surface of the tested samples was analyzed by X-ray photoelectron spectroscopy (XPS, Vg Scientific Escalab 200A, USA) using a non-monochromatized Mg  $K\alpha$  radiation (1253.6 eV) at chamber vacuum at  $1 \times 10^{-7}$  Pa. Moreover, the ion release in solutions due to the potentiodynamic polarization, was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Thermo X Series equipment, USA).

## **Results**

### *Open circuit potential measurements*



The evolution of the open circuit potential (OCP) versus time in artificial saliva solutions containing different amounts of fluoride ions is shown in Figures 2 and 3.

It was noticed that the OCP values of CP titanium are similar (aprox -0.4 V) after 1.5 h immersion in the artificial saliva without fluorides and with 20 and 30 ppm F<sup>-</sup> as shown in Figure 2A ( $p < .05$ ). In a solution containing 227 ppm F<sup>-</sup>, there is a significant decrease of the OCP values ( $-0.5 \pm 0,03$  V) during the first 1.5 h of immersion ( $p < .05$ ). A similar behavior of OCP is observed for Ti6Al4V (Fig. 2B). However, measurements in artificial saliva containing 12300 ppm F<sup>-</sup> have revealed a quick decrease of the OCP values of CP titanium during the first few minutes of immersion, and a stabilization at -1.2 V after 2 h of immersion (Fig. 2A). The same evolution of OCP with time was observed for Ti6Al4V immersed in a solution containing 12300 ppm F<sup>-</sup>.

Furthermore, the OCP value was measured before each EIS test performed during a period of 7 days of immersion. The evolution with immersion time of that OCP is shown in Fig. 3.

The OCP of CP titanium in artificial saliva containing 12300 ppm F<sup>-</sup> stabilized after 7 days of immersion at about  $-0.85 \pm 0,02$  V (Fig. 3A). On the contrary, the OCP of Ti6Al4V stabilized at about -0.6 V after 48 h of immersion in artificial saliva containing 12300 ppm F<sup>-</sup> (Fig. 3B).

### *Electrochemical Impedance spectroscopy measurements*

In Fig. 5A-B, the evolution of the polarization resistance of the oxide surface film ( $R_{pf}$ ) is shown as estimated from EIS spectra data (Fig.4). 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  $10^{-5}$ . From non-linear square fitting of EIS spectra, two equivalent circuits were derived that indicate the possible presence of a compact oxide film (passive state) or a porous oxide film (active state) on top of the test samples upon immersion in the electrolyte. These equivalent circuits are shown in Fig. 5C-D.

In artificial saliva containing 0 up to 227 ppm  $F^-$ , the equivalent electrical circuit fitting at best with the experimental EIS spectra consists of a constant phase element (CPE), that represents the capacitance of the titanium oxide film ( $C_f$ ) in parallel with the resistance of that passive film ( $R_{pf}$ ), as shown in Fig. 5C. This equivalent electrical circuit, also known as Randle's circuit, is valid in presence of a compact passive film on titanium. In our study, such equivalent electrical circuit indicated thus the presence of a compact film at a passive state on both materials during 7 days of immersion in these solutions. On the contrary, the EIS spectra recorded on both materials immersed in a solution containing 12300 ppm  $F^-$  (Fig. 4) were best fitted with an equivalent circuit containing two CPEs that represent the capacitance of the titanium oxide surface film ( $C_f$ ) and a double layer capacitance ( $C_{dl}$ ) in the circuit (Fig. 5D). This circuit suggests the presence of defects in the oxide surface film that thus has to be considered as a porous oxide film (Fig. 5D).

On CP titanium, high values of  $R_{pf}$  were recorded during 7 days of immersion in artificial saliva without and with 20-30 ppm  $F^-$  (Fig. 5A). That indicates a high electrical resistance of the surface. In other words, it reveals a high corrosion resistance of CP titanium in artificial saliva containing up to 30 ppm  $F^-$ . However, a decrease of the  $R_{pf}$  of CP titanium was noticed after 48 h of immersion in 227 ppm  $F^-$ . No significant differences between the  $R_{pf}$  of Ti6Al4V and CP titanium were noticed on immersion in 227 ppm  $F^-$  ( $p > .05$ ). In Fig. 5A-B, a significant decrease of the  $R_{pf}$  of CP titanium and Ti6Al4V was noticed after 2 h of immersion in a solution

containing 12300 ppm F<sup>-</sup> ( $p < .05$ ). A decrease of the electrolyte resistance ( $R_s$ ) containing 12300 ppm F<sup>-</sup> appeared also from non-linear square fitting analyses denoting the corrosive effect of these solutions.

#### *Potentiodynamic polarization measurements*

Potentiodynamic polarization curves recorded in this study on CP titanium and a Ti6Al4V alloy in artificial saliva solutions containing different concentrations of fluoride and pH's, are shown in Fig. 6.

Regarding the anodic part of the polarization curves, it can be observed that CP titanium (Fig. 5A) shows a large potential range where a stable passive current density,  $i_{pass}$ , is noticed starting from 0.3 V in artificial saliva free of F<sup>-</sup>. A large passive current plateau is also noticed on CP titanium in a solution containing 227 ppm F<sup>-</sup>, but that passive current plateau appears at a higher  $i_{pass}$  than under the previous conditions. Potentiodynamic polarization curves recorded on Ti6Al4V (Fig. 6B) are quite similar to the ones recorded on CP titanium in artificial saliva solutions free of fluoride and these containing up to 227 ppm F<sup>-</sup>.

In a solution containing 12300 ppm F<sup>-</sup>, CP titanium shows a short potential range where a passive state prevails, namely from 0.05 up to 0.2 V. Above that potential a slight increase of the anodic current density is noticed revealing a transpassivation behavior and that takes place up to 1.83 V where the potentiodynamic polarization indicates the occurrence of a second passive plateau on CP titanium (Fig. 6A). Nevertheless, the potentiodynamic polarization curves recorded on Ti6Al4V (Fig. 6B) immersed in a 12300 ppm F<sup>-</sup> solution, exhibit a different shape. A maximum anodic current density of about  $5.1 \times 10^{-4}$  A/cm<sup>2</sup> is noticed at 10 mV. Then, the anodic current density decreases with increasing potential till 0.78 V suggesting the formation of

a thick oxide film on the surface of the material. The further increase of the anodic current density between 0.85 and 1.35 V, suggests a degradation of that passive film. Finally, the anodic current density decreases again down to a stable value that is reached at 1.8 V.

In our study, the anodic part of the potentiodynamic polarization curves (Fig. 6) indicates a high corrosion resistance of CP titanium and Ti6Al4V in artificial saliva free of fluorides due to the formation of a protective passive film resulting in low passive current densities. However, an increase of the passive current density,  $i_{pass}$ , is noticed on both materials when the  $F^-$  concentration in artificial saliva solutions increases (Fig. 6C).

#### *Morphologic aspects of test sample surfaces after potentiodynamic polarization tests*

The surface morphology of CP titanium and Ti6Al4V inspected by SEM and AFM after a potentiodynamic polarization test performed between 1.5 V to 2.0 V and scan rate of 1.6 mV/s are shown in Figures 7 and 8.

The images obtained by secondary electrons on CP titanium and Ti6Al4V after potentiodynamic polarization in solutions free of  $F^-$  (Figures 7A, 8A, 7,8C), reveal mainly scratches and defects originating from the grinding and polishing operation done as pre-treatment. There were no clear signs of any general or localized corrosion on these samples. A similar finding was done on samples tested under similar conditions but in an artificial saliva solution containing 227 ppm  $F^-$ . However, SEM analyses done on samples after potentiodynamic polarization tests done in a 12300 ppm  $F^-$  solution, have revealed localized corrosion on both materials (Figures 7B,D and 8B,D). CP titanium . CP titanium surfaces revealed signs of pitting corrosion while Ti6Al4V surfaces showed characteristics of excessive oxidation and formation of microcracks in the active titanium oxide film (Figures 7D and 8D).

In order to confirm these findings on corrosion, the release of ions in the test solutions induced during the potentiodynamic polarization tests, was determined. Such ICP-MS analyses of the solutions are reported in Fig. 9A. On both CP Ti and Ti6Al4V, a clear decrease of the titanium ion content in the test solutions after potentiodynamic polarization is noticed when the concentration of fluorides increases from zero up to 20 ppm F<sup>-</sup>. This lowering of the selective dissolution kinetics of titanium suggests a beneficial effect of low fluoride content on the corrosion rate of titanium. In that range of fluoride concentrations, and notwithstanding the fact that range is limited, a progressive increase of Al-ions and V-ions is noticed after corrosion tests for Ti6Al4V. Thus, a significant release of Ti-, Al-, and V-ions were found after corrosion tests at 12300 ppm F<sup>-</sup> as shown in Fig. 9A ( $p < .05$ ).

On the other hand, the corrosive effect of high F<sup>-</sup> concentration revealed by SEM (Fig. 7) increases significantly the roughness of titanium as confirmed by AFM as noticed in Fig. 9B ( $p < .05$ ). The arithmetical roughness ( $Ra$ ) and the maximum distance from peak to valley ( $Rt$ ) of the surfaces were obtained from AFM analysis (Fig. 9B). The morphological aspect of the surfaces caused by localized corrosion on CP titanium (Fig. 7B) and Ti6Al4V (Fig. 7D) are probably responsible for the significant increase of the nano-roughness (Fig. 9B).

#### *Chemical analyses of sample surfaces*

XPS analyses of the sample surfaces were done after potentiodynamic polarization in the solutions containing different amounts of fluorides. A representative analysis outcome is shown in Fig. 10 from which the presence of the following elements at the sample surface can be deduced, namely Ti, C, O, Al, F, V, Ca, and P.

XPS analyses allow to evaluate the chemical energy state specific for each element, and to identify the photoelectric peak of chemical compounds. The Ti 2p<sub>3/2</sub> peak range found between 456.2 and 462 eV (Fig. 10B) that corresponds to the Ti oxidized forms, may be related to the formation of one or more of the following compounds on the surfaces after potentiodynamic polarization in artificial saliva: Ti<sub>2</sub>O<sub>3</sub> with a peak at 456.5 eV, Ti(OH)<sub>3</sub> with a peak at 457.5, and TiO<sub>2</sub> with a peak at 458.8 eV. On samples tested in fluoride containing solutions, the F s<sub>1/2</sub> peak range between 680.6 and 696.9 eV, suggests the presence of oxides as TiOF<sub>2</sub> and TiOHF on CP titanium surfaces, and heterogenic oxide layers on Ti6Al4V surfaces [8, 9]. On Ti6Al4V surfaces the detection of a low concentration of Al present as an oxidized form of Al<sup>+3</sup>, suggests the formation of Al<sub>2</sub>O<sub>3</sub> on the surface after potentiodynamic polarization. The XPS analyses on titanium after potentiodynamic polarization revealed the presence of TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>.

## **Discussion**

The results of the present study support the rejection of the null hypothesis. They showed significant differences in corrosion behaviour and topography between commercially pure titanium and Ti6Al4V immersed in fluoride solutions. After an immersion for 24 h in artificial saliva containing different amounts of fluorides, one can notice that: 1) at fluoride concentrations between 0 and 227 ppm, the open circuit potential (OCP) values evolve towards more and more noble values. That reveals an enhancement of the dielectric properties of the passive film with time. Taking into consideration the OCP values recorded, it may be stated that the global electrochemical reaction is cathodically controlled by the reduction of oxygen dissolved in

solution, and that the test material passivates [6, 10, 11, 37]; 2) at a fluoride concentration of 12300 ppm, the OCP almost stabilized at very less noble potentials. Taking into consideration the potential values recorded, the global electrochemical reaction is anodically controlled with an OCP value corresponding to  $E_{corr}$ , and the material corrodes. The cathodic reaction that takes place is the reduction of protons [6, 10, 11, 37]. These results were confirmed by Kruskal-Wallis analyses, indicating that no significant difference between the OCP values of both materials was found in the artificial saliva solutions, except in the solution containing 12300 ppm  $F^-$  ( $p < .05$ ). The lower value of the OCP of CP titanium in fluoride solutions noticed in this study, was also noticed in previous studies [10, 11,38].

Considering that the OCP value depends on the test environment and the exposure time, a variation of the OCP of CP titanium was observed on immersion for 7 days in solutions containing high and low  $F^-$  concentrations. A decrease of the OCP of a metallic material in contact with a certain environment reveals an increase of its chemical reactivity, and a subsequent pre-disposition to corrosion [6, 10, 11]. OCP curves recorded in this study (Figures 2 and 3) confirm 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. Based on literature, it can be stated that there is a large formation of HF that reacts with the titanium surface [15, 17, 20]. Therefore, a high  $F^-$  concentration combined with a low pH, can amplify the chemical reactivity of titanium [6, 17]. In this work, the OCP value recorded on titanium in a solution containing 12300 ppm  $F^-$  at pH 6.5, was similar to that reported in a previous study for titanium tested in a solution containing 554 ppm  $F^-$  at pH 2.5[38]. OCP values of CP titanium and Ti6Al4V immersed in artificial saliva solution (pH 5.2-5.5) reported in literature were similar to those ones found in this study. However, a large standard deviation of OCP values is reported

on CP titanium in the range from -0.15 V to 0.025 V vs. SCE and for Ti6Al4V in the range from -0.2 up to 0 V vs. SCE after 24 of immersion in Fusayama's artificial saliva solution at pH 5.5 that may be due to the high chemical reactivity of titanium exposed to the ambient air or the test solution before and during the OCP measurements [19, 38].

Comparing  $E_{(i=0)}$  values obtained from potentiodynamic polarization curves (Fig. 2) with OCP measurements recorded after 7 days of immersion (Fig. 3), the same value for  $E_{(i=0)}$  and OCP are found for CP titanium tested in a solution containing 12300 ppm  $F^-$ . However, Ti6Al4V shows a  $E_{(i=0)}$  value lower than the OCP value. The same fact was noticed on both materials immersed in solutions containing 0 up to 227 ppm  $F^-$ , whereas the  $E_{(i=0)}$  values are lower. Considering the high chemical reactivity of titanium, the cathodic polarization was used to promote a hydrogen reduction at the metal surface, and to bring the surface of the test samples in a standard state. As a consequence, this cathodic polarization decreases the spread in the test outcome, and allows a reliable comparison of the potentiodynamic polarization curves recorded on different test samples. In a previous study also reported a difference between OCP and  $E_{(i=0)}$  values related to different surface conditions induced during the cathodic-anodic polarization [37]. Potentiodynamic polarization curves recorded in our study revealed that the passive current density,  $i_{pass}$ , measured at 0.85 V on samples immersed in artificial saliva containing 20 or 30 ppm of  $F^-$  (Fig. 6), do not differ significantly up to 227 ppm  $F^-$ . Potentiodynamic polarization curves reveal a progressive degradation of CP titanium and Ti6Al4V in artificial saliva containing 12300 ppm  $F^-$ . Furthermore, CP titanium is much less corrosion resistant than Ti6Al4V in solutions containing 12300 ppm  $F^-$ .

EIS results were also correlated with OCP data shown in Fig. 3, whereas the lowering of  $E_{corr}$  in solutions containing 12300 ppm  $F^-$  is associated to a high chemical reactivity, and



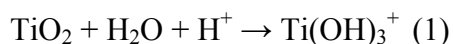
consequently to a localized corrosion of titanium. The values of  $R_{pf}$  found in this study for 24 h of immersion are in agreement with previous studies [12]. However, a previous study found a higher corrosion resistance of CP titanium than Ti6Al4V in artificial saliva solution based on their results on  $R_{pf}$  and  $C_f$  [19]. In fact,  $R_{pf}$  indicates the ability of the passive film to resist of a current flow on its surface, or else the corrosion resistance of the passive film. The increase of  $R_{pf}$  up to 24 or 48 h of immersion (Fig. 5) indicates an increase of corrosion resistance with time although that showed lower values compared to that recorded on lower fluoride contents. Then, the subsequently decrease of  $R_{pf}$  indicates a decrease of corrosion resistance.

As shown by the  $R_t$  roughness values obtained by AFM (Fig. 8B), there is an increased distance between peaks and valleys over the entire assessment length. Thus, the increase of roughness may facilitate the biofilm accumulation on the surfaces, and cause subsequently the inflammation of surrounding tissues [22], or it may cause the accumulation of acidic substances originating from biofilms and oral fluids [14, 17, 21]. A previous study has reported an increase of the roughness  $R_a$  of titanium after 9 days immersion in different test solutions, based on artificial saliva (pH 5.3) containing: 5000 and 25000 ppm  $F^-$ ,  $H_2O_2$  (0.1% and 10%) and/or lactic acid (pH 4.5) [17]. On the other hand, the increase of roughness recorded by AFM detected a degradation of titanium at nano-scale that is resultant from the ion release, and consequent material loss.

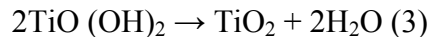
In line with the corrosion aspects noticed by SEM on sample surfaces tested in artificial saliva solutions containing 12300 ppm  $F^-$ , a significant release of Ti-, Al- and V-ions is noticed compared to what was noticed in the previous low fluoride solutions. Literature data have revealed the release of Al- and V-ions caused by passive film dissolution, though those alloying elements confer good mechanical properties to Ti-alloys [3]. A corrosion of metallic materials

has been classified in three classes based on the ion release: Class I) 10  $\mu\text{g}/\text{cm}^2$  week or less; Class II) 10-100  $\mu\text{g}/\text{cm}^2$  week or less; Class III) 100-1000  $\mu\text{g}/\text{cm}^2$  week [28]. Based on that study, alloys of class III could stimulate an adverse biological response in patients due the high release of ions. In that respect, CP titanium and Ti6Al4V alloy could induce adverse biological reactions when in contact with high fluoride concentrations [3, 28, 32]. The release of aluminum ions may however be considered as a toxic element, while vanadium ions as a mutagenic agent [3, 28]. Furthermore, some studies mentioned that the enrichment of the  $\alpha$ -phase with Al may cause prejudice to the passivity and thus decrease the corrosion resistance of Ti-alloys [3, 5, 7]. The development of vanadium-free titanium alloys is actually considered without depreciating the mechanical and chemical properties of the titanium alloys [3, 15, 18, 35]. Studies about Ti-5Al-2Fe, Ti13Nb13Zr, and Ti6Al7Nb alloys have shown an increased corrosion resistance and good biocompatibility although CP titanium behaves well too [3, 8, 9, 14].

On chemical analyses of the surfaces, titanium dioxide ( $\text{TiO}_2$ ) was also found on titanium as one of the main compounds of the protective passive layer formed after potentiodynamic polarization in modified Fusayama's artificial saliva (pH 6.1-7.9) in the  $E$ -range from -1.2V up to 1.2V [9] and in physiological solutions (Hank's and MEM solutions, pH 3-7) in the range from -0.02 up to 1.0 V vs. SCE [39]. Then, the dissolution reaction of the titanium oxide film depends on the saliva pH and consequently the proton concentration. The following reaction has been proposed to explain the dissolution of titanium oxide compounds [6]:

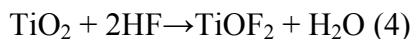


$\text{Ti}_2\text{O}_3$  formed on titanium surfaces can also rapidly oxidize to  $\text{TiO}(\text{OH})_2$  when brought in contact with acidic aqueous solutions, and further on to  $\text{TiO}_2$  by dehydration according the following reactions [40].

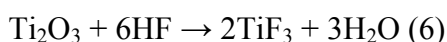
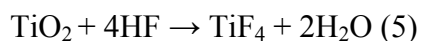


The  $\text{TiO}_2$  layer was reported in literature to be thicker on titanium alloys than on CP titanium [9, 12]. That increase of the thickness of the oxide layer on titanium alloys can be due to the alloying which amplifies the diffusion of  $\text{Ti}^{3+}$  in the oxide film [12]. The formation of oxide layers on Ti6Al4V surfaces (Fig. 7D) can be enhanced by the presence of Al in these alloys. The impedance (EIS) spectra and potentiodynamic polarization curves performed in this work, revealed a growth and dissolution of a titanium oxide film on Ti6Al4V in artificial saliva containing 12300 ppm  $\text{F}^-$ .

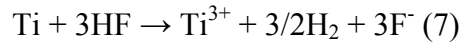
The presence of  $\text{TiOF}_2$  detected at 680.6 eV by XPS analyses (Fig. 8A) in this and previous studies [25] can be associated to the following reaction:



In fact, gels, varnishes or solutions including high  $\text{F}^-$  content (9000-2600 ppm $\text{F}^-$ ) often used after dental bleaching or treatment of natural teeth can also contact titanium-based surfaces of prosthetic structures, abutment and implant systems in the oral cavity. The degradation of titanium-base surface at high fluoride concentrations was found in this work to be consistent with previous reports revealing the occurrence of a localized corrosion process, namely pitting corrosion [17, 20]. The occurrence of pitting corrosion was described as resulting from the formation of hydrated Ti oxides as  $\text{Ti}(\text{OH})_2\text{F}^+$ , and salts as  $[\text{TiF}_6]^{2-}$ ,  $\text{TiH}_2$ ,  $\text{Na}_3\text{Ti}_3\text{F}_{14}$ ,  $\text{TiF}_4$   $[\text{TiF}_6]^{3-}$  in presence of HF according the following reactions [20]:



Once the protective passive layer is dissolved, a release of Ti ions from the metal takes place promoting a localized corrosion according the following reaction [20]:



Previous studies have revealed that a minimum concentration of 30 ppm HF is enough to promote a localized corrosion of titanium in fluoride solutions [20]. Hydrofluoric acid (HF) is chemically classified as a weak acid due to its limited ionic dissociation in H<sub>2</sub>O at 25 °C [26]. In water at equilibrium, non-ionized molecules, HF, remain present and provides slowly H<sup>+</sup> and F<sup>-</sup> to form F<sup>-</sup>.H<sub>3</sub>O<sup>+</sup> [26, 27]. However, hydrofluoric acid is extremely corrosive to glass, metals, and semi-metal oxides, and can penetrate dangerously into tissues [26, 27]. 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<sup>+</sup> and F<sup>-</sup> ions [15, 20, 38]. The relation between pH and F<sup>-</sup> concentration might be expressed by the following equation [20]:

$$\text{pH} = 1.49 \log F + 0.422 \quad (8)$$

Taking this reaction into consideration, a localized corrosion on titanium surfaces might occur in a solution containing 452.5 ppm F<sup>-</sup> at pH 4.2 or in a solution containing 227 ppm F<sup>-</sup> at pH 3.8 [20]. This reaction appears to be correct in our study where pitting corrosion was promoted on CP titanium in a solution containing 12300 ppmF<sup>-</sup> at pH 6.5 (Fig. 7B). The formation of pits on CP titanium was also found in a previous study after immersion in artificial saliva containing NaF 2.5% (11,180 ppm F<sup>-</sup>) [17]. Sodium fluortitanate (Na<sub>2</sub>TiF) and Ca/P globular deposits were detected by EDX analyses after 3 days of immersion [17].

## **Conclusion**

Within the limitations of this study, the main outcome of this work can be summarized as follow:

- CP titanium and Ti6Al4V showed a high corrosion resistance after potentiodynamic polarization and immersion for 7 days in artificial saliva free of fluorides or containing a low F<sup>-</sup> concentration;
- however, a significant decrease of the corrosion resistance of both materials occurred in artificial saliva containing 227 and 12300 ppm F<sup>-</sup>;
- topographic aspects of the corrosion process differed between CP titanium and Ti6Al4V in artificial saliva containing 12300 ppm F<sup>-</sup>. CP titanium degraded by pitting corrosion while Ti6Al4V suffered from general corrosion showing micro-cracks;
- the roughness increased on both materials as a result of the corrosion process;
- consequently, a high amount of metallic ions were released from both materials to the surrounding environment on immersion in concentrated fluoride solutions;

## *Acknowledgments:*

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## TABLE LEGEND

Table 1. Composition of the artificial saliva used as electrolyte solution of pH 5.5 in this study.

## FIGURE CAPTIONS

Figure 1. Schematics of the experimental set up used for corrosion tests.

Figure 2. Open circuit potential (OCP) *vs.* time of immersion for (A) CP titanium and (B) Ti6Al4V in artificial saliva containing different amounts of fluoride ions.

Figure 3. OCP measurements for 7 days of immersion in artificial saliva without and with fluorides. (A) CP titanium and (B) Ti6Al4V.

Figure 4. Nyquist and Bode spectra recorded on (A,C) CP titanium or (B,D) Ti6Al4V immersed in artificial saliva solutions containing different amount of fluorides for 7 days.

Figure 5. Evolution of the polarization resistance with immersion time for (A) CP titanium and (B) Ti6Al4V immersed in solutions containing different amounts of fluorides. Equivalent circuit proposed for (C) a compact oxide surface film, and (D) a porous oxide surface film.

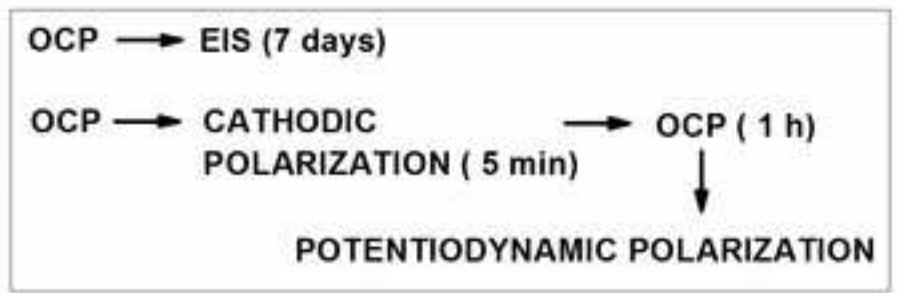
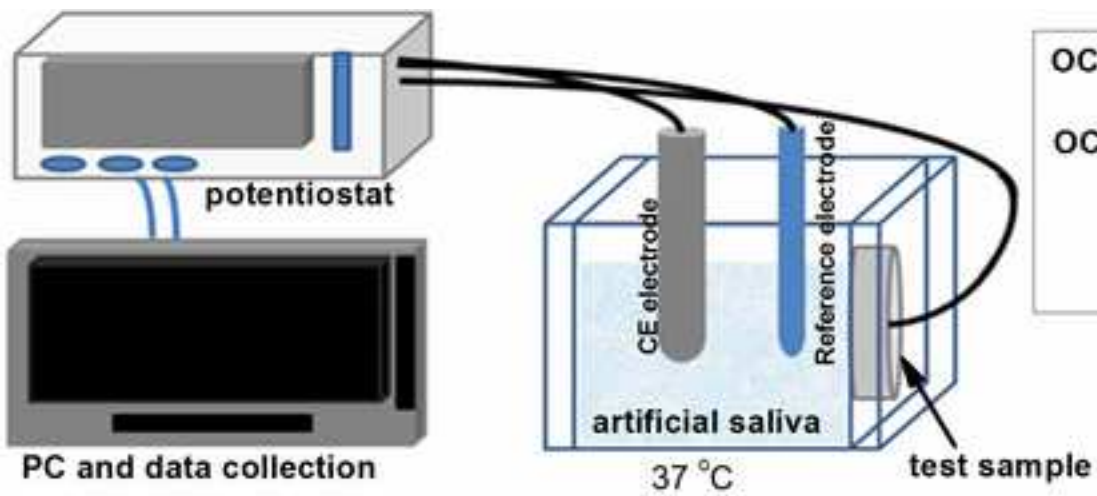
Figure 6. Potentiodynamic polarization plots in artificial saliva solutions containing different concentrations of fluorides: (A) CP titanium and (B) Ti6Al4V. Potential scan rate was 1.6 mV/s and curves were recorded starting at the lowest potential. (C) Passive current density *vs.*  $F^-$  concentration measured during potentiodynamic polarization tests at a potential of 0.85V *vs.* SCE on either CP titanium or Ti6Al4V.

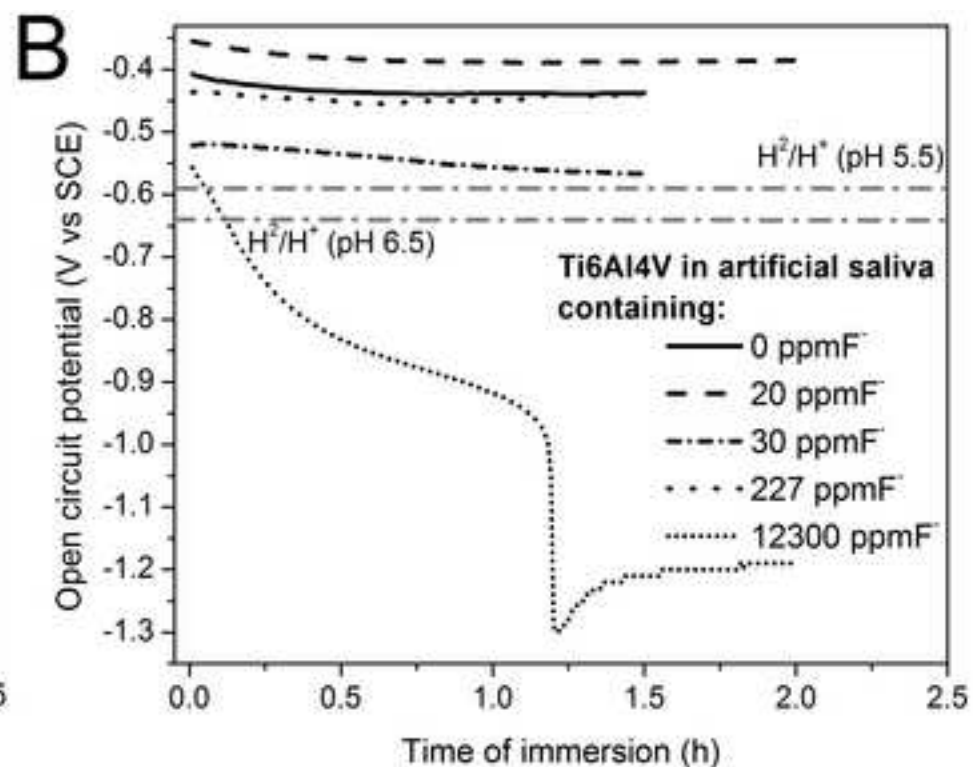
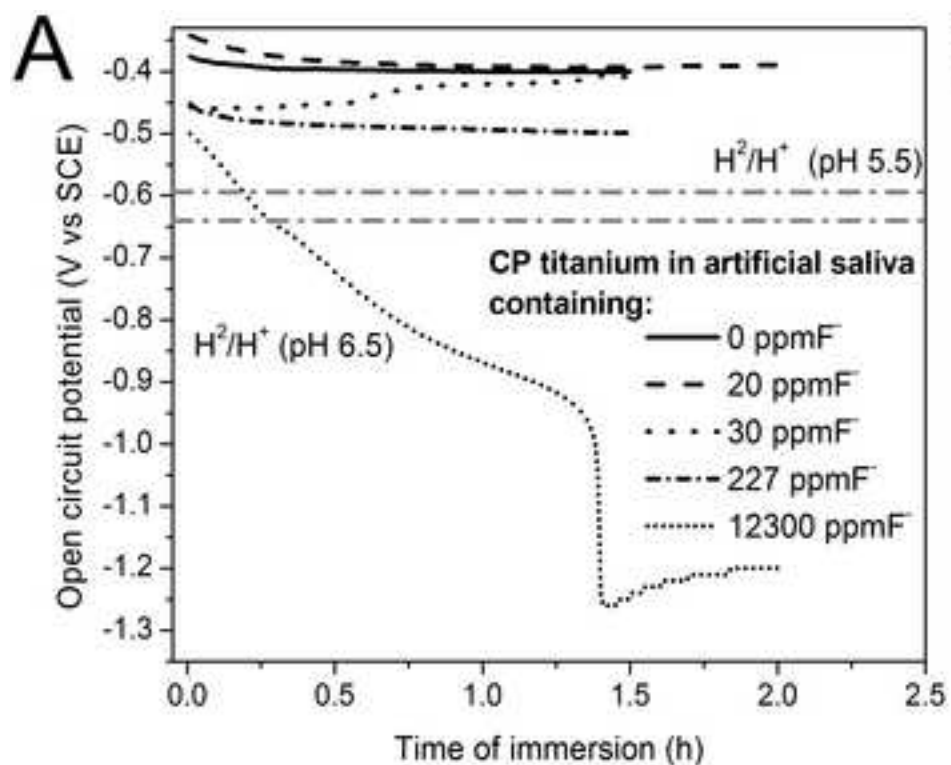
Figure 7. Topography as appearing in SEM analyses of samples after potentiodynamic polarization tests for: CP titanium in (A) artificial saliva solutions free of  $F^-$  and (B) containing 12,300 ppm  $F^-$  ; and, for Ti6Al4V in (C) artificial saliva solutions free of  $F^-$  and (D) containing 12,300 ppm  $F^-$ . The tests were performed between -1.5 V *vs.* SCE and 2.0 V *vs.* SCE at a scan rate of 1.6 mV/s.

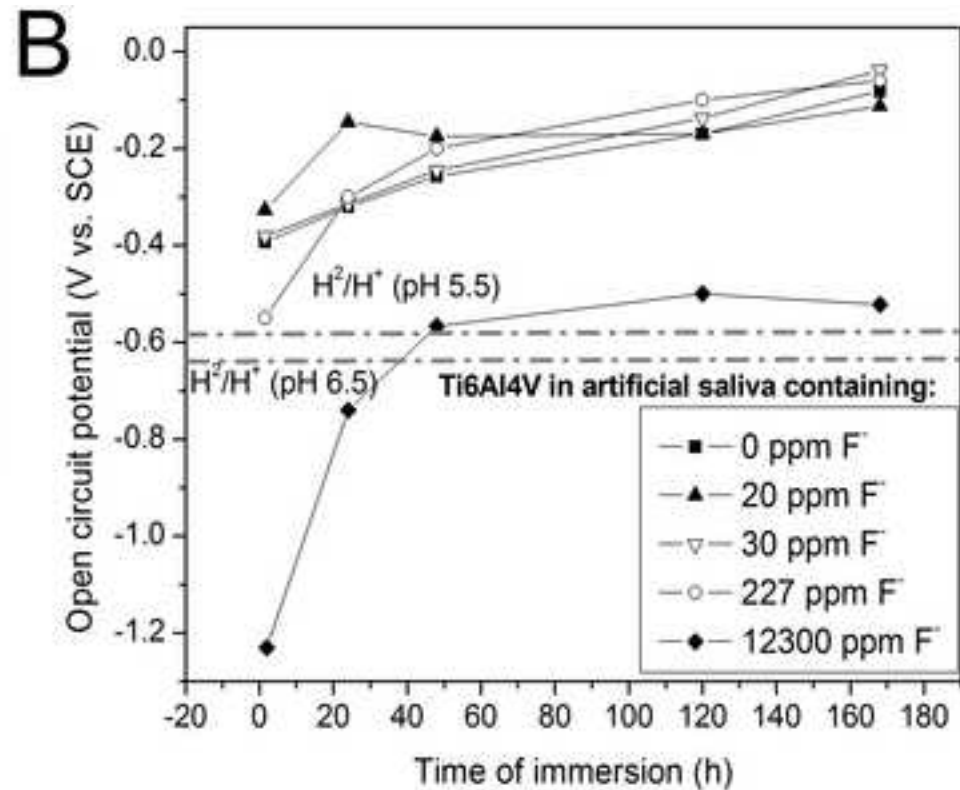
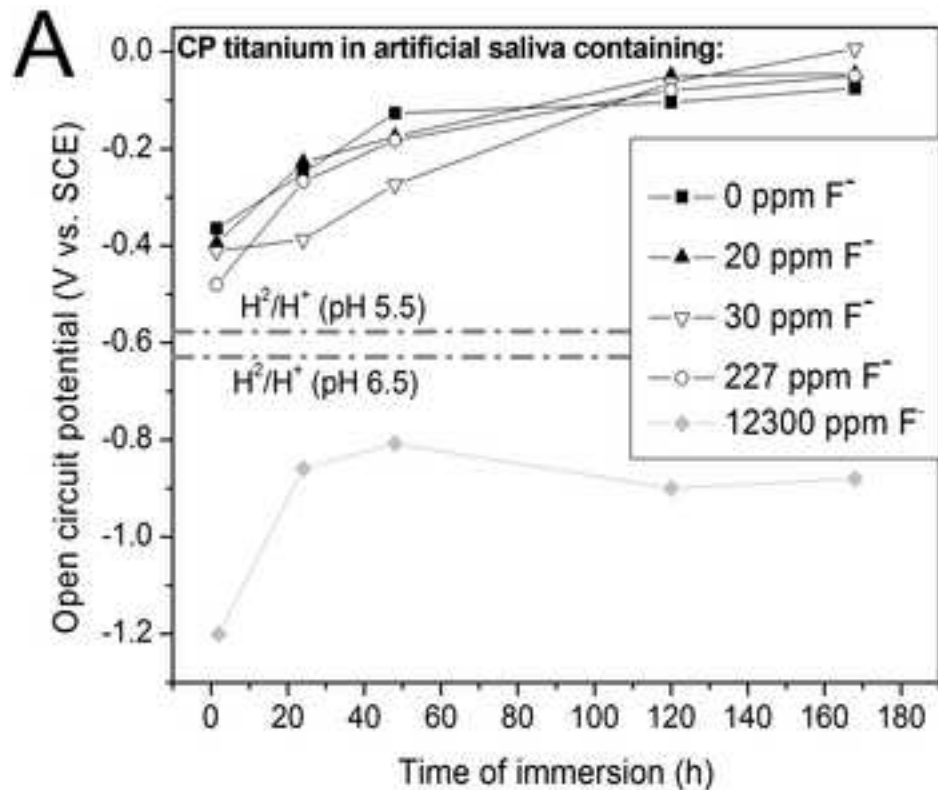
Figure 8. AFM images after potentiodynamic polarization tests of (A, B) CP titanium, and (C, D) Ti6Al4V performed between -1.5 V vs. SCE and 2.0 V vs. SCE at a scan rate of 1.6 mV/s, in (A, C) artificial saliva solution free of F<sup>-</sup> and (B, D) containing 12,300 ppm F<sup>-</sup>.

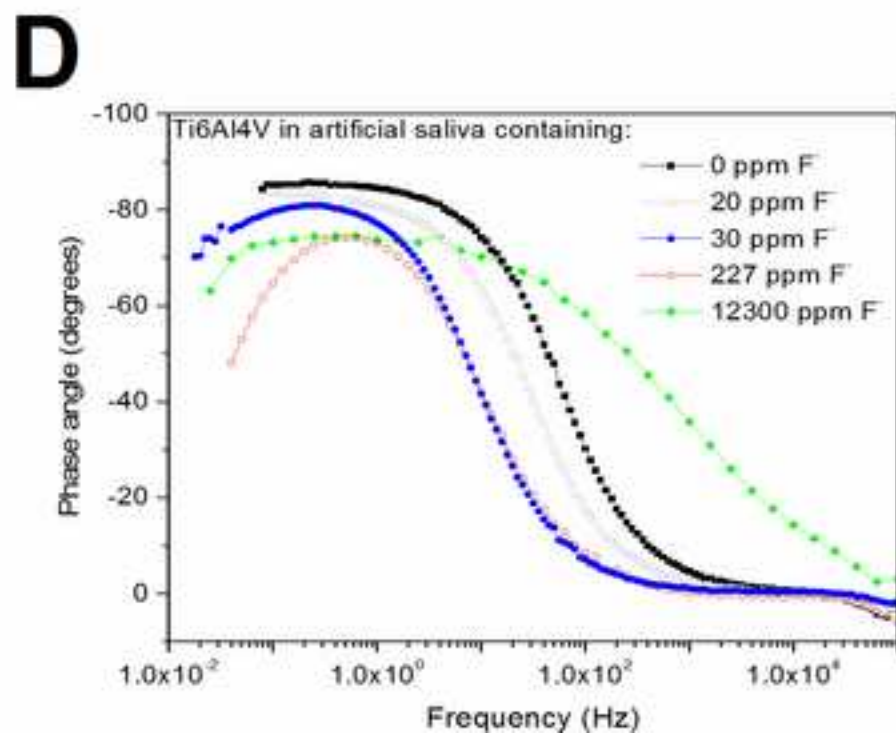
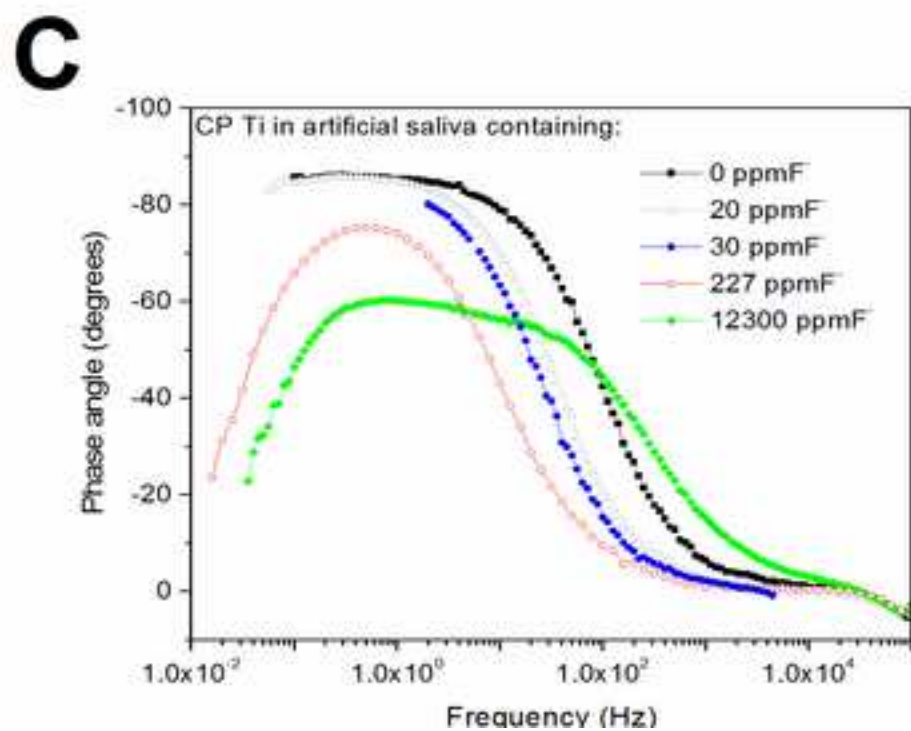
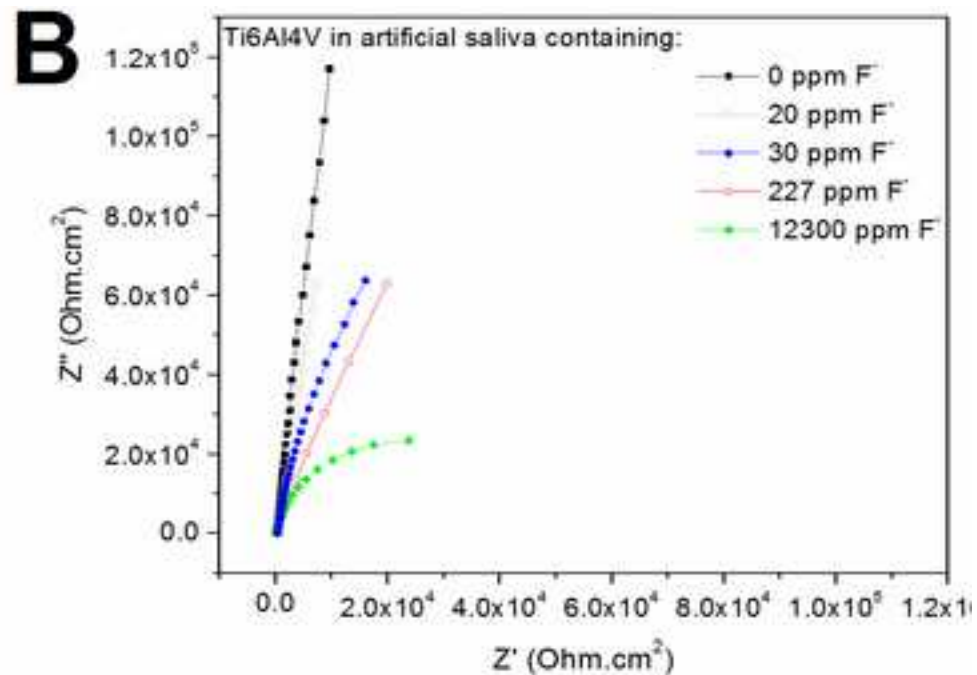
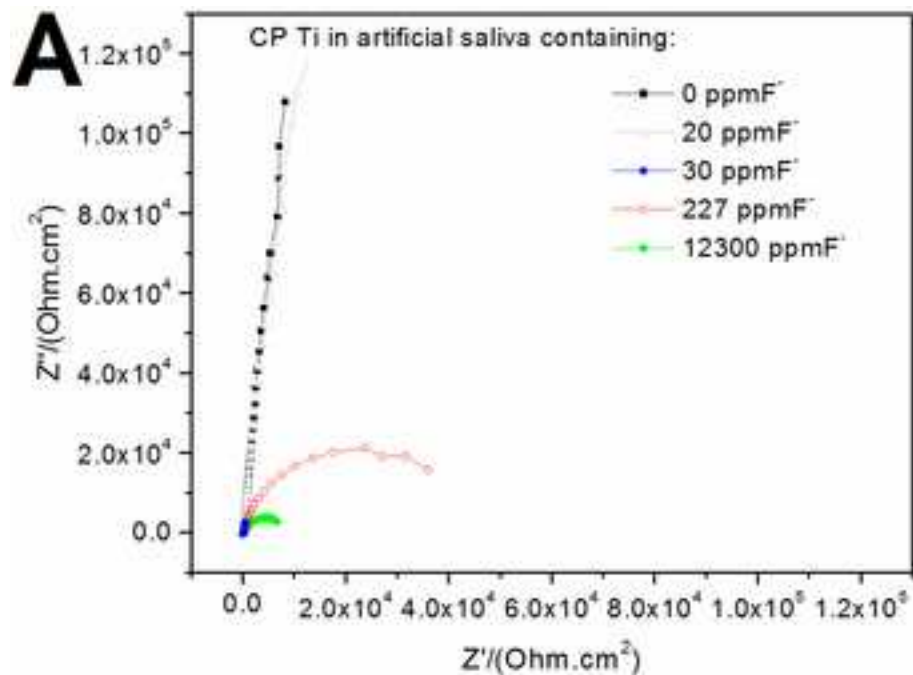
Figure 9. (A) Release of metallic ions from CP titanium and Ti6Al4V in solutions induced by the potentiodynamic polarization tests and (B) consequent roughness of the surfaces obtained by AFM. The tests were performed between -1.5 V vs. SCE and 2.0 V vs. SCE at a scan rate of 1.6 mV/s, in artificial saliva solutions with 0, 20 and 12300 ppm F<sup>-</sup>.

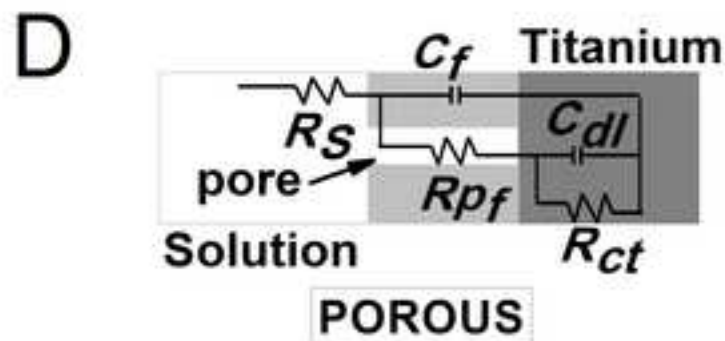
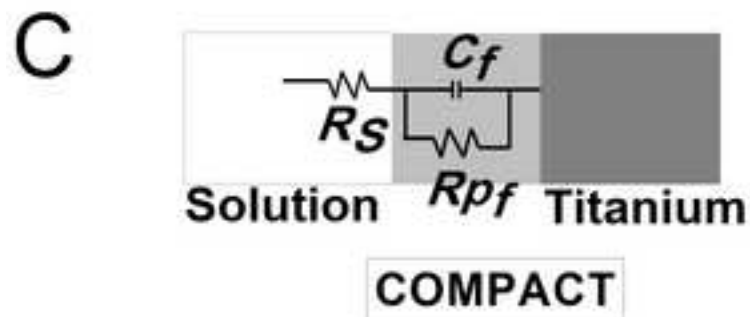
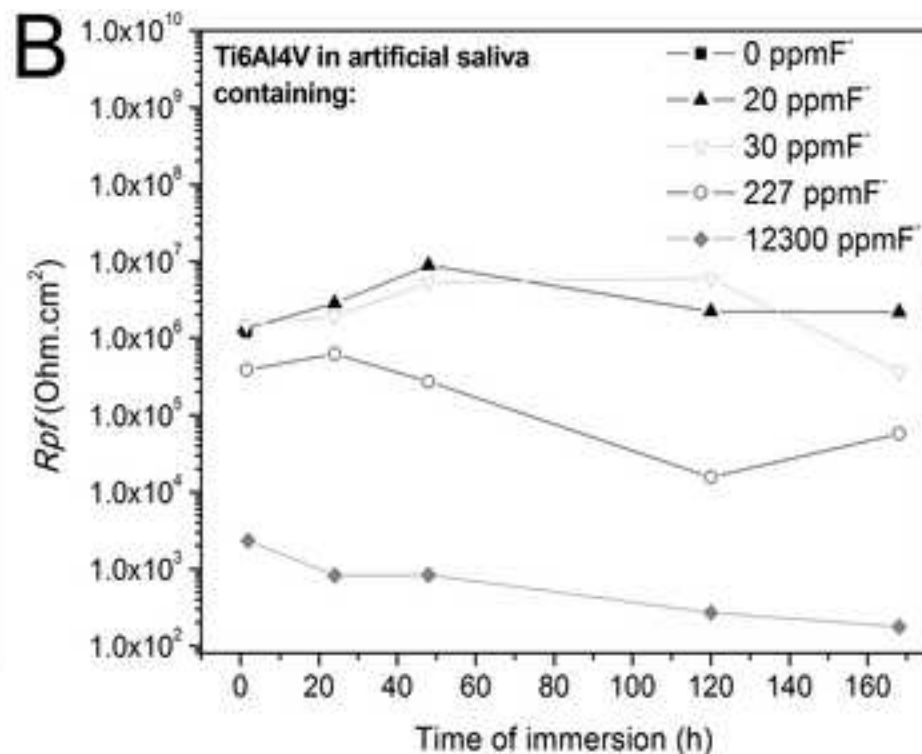
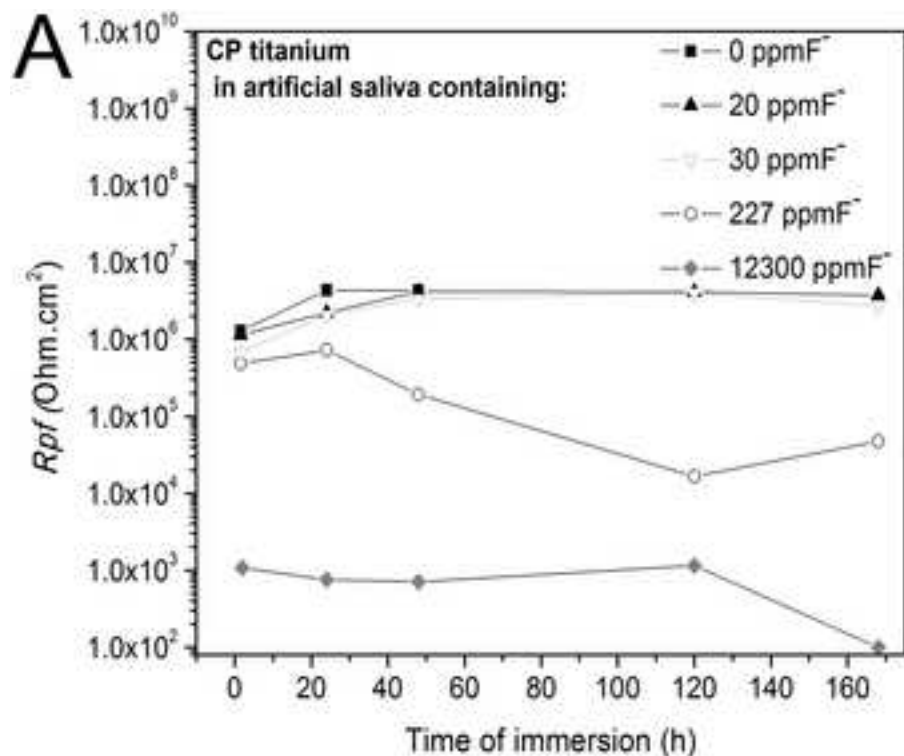
Figure 10. XPS spectra of the titanium surfaces after potentiodynamic polarization of CP titanium performed between -1.5 V vs. SCE and 2.0 V vs. SCE at a scan rate of 1.6 mV/s in 12300 ppm F<sup>-</sup> solution (pH 6.5).



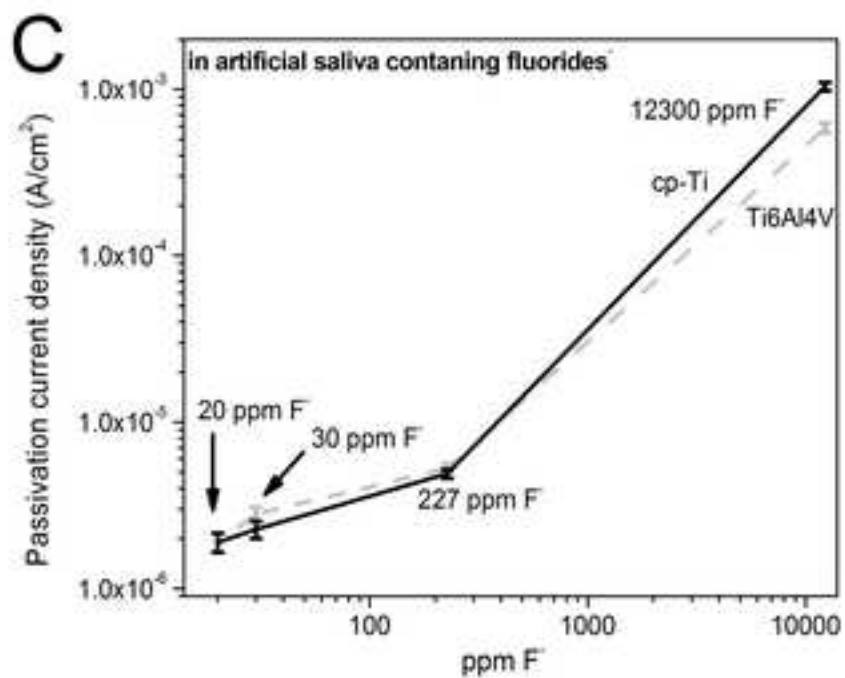
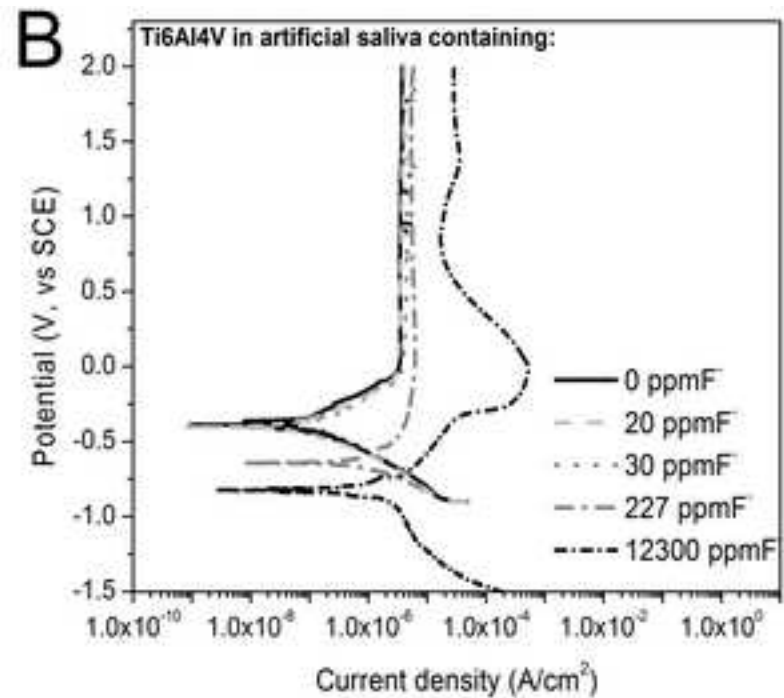
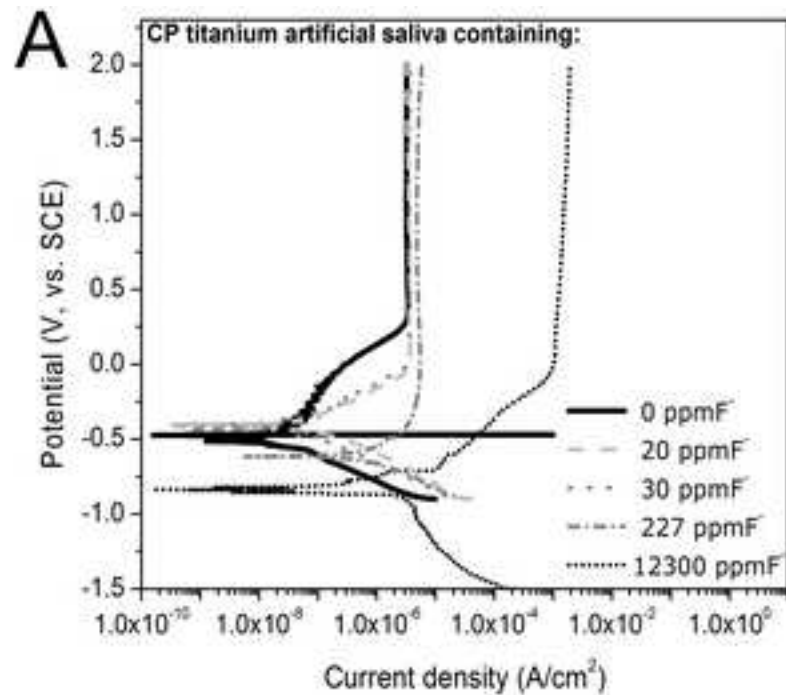


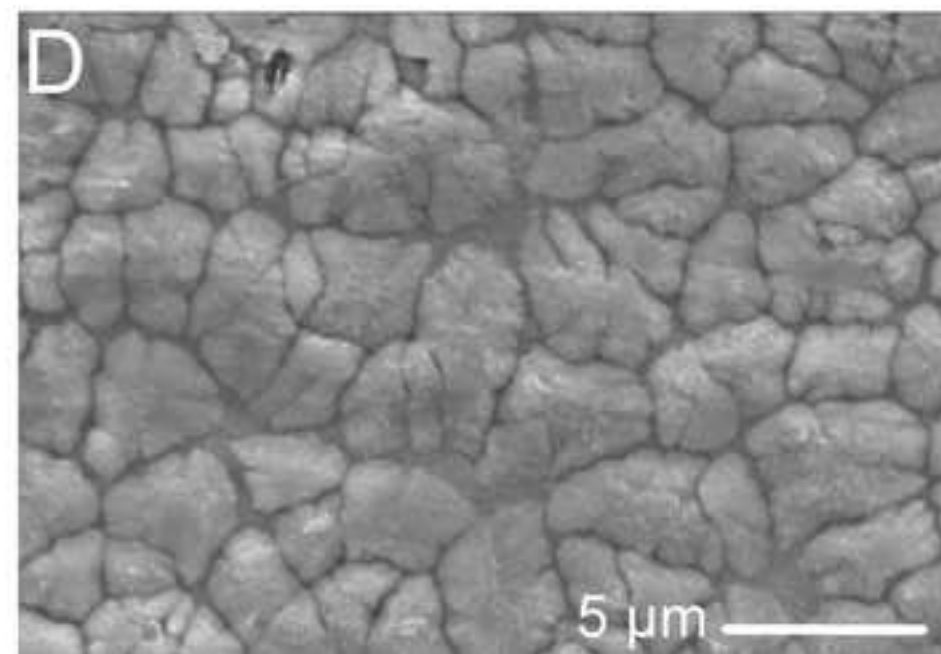
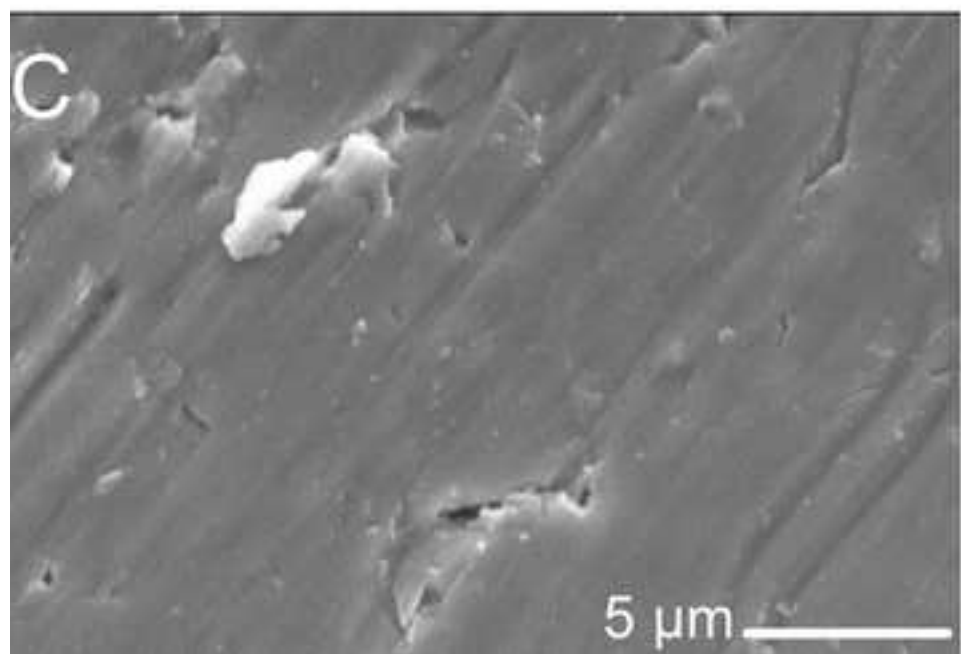
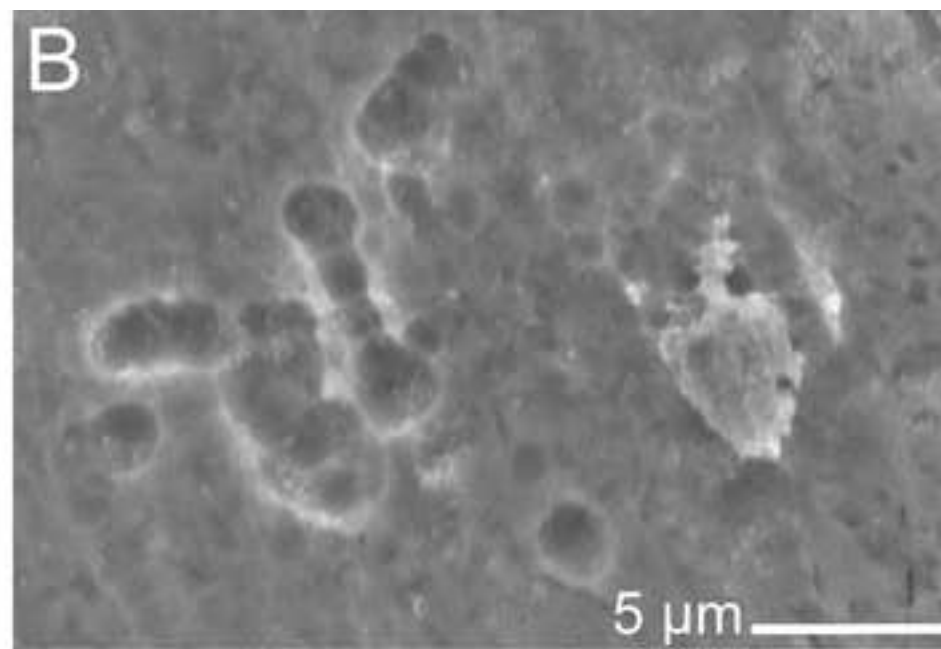
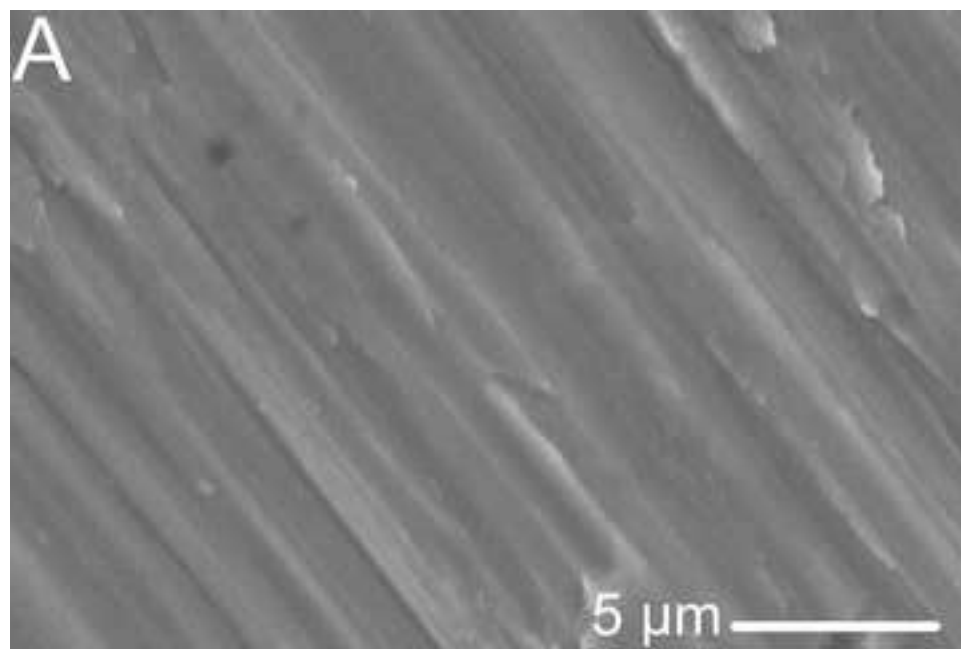


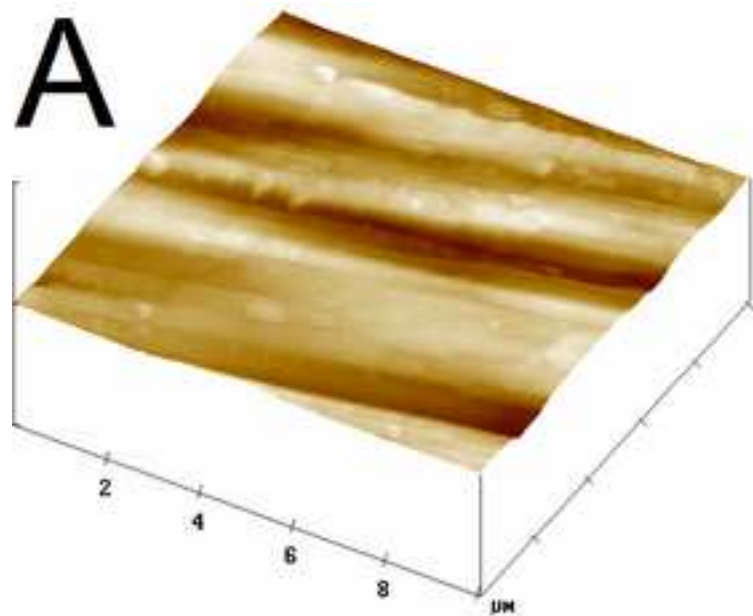




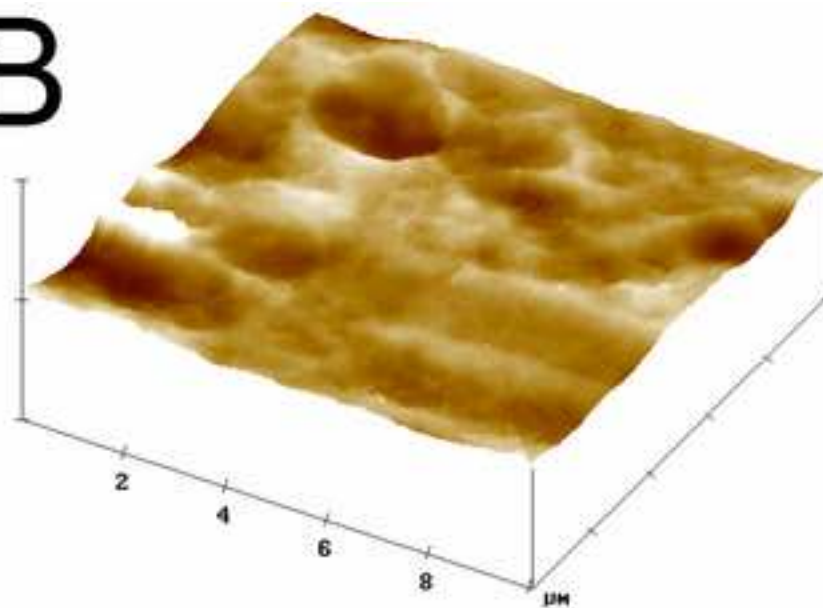




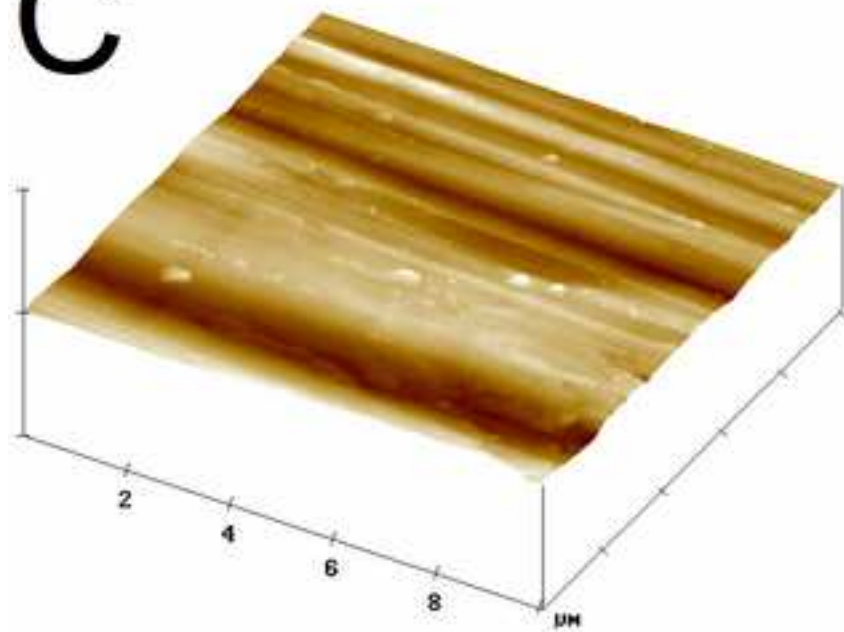


**A**

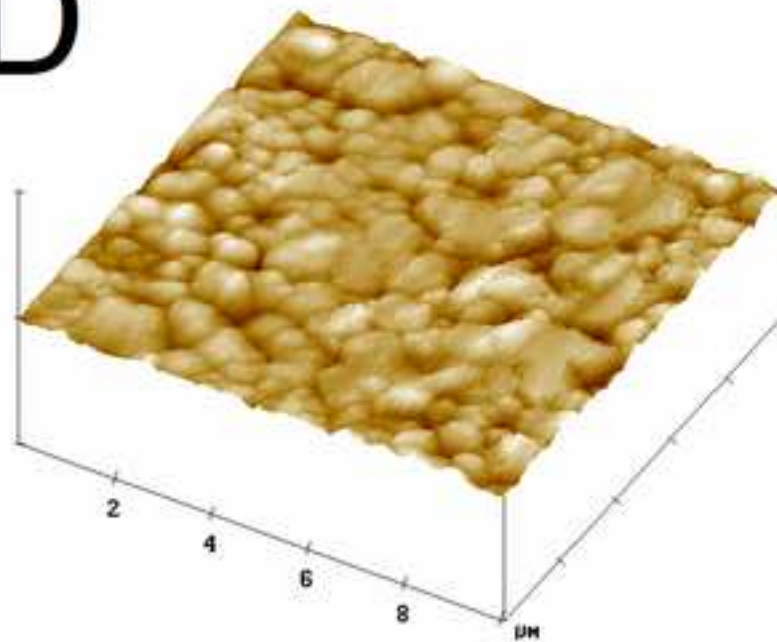
X 2.000  $\mu\text{m}/\text{div}$   
Z 3500.000  $\text{nm}/\text{div}$

**B**

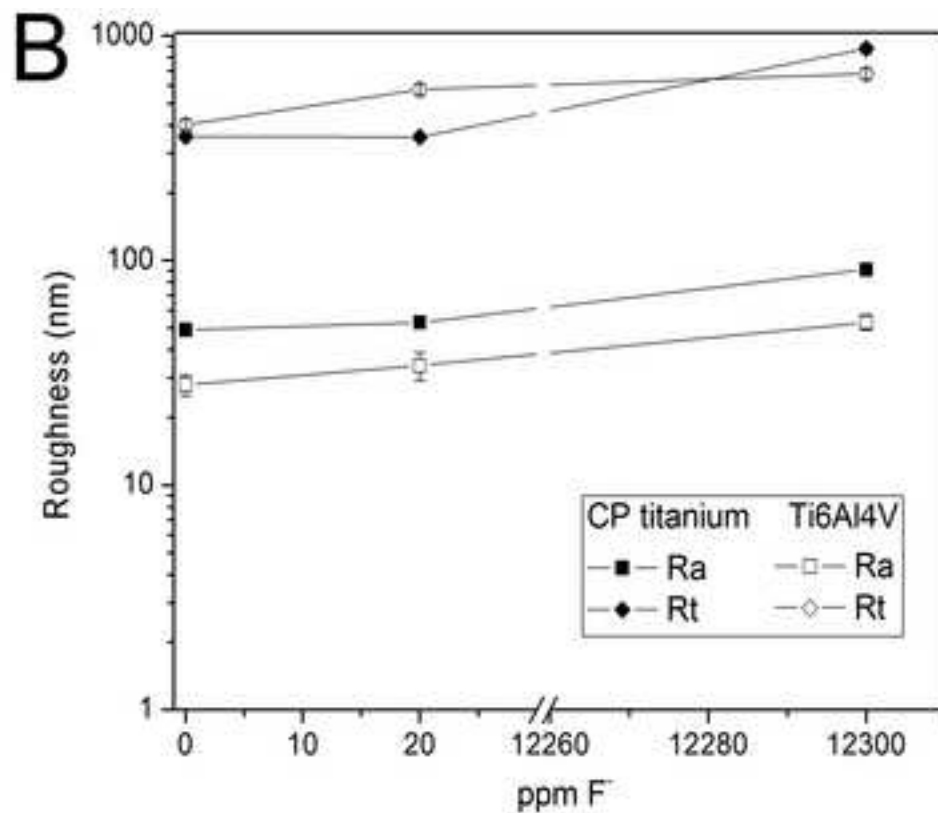
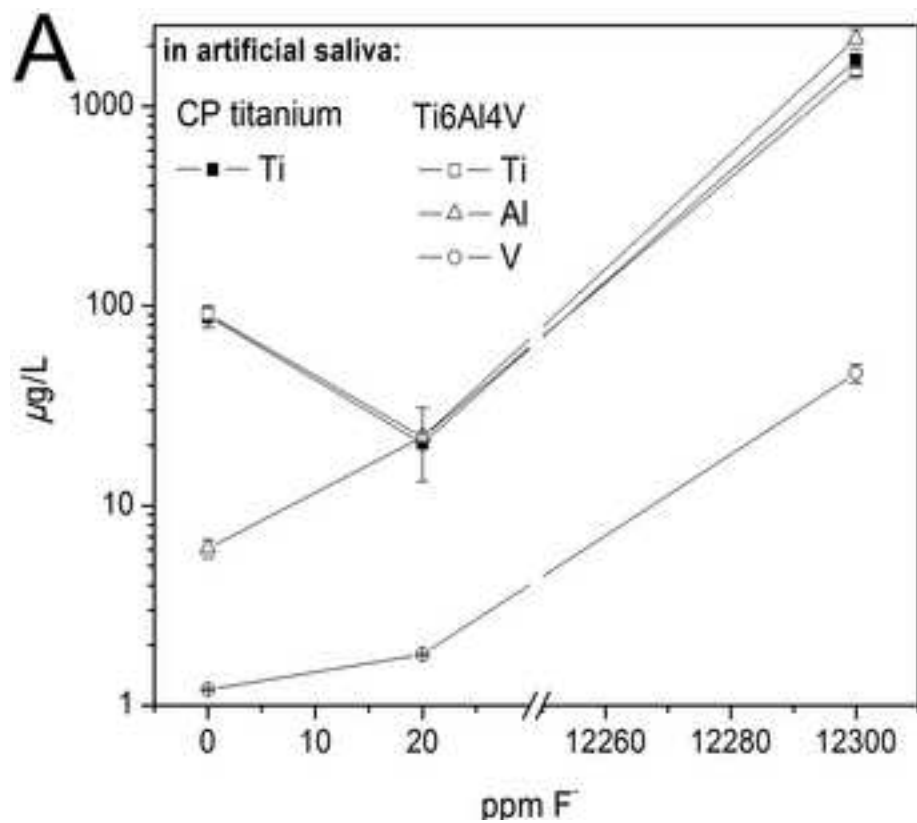
X 2.000  $\mu\text{m}/\text{div}$   
Z 3500.000  $\text{nm}/\text{div}$

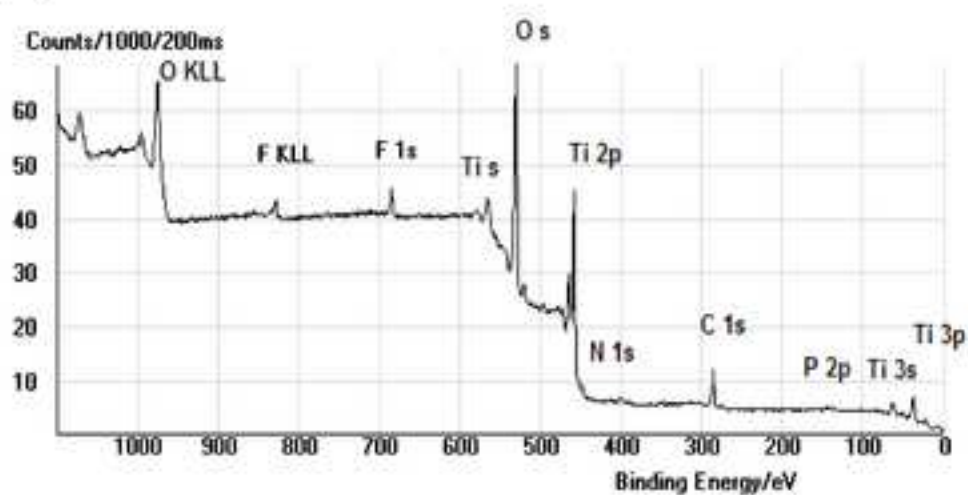
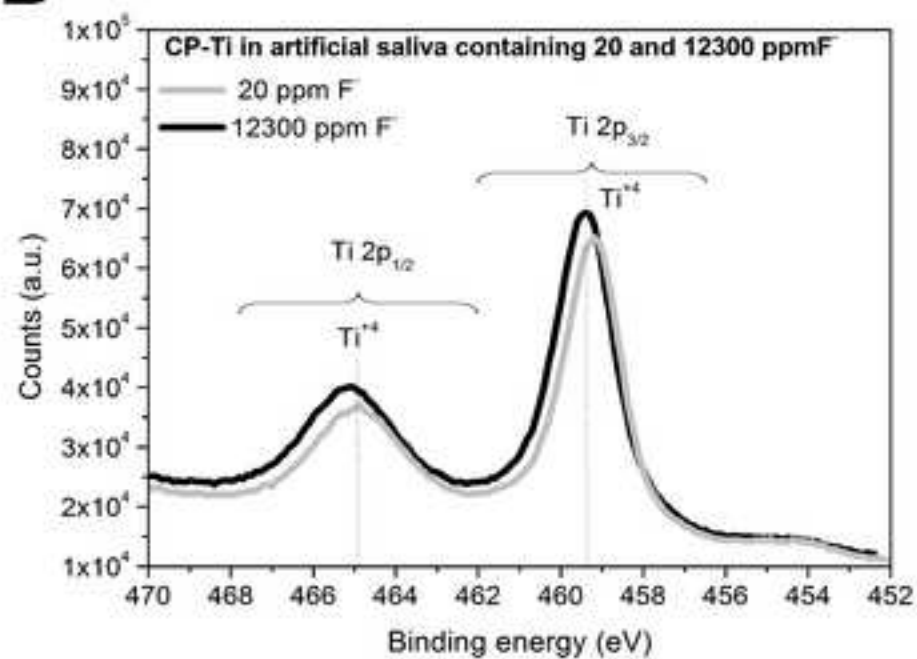
**C**

X 2.000  $\mu\text{m}/\text{div}$   
Z 3500.000  $\text{nm}/\text{div}$

**D**

X 2.000  $\mu\text{m}/\text{div}$   
Z 3500.000  $\text{nm}/\text{div}$



**A****B**

**TABLE**

Table 1. Composition of the Fusayama's artificial saliva used as ~~stock~~electrolyte solution of pH 5.5 in this study.

Compounds	(g/l)
NaCl	0.4
KCl	0.4
CaCl <sub>2</sub> .2H <sub>2</sub> O	0.795
Na <sub>2</sub> S.9H <sub>2</sub> O	0.005
NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O	0.69
Urea	1