Electrochemical Behavior of Ti and TiAlV in Tani-Zucchi Artificial Saliva

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The main objective of this work is to study the corrosion susceptibility of Ti and TiAlV in artificial saliva Tani-Zucchi at 37°C with and without fluoride and chloride anions. The addition of anions was performed at various time of the local process on the passive film: breakdown and regeneration.

Artificial saliva Tani-Zucchi was chosen for its agresivity related to high concentration of Cl⁻ anions. The composition of Tani-Zucchi saliva is very closed to the actual conditions existent in a cavity media.

Monitoring and controlling the implant interface into oral cavity media include the following techniques:

– open circuit potential during 600 hours;

– ion release identification during 600 hours (Atomic Absorption Spectroscopy);

– electrochemical hysteresis curves;

– surface analysis (Atomic Force Microscopy).

The surface parameters (roughness) and the susceptibility to local corrosion data (breakdown potential and protection potential) are evaluated, and their trend variations suggested a direct correlation.

A model based on double layer concept and the surface analysis was proposed and discussed.

As a conclusion it was revealed a strong and complex effect of floride and chloride anions on the behavior of titanium and titanium alloy in artificial saliva.

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INTRODUCTION

Electrochemical behavior involved in dental and orthopaedic corrosion processes is of high interest to value biocompatibility.

Corrosion processes may affect dental alloys biologically, functionally and aesthetically.

During the corrosion processes metallic ions are released; they may come across cells or tissues which are adjacent to the implant or may spread to various parts of the body. Unless the implant is made up of biocompatible materials, the ions released into the physiological environment may have toxic effects or hamper the growth of bony cells on the implant surface [1].

Titanium and its alloys are widely used for dental implantology because of their mechanical properties, electrochemical parameters, absence of toxicity and their biocompatibility. Nevertheless, the very complex chemistry of the oral cavity may reveal surprises concerning corrosion processes.

The surface morphology and the oxide layer thickness, have been shown to influence the final interactions of the implant with the surrounding media [2].

Titanium implants are covered by 2–6 nm thick oxide layer, spontaneously formed in the presence of oxygen and contributing to the high biocompatibility of titanium systems by preventing corrosion of the implant and ion release from the metal surface.

However it has been reported that fluoride containing environment, used in preventing dental caries, can attack titanium systems [3,4].

In vitro electrochemical studies are relevant even for corrosion processes which are very slow due to a protective passive film. The aim of this paper is to compare the susceptibility to corrosion of Ti and TiAlV in Tani-Zucchi artificial saliva solutions in different conditions, by doping with fluoride anions. The variation in time of the corrosion potential, of the ions dissolved in the artificial saliva solution and of the surface topography was monitored by various methods. The susceptibility to local corrosion was evaluated by means of potentiodynamic polarization curve measurement technique.

MATERIALS AND METHODS

The biomaterials used in this study, as test specimen, were Ti and TiAlV. Their composition is presented in Table 1.

The electrodes were shaped cylindrically out of massive cast metal bars. Before each measurement the electrode surface was polished down to 1200 grit specification with a grinding wheel with carborundum-based abrasive paste of different gradings; it was then polished using 6, 1, 0.25 µm slurried aluminium oxide (Buehler). For washing and removing the residues the

TABLE 1 Lipsa Titlu !!!!!!!

Electrode	C	N	H	O	Al	V	Fe	Ti
Ti	0.1	0.036	0.015	0.2	0.05	–	0.015	balance
Ti6Al4V	0.08	0.05	0.015	0.2	6.7	4.5	0.3	balance

electrode was placed in an ultrasound settling tank with ethanol 15 min, then rinsed with deionized water during 30 minutes.

The electrolyte cell was maintained at 37°C, the temperature of human body, using a suitable water bath. All tests were carried out under aerated condition.

The electrolyte solutions used in these tests were Tani-Zucchi artificial saliva, doped or not doped with fluorine ions.

The composition of the Tani-Zucchi artificial saliva [5] used was: $1.5\,g/l$ KCl, $1.5\,g/l$ NaHCO$_3$, $0.5\,g/l$ NaH$_2$PO$_4$·H$_2$O, $0.5\,g/l$ KSCN, $0.9\,g/l$ lactic acid.

Note that Tani-Zucchi saliva contains lactic acid, which ensures working conditions close to the clinical reality, as it is naturally released by bacteria in the oral cavity. Tani-Zucchi saliva also has a pH of 7.5, it contains a greater amount of chlorine ions than Fusayama saliva and does not contain calcium ions.

Electrochemical tests in evaluating the implant material susceptibility to local corrosion were pitting or crevice included measurements of the potential variation in open circuit and cyclic polarisation data. Atomic absorption analysis and Atomic Force Microscopy (AFM) have completed electrochemical measurements for the surface characterization of biomaterials.

The implant corrosion potential variation in time, in doped and not doped artificial saliva was monitored with ITT- Matrix instrument. The influence of the time of doping with fluorine anions on the evolution of the corrosion potential was also taken noticed.

The VoltaMaster software, using the A.S.M. standard [6] based on Stern's theory [7], indicates from polarisation resistance the values of the corrosion current I_{cor} and of the corrosion rate v_{cor} in mm/year by means of the relation:

$$V_{cor} = 3.27 \times 10^{-3} I_{cor} E/d,$$

where E is the chemical equivalent for titanium. For TiAlV, the chemical equivalent was calculated using the formula

$$E_{TiAlV} = f_{Ti}M_{TiAlV}/Z_{Ti} + f_{Al}M_{Al}/Z_{Al} + f_V M_V/Z_V,$$

where 'f' stands for the atomic fractions of the alloying elements; M is the atomic mass of each of the alloying elements and 'z' indicates the alloying element valence.

Cyclic polarization potentiodynamic curves were obtained in the form of potential *vs.* current density curves between a range of $-0.8\,V$ to $3\,V$ using VoltaLab21 with VOLTAMASTER 2 electrochemistry software, license for Windows 95. The potential was increased at a rate of $2\,mV/sec$. The electrolyte cell was made of glass and had a capacity of $200\,mL$. The specimen (Ti and TiAlV) acting as a "working" electrode (anode) was placed in the cell facing a platinum "auxiliary" electrod (catode). A saturated calomel electrode was used as the "reference" electrode. The voltamograms allowed to determine the main electrochemical parameters which characterize the corrosion process of the studied biomaterials: E_{cor} – corrosion potential, I_{cor} – corrosion current, E_{br} – breakdown potential was noted to be value at which the potential-current density plot was seen to show a sudden increase in current density, E_{pr} – protection (repassivation) potential was noted as the value of potential at which the current density returned to the passive current density on the reverse scan. Generally, smaller differences between these two values ($E_{br} - E_{pr}$) indicated a better corrosion resistance.

Atomic absorption analysis was used to determine the amount of Ti ions released by the biomaterial during 20 days. The experiments were performed using an AAS 6 Vario atomic absorption spectrometer, with electrothermal atomization with the detection limit of $10^{-9}g$.

Surface average roughness measurements (R_a) were undertaken for each specimen before and after corrosion using atomic force microscopy (AFM) program in order to correlate roughness to electrochemical parameters: E_{cor}, E_{br}, E_{pr} and difference ($E_{br} - E_{pr}$).

Atomic force microscopy with image analysis was performed with a non-commercial model developed at Twente University Netherlands. A Park Scientific type to make microfabricated cantilever – type assembly was used in the investigation images were acquired in standard contact mode, in close loop (height mode) at scan size ranging from $20 \times 20\,\mu m^2$ to $2 \times 2\,\mu m^2$. Delay (time between two measurements points) ranged from $3000\,\mu s$ to $8000\,\mu s$. For quantitative analysis purposes maximum area images were selected and processed with AFM IMAGES ANALYSIS a Windows application with Single Document Interface used in surface topography characterization. The program provide 2D and 3D visualization of AFM data, software techniques for image improvement and various functions for granulometric measurements and statistical analysis.

RESULTS AND DISCUSSION

The evolution in time of the corrosion potential in open circuit for the Tiand TiAlV working electrodes in solutions simulating physiological

environment in the oral cavity revealed the following aspects. During the first minutes, the electrode potential became more negative. After 2 to 5 hours, the stationary potential changed towards much more positive values than those registered during the immersion. The initial variation of the corrosion potential towards more negative values can be explained by the break of the oxide film already existing at the bioma- terial surface, due to the latter interaction with the artificial saliva. The positive values registered afterwards show that the film recovered and grew thicker. The width of the oxide film on the biomaterial surface may increase at different rates, depending on the composition of the sol- ution, of the anions adsorption within the oxide film, on the surface mor- phology, etc. [8,9].

The variation of the Ti and Ti6Al4V electrode potential in artificial saliva is presented in Figure 1. This curve shows that passivation proceeds in artificial saliva right after immersion.

Titanium reaches positive values of the corrosion potential after only five days from immersion, therefore its tendency to oxidation is bigger than the alloy's containing vanadium, whose potential stays negative even after 25 days.

Considering the multiple factors (pH, temperature, anions and cations of the simulated physiological environment, etc.) which may affect the
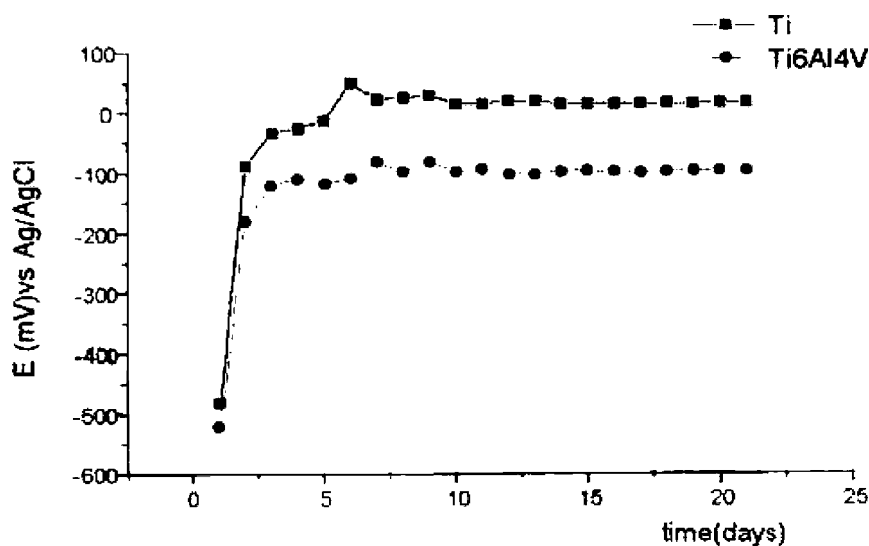
FIGURE 1 The variation of the potential in open circuit for titanium and titanium alloys in artificial saliva.

biomaterial behavior in the oral cavity, we studied the influence of the fluorine ion, added in different ways. The concentration of the fluorine ions in the oral cavity depending on function of the prophylactic treatment and of the gel nature. For instance, in toothpastes the fluorine concentration is around 1%, while in different dental hygienic solutions (mouth water) it can reach 2%.

For the Ti electrode, we made both tests regarding the corrosion potential variation in time in saliva doped with NaF at different moments and measurements for the saliva containing fluorine ions have been performed from the very beginning. Doping was made before and after reaching the stationary potential. Note that the moment of doping plays a very important role in the evolution of the corrosion potential in open circuit. Adding fluoride anions before the stationary potential to be reached triggers the latter movement towards more negative values, at -275 mV. This suggests a local break of the oxide layer on the Ti surface, followed by the film recovery and by the restoration of protective qualities. Doping with NaF after the stationary potential was reached has no major influence on its variation in time, indicating the passive film stability at the action of the fluorine ions. (Fig. 2).

The metallic ions release is evident by the modification of the corrosion potential in open circuit, after the deterioration of the passive film and can be also estimated by means of corrosion rate evaluated from polarisation resistance.

The results in Table 2 show that the corrosion rate for Ti and TiAlV rises in the presence of F^- anions, proving that the resistance to corrosion decreases, function of their concentration. The values of corrosion rate for TiAlV are bigger than for pure titanium. These data should be widely diffused to all dental practitioners.

Using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) we have been recently able to demonstrate that the pasive film in physiological media is a mixture of oxides TiO, TiO_2, Ti_2O_3 Ti_3O_5 and the predominate species is the TiO_2 [10] in two crystaline forms, rutile and anatase [11]. All the titanium oxides on the metallic surface contribute to a part of the interface with the molecular constituents of the biological systems, where interactions exist on the molecular level in a very narrow zone having a thickness of less than 1 nm.

In order to understand how corrosion proceeds in terms of charge transfer at the metal-physiological electrolyte interface, it is necessary to consider an accepted model $Ti/TiO_2 \cdot TiOOH$ [12]. In this case, due to hydroxilated ions at the metal surface, charge transfer can occur within the layer depending on whether the metal oxide is stable or it is passivated up to and beyond removal of its protective oxide layer. These are shown by the results presented in Tables 2 and 3.
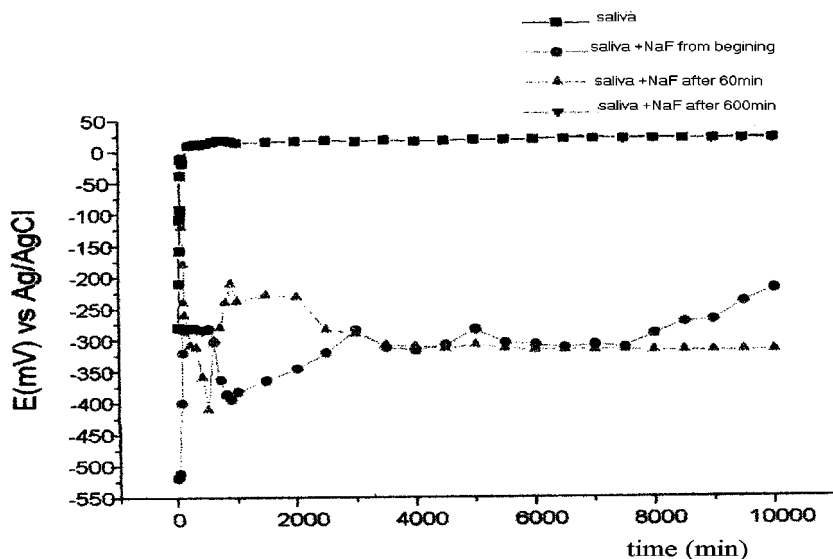
FIGURE 2 The variation of the potential in open circuit for Ti doped with NaF in saliva.

Potentiodynamic curves were traced for the Ti and Ti6Al4V electrode in Tani-Zucchi simulated saliva. The polarization curves are rendered in Figure 3 and the electrochemical parameters are presented in Table 3.

Potentiodynamic curves for titanium in Tani-Zucchi saliva with fluoride ions addition are presented in Figure 4.

It could be noticed that, in the case of a 0.01 M NaF addition, Ti remains passive up to 0.7 V and the passivation current's density rises up to $1 \, mA/cm^2$ approximately, as compared to only $1–5 \, \mu A/cm^2$ in the absence of fluorine ions. It is a three size grade increase. In the same time the passive domain diminishes, and the values of the breakdown potential (E_{br}) tend to be more negative than those registered in the absence of fluorine ions. This may be explained by local breakdowns provoked by the fluoride

TABLE 2 The Values of the Corrosion Rate (mm/year) for Ti and Ti$_6$Al$_4$V in Tani Zucchi Saliva

$[F^-]$, mol/L	0	0.01^-	0.1	0.5
Ti	0.0008780	0.0035	0.00735	0.009395
Ti$_6$Al$_4$V	0.002	0.039	0.1121	0.217

TABLE 3 Electrochemical Parameters Resulted from Polarization Curves for Non-doped Saliva

| Biomaterial	E_{br} (mV)	E_{pr} (mV)	$E_{br} - E_{pr}$ (mV)
Ti	1250	1120	130
Ti6Al4V	958	543	415

anions. The local breakdowns of the passive film lead to local depassivations of the surface, followed by repassivations, as shown in literature [13] by means of microscopic analyses of the surface.

From the passivation curves we deduce a slight increase of the passive current as long as the morphology of the exposed surfaces alters.

The electrochemical parameters of Ti which results from the anodic polarization curves are presented in Table 4.

The passive protective film (titanium oxides and different ions and molecules as HPO_4^{2-}, $H_2PO_4^{-}$, water, and adsorbed oxygen) formed on the biomaterial surface in Tani-Zucchi artificial saliva stays in a permanent dynamic balance, dissolving and regenerating in the vicinity of the present ion species [14]. When the passive layer is broken the titanium alloy is able to realease ions into solution until the passive stratum is rebuilt. The action of rebuilding this oxide film results from the chemical interaction of anions
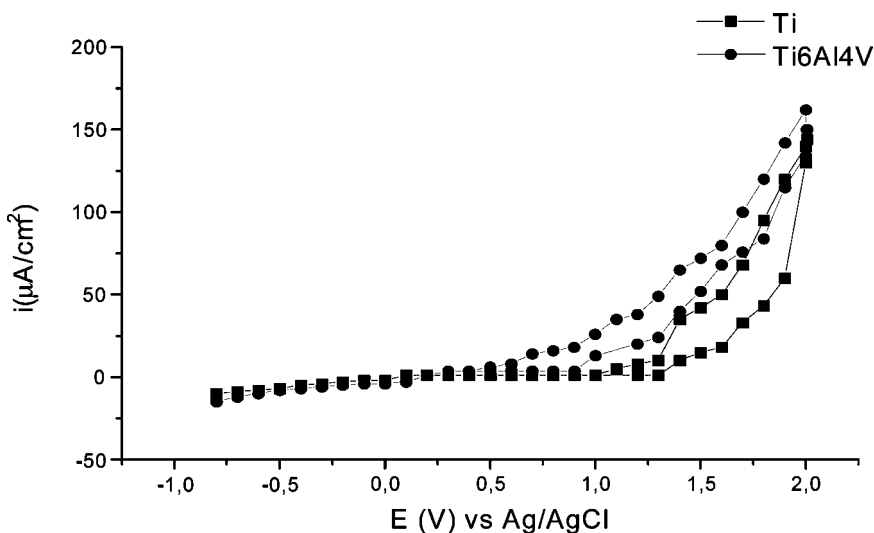
FIGURE 3 Cyclic polarization curves for Ti and Ti6Al4V in artificial saliva.
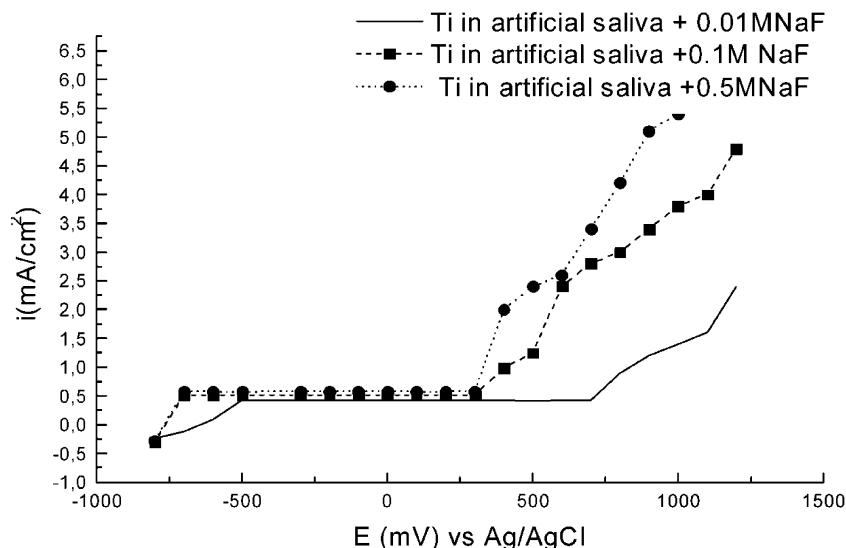
FIGURE 4 Potentiodynamic curves for Ti in doped saliva.

in the environment reacting with the surface [15]. In certain conditions the protective stratum at the implant surface may be destroyed, but even in a passive state we detect metallic ions in the implant area, free or in chemical combinations, due to the ions migration or dissolution through the protective film.

The corrosion products, i.e., metallic ions, pile locally, lead to inflammations, the destruction of the tissue and the implant's surrounding with fibre, followed by the rejection of the implant.

Comparison of the change in time of potential (Fig. 1) and ion realease (Fig. 5) results in a correlation between the ion quantity and the potential at several identical times.

During the first days the quantity of ions is bigger in all kinds of solution, then they are released with lesser rate, function of the environment aggressiveness.

TABLE 4 Electrochemical Parameters of Ti in Doped Artificial Saliva

Physiological environment	E_{cor} (mV)	I_{pas} (mA/cm^2)	E_{br} (mV)
Artificial saliva	−485	0.01	1250
Artificial saliva + NaF 0.01 M	−507	0.4	625
Artificial saliva + NaF 0.1 M	−608	0.63	374
Artificial saliva + NaF 0.5 M	−680	0.83	180

Ti passive dissolution in doped and not doped artificial saliva takes place in two phases. The first kinetic phase is governed by the oxide hydrolysis and by the surface hydration. In the second phase, the dissolution rate alters due to the exchange of ions between the hydrated surface and the newly formed oxide. The transition between them takes place 5–10 days after the immersion. The electrolytes from the environment interfere in the dissolution kinetics, so that the ions released from the oxide's surface are transferred in the hydrated stratum.

The continuous anodic dissolution through the passive film determines a small increase of the passive current, doubled by the modification of the exposed surface morphology.

The role of surface roughness on the biocompatibility of titanium implants has been discussed by various authors being a very complex process [16,17]. They remarked that rough surfaces in dental implants promote better osteointegration than smooth surfaces in spite of a trend in increasing corrosion susceptibility [18]. The analysis of the surface consisted in determining the surface roughness, considering that the latter contributes to the increase of the bone mechanical adhesion and also allows it to grow through the pores in the surface and fix on the implant. Roughness not only contributes to the osteointegration process mechanically, but also influences the biomolecules adsorption process. The surface ability to adsorb molecules is directly correlated with biocompatibility. All the AFM images that were obtained show a deep alteration of the exposed surfaces in simulated saliva. In doped environments, which are the most aggressive, Ti surfaces are characterized by a local attack, either in pitting or in the crevice.
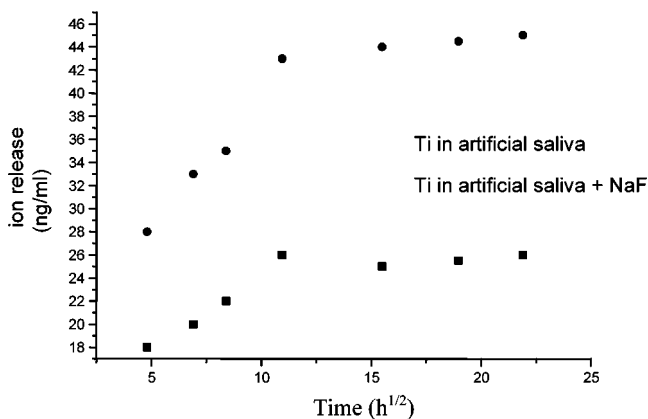
FIGURE 5 The variation in time of the quantity of Ti ions which are released in doped and not doped artificial saliva.

TABLE 5 Roughness Parameters for Ti and TiAlV

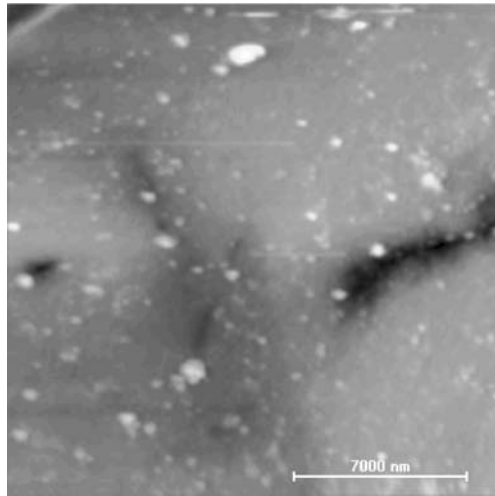| Immersion time (days)	Environment	Ti		Ti6Al4V	
		R_a (nm)	R_{rms} (nm)	R_a (nm)	R_{rms} (nm)
1	Artificial saliva	281.40	517.63	68.35	98.57
50		362.68	664.68	198.74	302.54
1	Artificial saliva doped	301.28	612.85	–	–
50	with NaF	425.28	708.9	–	–

Considering the importance of the surface roughness within the system implant-host environment, the variation in time of roughness parameters was monitored, in an attempt to correlate them with the electrochemical parameters. The values of the roughness parameters are presented in Table 5.

The 2D images obtained through AFM analysis of the electrode surfaces after exposure in solutions are presented in Figures 6, 7.

The roughness of the samples immersed in artificial saliva is growing in time. Doping the saliva with fluoride ions led to a considerable rise of the roughness, even though the sample roughness was approximately the same at the immersion time. In Table 6 the electrochemical parameters and the roughness parameters are presented. We notice that the rougher surface has a more electronegative pitting potential than the homogenous surface.
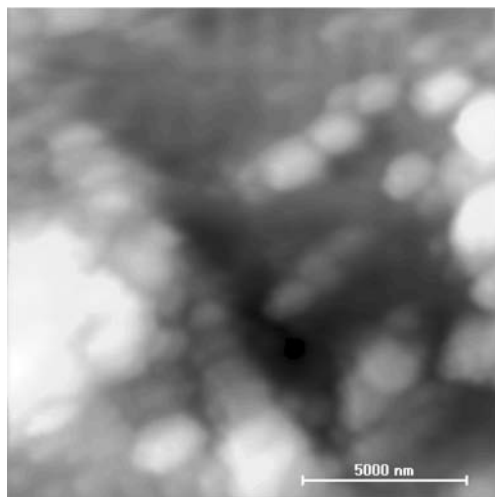
FIGURE 6 AFM image of Ti in artificial saliva with NaF after 50 days imersion. Scan size $20 \times 20\,\mu m$.

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FIGURE 7 AFM image of Ti in saliva without NaF after 50 days immersion. Scan size $20 \times 20\,\mu$m.

TABLE 6 Correlation of the Electrochemical Parameters and the Roughness Parameters for the Ti Electrode

Simulated saliva	$E_{br} - E_{pr}$ (mv)	Ra (nm)	R_{rms} (nm)
Tani-Zucchi saliva	200	281.40	517.63
Tani-Zucchi saliva doped with 0.01 M F ions	265	301.28	708.9

Generally, the quality of the protective film is the most important parameter affecting the resistance to corrosion of metallic biomaterials.

CONCLUSION

1. All the obtained results with regards to the ion release within the process of local electrochemical corrosion in simulated saliva Tani-Zucchi, as well as those concerning the Ti and TiAlV surface analysis show that the passive protective film characteristics thoroughly depend on the composition of the simulated saliva solution.
2. From corrosion rates and amount of ion released to the environment these studies offer information about negative effect of F^- and about limit concentration of fluorine ions in dental products.

3. In Tani-Zucchi simulated saliva, when Ti and TiAlV is subject matter of anodic polarization it presents an extended passive domain, proving the existence of a passive protective film, with a continuous change in the composition.
4. In the presence of fluorine ions, titanium and its alloy react with ions and molecules from physiological media as showed average roughness R_a from microscopic surface examination (AFM) and electrochemical results regarding susceptibility to local corrosion.

As a practical conclusion, dental products based on fluorine must be forbidden to patients with Ti and TiAlV implants, or with titanium wire used in dental rebuilding.

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