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Long-term assessment of the implant titanium material—artificial saliva interface

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Abstract This paper studies the long-term (20,000 exposure hours) behavior of titanium and Ti–5Al–4V alloy—Carter–Brugirard saliva interface and the short-term (500 exposure hours) resistance of titanium and Ti–5Al–4V alloy—Tani&Zucchi saliva interface. Potentiodynamic polarization method was applied for the determination of the main electrochemical parameters. Linear polarization measurements for to obtain the corrosion rates were used. Monitoring of the open circuit potentials (E_{oc}) for long-term have permitted to calculate the potential gradients due to the pH, ΔE_{oc}(pH) and to the saliva composition ΔE_{oc}(c) changes which can appear "in vivo" conditions and can generate local corrosion. Atomic force microscopy (AFM) has analyzed the surface roughness. Ion release was studied by atomic absorption spectroscopy (AAS). In Carter–Brugirard saliva both titanium and Ti–5Al–4V alloy present very stable passive films, long-term stability, "very good" resistance, low values of the open circuit potential gradients, which cannot generate local corrosion. In Tani&Zucchi artificial saliva, pitting corrosion and noble pitting protection potentials (which cannot be reached in oral cavity) were registered; titanium ion release is very low; surface roughness increase in time and in the presence of the fluoride ions, denoting some increase in the anodic activity.

1 Introduction

In implantology it is necessary to know the interaction between biomaterials and the oral or physiological environment and surrounding tissues and, specially, the longevity of these biomedical implants. The degradation by corrosion of the materials within the body can release toxic elements in time [1–9].

For a dental implant, to be successful, it must be able to bond to bone, to provide rigid fixation and to connective and epithelial tissue, in order to prevent the ingress of bacteria and to be in functional service 5 or 10 or more years [10–12]. Also, these implants must not release ions or metal dissolution products [13, 14].

In odontology, fluoride ions and changes of pH values and saliva content appear and could alter the behavior of titanium implants [15–21]. Corrosion resistance of biomaterials depends of the passive films formed on their surfaces. So, in literature, the implant–environment interface is studied both by the electrochemical methods [22–26] and spectroscopic techniques [27–29].

Passive films on titanium and its alloy surface are resistant in artificial saliva with medium chloride and fluoride ion content [15–18]. But, in very aggressive artificial saliva with high chloride and fluoride ion level, titanium and its dental alloys can undergo a corrosive process, in the form of crevice or pitting [18, 30, 31].

The aim of this paper is to study the long-term (20,000 exposure hours) behavior of titanium and Ti–5Al–4V alloy—Carter–Brugirard saliva interface and the short-term

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(500 exposure hours) resistance of titanium and Ti–5Al–4V alloy—Tani&Zucchi saliva interface.

2 Experimental

Titanium and its alloy Ti–5Al–4V (donated by Institute for Non Ferrous and Rare Metals, Bucharest, Romania) were obtained by vacuum melting. The composition is given in Table 1. Cylindrical electrodes were abraded with emery paper, fixed in a Stern–Makrides mount system, rinsed with distilled water, degreased in boiling benzene and dried.

The experiments were performed in a three-electrode electrochemical glass cell; a large cylindrical platinum grid has been used as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

The experimental measurements were carried out in:

- Carter–Brugirard artificial saliva of different pH values (7.88; 5.75; 2.13; acid pH was obtained by hydrochloric acid addition) with the composition (g/L): sodium chloride (NaCl)—0.7; potassium phosphoricum monobasicum (KH_2PO_4)—0.26; potassium sulphocyanide (KSCN)—0.33; sodium phosphoricum monobasicum ($NaH_2PO_4 \cdot H_2O$)—0.19; urea—1.3; sodium hydrogen carbonate ($NaHCO_3$)—1.5; doped saliva contained 0.02 M sodium fluoride (NaF);
- Tani&Zucchi artificial saliva (pH = 5) of composition (g/L): potassium chloride (KCl)—15; sodium hydrogen carbonate ($NaHCO_3$)—1.5; sodium phosphoricum bibasicum ($Na_2HPO_4 \cdot 12H_2O$)—0.5; potassium sulphocyanide (KSCN)—0.5; lactic acid—0.9; doped saliva contained 0.01 M sodium fluoride (NaF).

The temperature of the solutions was kept at 37° ± 1 °C (human body temperature).

The following experimental techniques were used.

Potentiodynamic polarization for to obtain the main electrochemical parameters: corrosion potential, E_{corr}; breakdown (pitting) potential, E_b, being the potential at which a sharp increase of the current appears; pitting protection potential, E_{pp}, as the potential at which the current density on the negative sweep equals the current density in the passive region; below this potential value, no pit can be initiated, while at higher values, the already initiated pits can grow; the difference $E_b - E_{pp}$ is defined as "pitting corrosion resistance"; the low values means a high pitting resistance, namely pit re-passivation ability; this ability depends on this potential difference; low values express high tendency to re-passivation; the pitting corrosion tendency is $E_{corrr} - E_b$; high values denotes low tendency to pitting corrosion. A Voltalab 21 system with analysis corrosion program Voltamaster was used.

Linear polarization measurements for to determine the corrosion current density and then to obtain the corrosion rate. The electrochemical set-up consisting of a potentiostat (PAR 173 type), a XY recorder (Endim 62002 type) and a universal pulse generator (AT type); impulse of ±10 mV around the open circuit potential (E_{oc}) was applied. The corrosion current densities were calculated from Stern formula [32]:

$$i_{corr} = k(di/dE)_{E_{oc}} \tag{1}$$

considering $k = 26.8$ mV.

Monitoring of the open circuit potentials (E_{oc}) for long-term using a high performance multimeter Hullett–Pakard. Variations of these potentials with the pH value and saliva composition have permitted to calculate the potential gradients due to the pH changes, ΔE_{oc}(pH) and to the saliva composition changes, ΔE_{oc}(c). These gradients can appear "in vivo" conditions and can generate local corrosion.

Biostatistical analysis of the open circuit potentials was applied using Medcalc. Program. By this statistical treatment can be obtained: histograms, scatter diagrams and regression equations which can supply a prognosis of the biomaterial behavior for longer term than the experimental one. The coefficients of determination (D) characterize the credibility degree of the prognosis: a good credibility signifies values from 0.7 to 1.

Atomic absorption spectroscopy (AAS) analyzed the titanium ion release and its variation for short-term (500 exposure hours). An atomic absorption flame spectrophotometer, type Zeiss AIS L 30 was used.

Atomic force microscopy (AFM) was used for surface analysis. Images were acquired in standard contact mode and were processed with AFM Images Analysis, a window application with single document interface. The surface characterization in 2D and 3D visualization and statistical analysis can be realized with this program. Average roughness, R_a, and root mean square roughness, R_{rms}, were determined.

Table 1 Composition of biomaterials

TYPE	% Wt.							Structure
	Al	Fe	V	C	O	N	Ti	
Titanium	0.005	0.095	–	0.040	0.056	0.045	Balance	–
Ti–5Al–4V	4.88	0.021	3.72	0.048	0.175	0.0153	Balance	$\alpha + \beta$

3 Results and discussions

3.1 Long-term behavior of titanium and Ti–5Al–4V alloy in Carter–Brugirard artificial saliva

The long-term behavior, for 20,000 exposure hours in Carter–Brugirard artificial saliva of different pH values was studied by the monitoring of the open circuit potentials and corrosion rates and the determination of the potential gradients due to the saliva pH and composition non-uniformity.

3.1.1 Monitoring of the open circuit potentials for 20,000 exposure hours

In Carter–Brugirard saliva of pH = 7.88 (Fig. 1), both titanium and its dental implant alloy Ti–5Al–4V present some variations of their open circuit potentials (E_{oc}). But, these potentials tend to more electropositive values in time, indicating a consolidation of the passive films. Ti–5Al–4V alloy realized nobler values than titanium, consequently a better stability.

In the case of Carter–Brugirard saliva of pH = 5.73 (Fig. 2), the same behavior is observed: some oscillations and ennobling tendency of the open circuit potentials with the exposure time characterizing a stable state. The same better behavior of Ti–5Al–4V alloy than titanium was registered.

In very acid Carter–Brugirard saliva of pH = 2.13 (Fig. 3) have appeared some differences between titanium and its alloy Ti–5Al–4V behavior; for 15,000 exposure hours, the alloy open circuit potentials present more electronegative values, but after this period, these values became more electropositive. This fact is due to the thinning and re-modeling processes of the passive films. From 15,000 to 20,000 h both biomaterials realized very noble open circuit potentials (about+100 mV ÷ +300 mV) denoting an increase in the corrosion resistance.

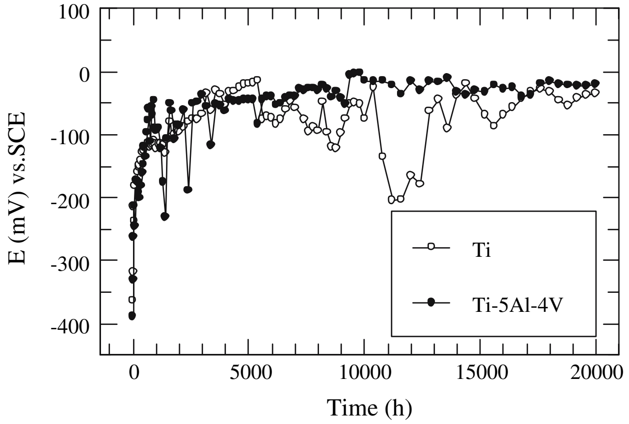

Fig. 2 E_{oc} vs. time in Carter–Brugirard saliva of pH = 5.73, for 20,000 exposure hours

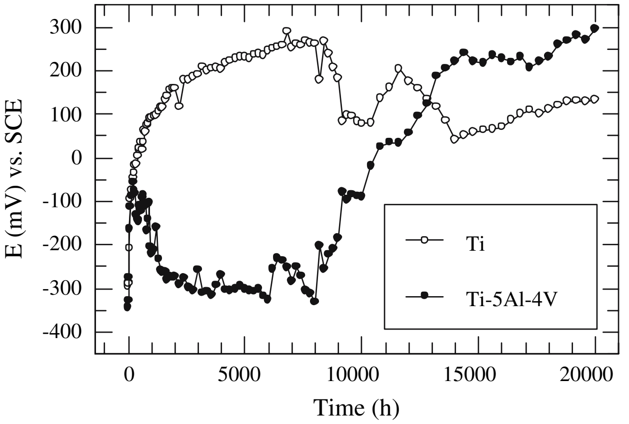

Fig. 3 E_{oc} vs. time in Carter–Brugirard saliva of pH = 2.13, for 20,000 exposure hours

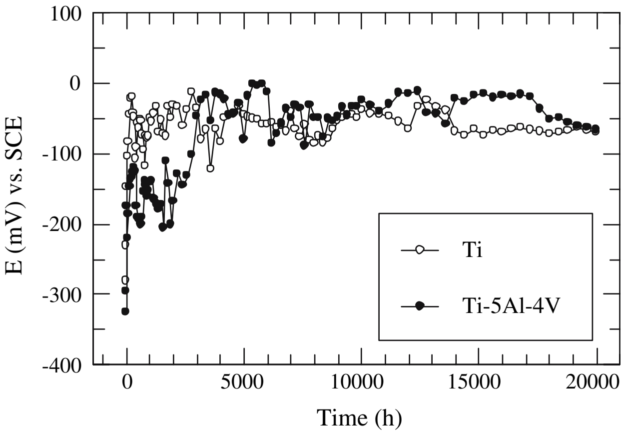

Fig. 1 E_{oc} vs. time in Carter–Brugirard saliva of pH = 7.88, for 20,000 exposure hours

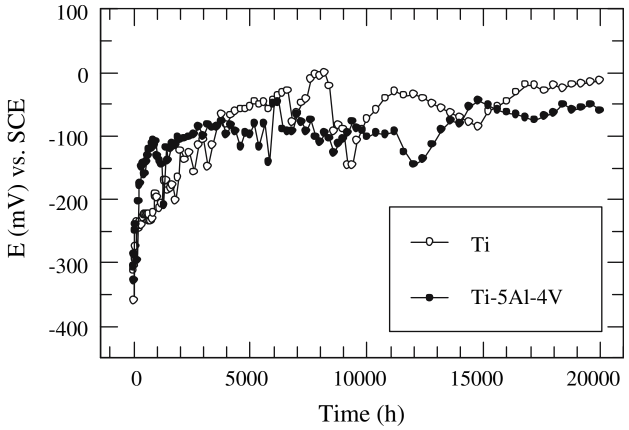

Fig. 4 E_{oc} vs. time in Carter–Brugirard saliva of pH = 7.88, doped with 0.02 M NaF, for 20,000 exposure hours

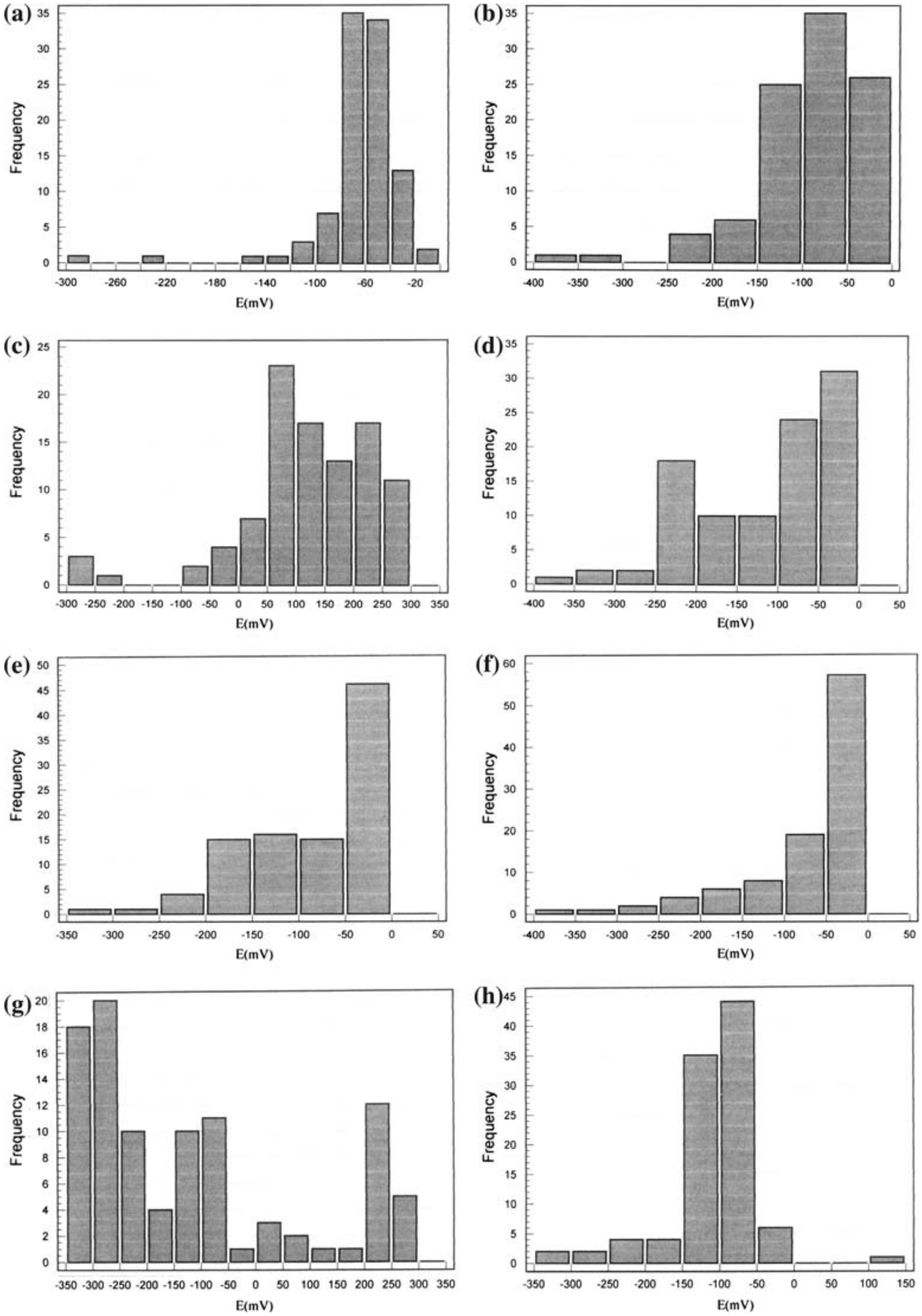

Fig. 5 Histograms in Carter–Brugirard artificial saliva for: (**a**) Ti at pH = 7.88; (**b**) Ti at pH = 5.73; (**c**) Ti at pH = 2.13; (**d**) Ti at pH = 7.88 doped with 0.02 M NaF; (**e**) Ti–5Al–4V alloy at pH = 7.88; (**f**) Ti–5Al–4V alloy at pH = 5.73; (**g**) Ti–5Al–4V alloy at pH = 2.13; (**h**) Ti–5Al–4V alloy at pH = 7.88 doped with 0.02 M NaF

In the presence of 0.02 M sodium fluoride (NaF), the open circuit potentials (Fig. 4) do not change in comparison with undoped saliva and tend to noble values. So, both biomaterials are very resistant to the fluoride ion action in Carter–Brugirard saliva.

All open circuit potential values are placed in the passive potential range on the Pourbaix diagram of titanium [33], attesting very stable passive films and long-term stability. No form of local corrosion was detected for 20,000 exposure hours.

The histograms obtained by statistical method (Fig. 5) show the frequency and distribution of the open circuit potential values; it can be observed that the majority values are distributed around the electropositive values.

Medcalc. Program allowed the obtaining of the scatter diagrams (Fig. 6), which are described by the corresponding (Table 2) regression equations and are characterized by the determination coefficients (*D*). The values of these coefficients revealed a good percent of the

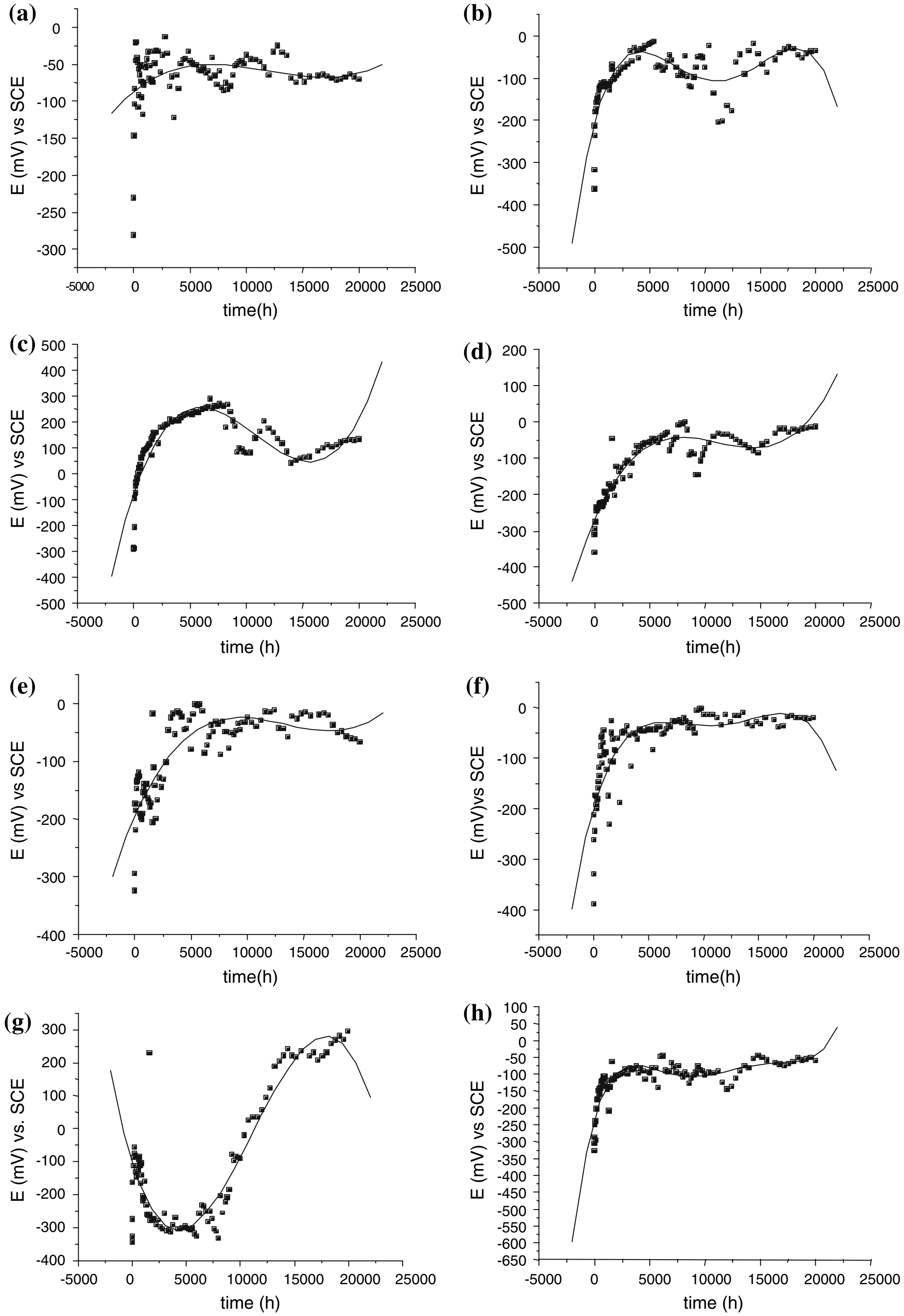

Fig. 6 Scatter diagrams in Carter–Brugirard artificial saliva for: (**a**) Ti at pH = 7.88; (**b**) Ti at pH = 5.73; (**c**) Ti at pH = 2.13; (**d**) Ti at pH = 7.88 doped with 0.02 M NaF; (**e**) Ti–5Al–4V alloy at pH = 7.88; (**f**) Ti–5Al–4V alloy at pH = 5.73; (**g**) Ti–5Al–4V alloy at pH = 2.13; (**h**) Ti–5Al–4V alloy at pH = 7.88 doped with 0.02 M NaF

Table 2 Regression equations and determination coefficients (*D*) in Carter–Brugirard artificial saliva of different pH values

Biomaterial	pH	Regression equation	D
Titanium	7.88	$Y = 0.012 - 1.246X + 3.475X^2$	0.692
Ti–5Al–4V	7.88	$Y = 0.0446 - 3.665X + 9.121X^2$	0.913
Titanium	5.73	$Y = -204.8 + 0.099X - 1.92X^2 + 1.3327X^3 - 2.993X^4$	0.838
Ti–5Al–4V	5.73	$Y = -196.52 + 0.074X - 1.1686X^2 + 7.487X^3 - 1.659X^4$	0.858
Titanium	2.13	$Y = -77.157 + 0.128X - 1.484X^2 + 4.582X^3$	0.915
Ti–5Al–4V	2.13	$Y = -101.48 - 0.106X + 1.5401X^2 - 4.6236X^3$	0.864
Titanium	7.88 + NaF	$Y = -269.9 + 0.0703X - 6.874X^2 + 2.049X^3$	0.879
Ti–5Al–4V	7.88 + NaF	$Y = -231.03 + 0.113X - 2.851X^2 + 2.997X^3 - 1.394X^4$	0.812

credibility. The computing of the regression equations permit the prediction of the open circuit potential values for longer time than the experimental one. But, such prognosis needs more precautions because that, in the human body can appear unexpected phenomenon, which can vitiate the theoretical results [7, 9].

3.1.2 *Potential gradients due to the saliva pH and content non-uniformity*

In dental implant applications, due to the corrosion products hydrolysis or in distress periods of the body, it is possible that some implant zones to be in contact with acid pH saliva and another with neutral or alkaline pH saliva. So, open circuit potentials will have various values on different zones of the implant, producing potential gradients ΔE_{oc} that can intensify the corrosion. Therefore, the open circuit potential gradients which can appear due to the non-uniformity of the saliva pH, ΔE_{oc}(pH), and composition, ΔE_{oc}(c), were simulated and calculated (Table 3):

$$\Delta E_{oc1}(\mathrm{pH}) = E_{oc}^{\mathrm{pH}=2.13} - E_{oc}^{\mathrm{pH}=7.88} \qquad (2)$$

$$\Delta E_{oc2}(\mathrm{pH}) = E_{oc}^{\mathrm{pH}=2.13} - E_{oc}^{\mathrm{pH}=5.73} \qquad (3)$$

$$\Delta E_{oc3}(\mathrm{pH}) = E_{oc}^{\mathrm{pH}=5.73} - E_{oc}^{\mathrm{pH}=7.88} \qquad (4)$$

$$\Delta E_{oc4}(\mathrm{c}) = E_{oc}^{\mathrm{pH}=7.88} - E_{oc}^{\mathrm{NaF}} \qquad (5)$$

$$\Delta E_{oc5}(\mathrm{c}) = E_{oc}^{\mathrm{pH}=5.73} - E_{oc}^{\mathrm{NaF}} \qquad (6)$$

$$\Delta E_{oc6}(\mathrm{c}) = E_{oc}^{\mathrm{pH}=2.13} - E_{ocr}^{\mathrm{NaF}} \qquad (7)$$

The resulted open circuit potential gradients have low values, which do not exceed 0.416 V for titanium and 0.368 V for Ti–5Al–4V alloy; these values cannot generate local corrosion. This observation is justified by the large passive plateau of the anodic polarization curves obtained both for titanium and its alloy Ti–5Al–4V [30]. Also, studies concerning titanium and Ti-6Al-4V alloy when are galvanically coupled with other metals [34–36] have revealed that these biomaterials do not exhibit accelerated corrosion.

3.1.3 *Corrosion rates for long-term*

The corrosion rates were periodically determined using linear polarization method. It can be observed from Table 4, that the both biomaterials present very low corrosion rates, describing a “very good” resistance for 20,000 exposure hours.

Table 3 Open circuit potential gradients ΔE_{oc} (V) for titanium and Ti–5Al–4V alloy in Carter–Brugirard artificial saliva

Biomaterial	Time (h)	ΔE_{oc1}	ΔE_{oc2}	ΔE_{oc3}	ΔE_{oc4}	ΔE_{oc5}	ΔE_{oc6}
Titanium	1,000	0.143	0.214	–0.071	0.146	0.075	0.005
	5,000	0.277	0.416	–0.138	0.088	–0.130	0.290
	10,000	0.129	0.334	–0.334	0.023	–0.183	0.005
	15,000	0.126	0.185	–0.059	–0.029	–0.081	0.097
	20,000	0.203	0.169	0.348	–0.042	–0.077	0.246
Ti–5Al–4V	1,000	–0.008	–0.126	0.046	–0.008	0.038	–0.008
	5,000	–0.025	–0.207	–0.046	0.081	0.035	–0.123
	10,000	–0.060	–0.064	0.004	–0.076	–0.081	–0.017
	15,000	0.328	0.356	–0.028	0.039	0.012	0.368
	20,000	0.282	0.279	0.003	–0.043	–0.046	0.325

Table 4 Corrosion rates (mm/yr) for titanium and Ti–5Al–4V alloy in Carter–Brugirard artificial saliva

Biomaterial	Time (h)	Carter–Brugirard saliva of pH:		
		7.88	5.73	2.13
Titanium	1,000	1.8×10^{-3}	1.9×10^{-3}	2.7×10^{-3}
	5,000	2.4×10^{-3}	2.5×10^{-3}	3.2×10^{-3}
	10,000	2.7×10^{-3}	2.6×10^{-3}	3.5×10^{-3}
	15,000	2.9×10^{-3}	3.0×10^{-3}	3.8×10^{-3}
	20,000	3.2×10^{-3}	3.3×10^{-3}	4.1×10^{-3}
Ti–5Al–4V	1,000	2.4×10^{-3}	1.8×10^{-3}	1.9×10^{-3}
	5,000	2.9×10^{-3}	2.4×10^{-3}	2.7×10^{-3}
	10,000	3.0×10^{-3}	2.6×10^{-3}	3.1×10^{-3}
	15,000	3.1×10^{-3}	2.9×10^{-3}	3.6×10^{-3}
	20,000	3.4×10^{-3}	3.2×10^{-3}	3.9×10^{-3}

3.2 Short-term behavior of titanium and Ti–5Al–4V alloy in Tani&Zucchi artificial saliva

The short-term behavior was estimated from the potentiodynamic curves, variation in time (500 exposure hours) of the ion release and surface roughness (from AFM). Tani&Zucchi saliva contains high level of chloride ions (15 g/L sodium chloride) and it is more aggressive than Carter–Brugirard saliva (0.7 g/L sodium chloride).

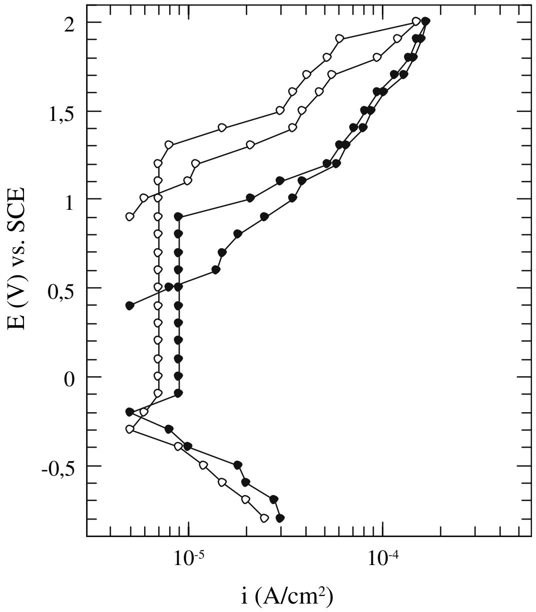

Fig. 7 Potentiodynamic polarization curves for Ti (○) and Ti–5Al–4V (●) alloy in Tani&Zucchi artificial saliva

Table 5 Pitting corrosion parameters for titanium and Ti–5Al–4V alloy in Tani&Zucchi artificial saliva

Biomaterial	E_{corr} (V)	E_b (V)	E_{pp} (V)	$E_b - E_{pp}$ (V)	$E_{corr} - E_b$ (V)
Titanium	–0.30	1.25	1.12	0.13	–1.55
Ti–5Al–4V	–0.15	0.96	0.55	0.41	–1.11

3.2.1 *Anodic potentiodynamic curves*

Pitting corrosion was registered (Fig. 7) both for titanium and Ti–5Al–4V alloy. The pitting corrosion parameters from Table 5 revealed that, the pitting corrosion resistance ($E_b - E_{pp}$) is better for titanium (0.13 V) than for its alloy (0.41 V); but, the value obtained for Ti–5Al–4V alloy characterizes a good ability to re-passivation. The pitting protection potential (E_{pp}) presents noble values both for titanium (+1.12 V) and its alloy (+0.55 V); these values

Table 6 Roughness parameters for titanium and Ti–5Al–4V alloy in Tani&Zucchi artificial saliva

Environment	Time (h)	Titanium		Ti–5Al–4V	
		R_a (nm)	R_{rms} (nm)	R_a (nm)	R_{rms} (nm)
Tani&Zucchi saliva	1	261.40	517.63	68.35	98.57
	50	362.68	664.68	198.74	302.54
Tani&Zucchi saliva doped with 0.01 M NaF	1	301.28	612.85	232.57	475.84
	50	425.28	708.90	498.97	789.48

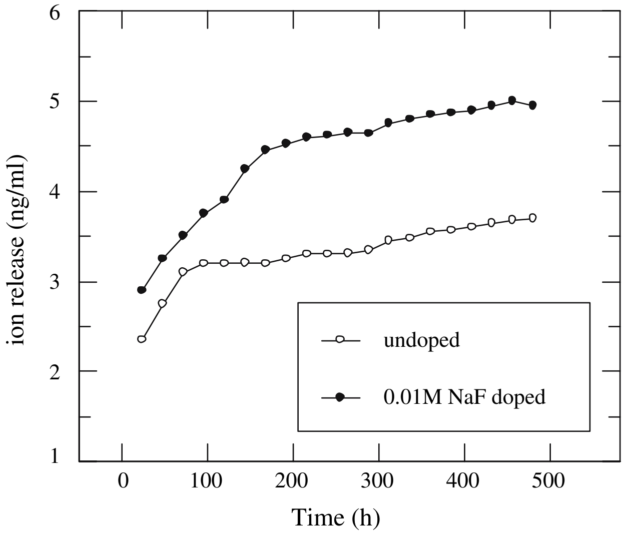

Fig. 8 Titanium ion release in Tani&Zucchi artificial saliva

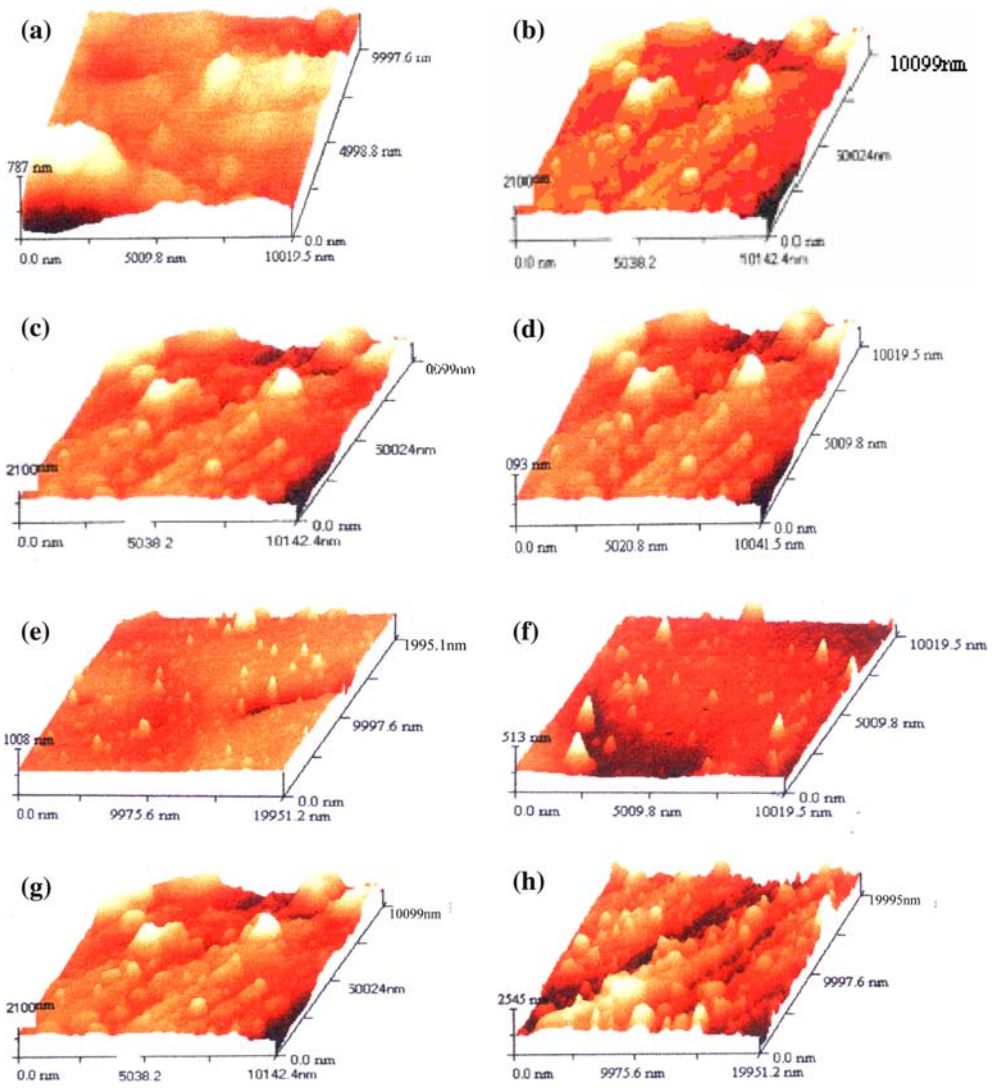

Fig. 9 AFM images in Tani&Zucchi artificial saliva: (**a**) Ti after 1 day; (**b**) Ti after 50 days; (**c**) Ti after 1 day in doped saliva with 0.01 M NaF; (**d**) Ti after 50 days in doped saliva with 0.01 M NaF; (**e**) Ti–5Al–4V alloy after 1 day; (**f**) Ti–5Al–4V alloy after 50 days; (**g**) Ti–5Al–4V alloy after 1 day in doped saliva with 0.01 M NaF; (**h**) Ti–5Al–4V alloy after 50 days in doped saliva with 0.01 M NaF

cannot be reached in oral cavity. Also, the difference $E_{corr} - E_b$ is very large, denoting a very low pitting corrosion tendency for both biomaterials.

3.2.2 *Ion release*

The titanium ion release was determined using atomic absorption spectroscopy. In the first days, the ion release level increased and, after 5–10 days, the ion release rate reached a constant level (Fig. 8). Fluoride ions product a slight increase of the ion release amount due to its higher aggressivity. But, the quantity of the ion release is very low, about 30–40 μg/L and cannot be considered dangerous for the human body.

3.2.3 *Surface roughness*

The roughness values increased in time (Table 6) due to low corrosion processes (Fig. 9). Also, these values are higher in doped saliva denoting an increase in the anodic activity of the biomaterials in the presence of the fluoride ions. Nevertheless, no form of local corrosion was put in evidence.

4 Conclusions

1. Long-term (20,000 h) behavior of titanium and Ti–5Al–4V alloy—Carter–Brugirard saliva interface revealed that:

- all open circuit potential values are placed in the passive potential range on the Pourbaix diagram of titanium, attesting very stable passive film and long-term stability;
- no form of local corrosion was detected for 20,000 exposure hours;
- statistical treatment applied to the variations of the open circuit potentials have shown a good percent of the credibility of the prognosis, but with precautions;
- the calculated open circuit potential gradients have low values which cannot generate local corrosion;
- both biomaterials present very low corrosion rates, describing a "very good" resistance for the whole tested period (20,000 h).

2. Short-term (500 h) behavior of titanium and Ti–5Al–4V alloy—Tani&Zucchi saliva interface pointed-out that:

- pitting corrosion and noble pitting protection potentials (which cannot be reached in oral cavity) were registered; also, the ability to the pit re-passivation and the pitting corrosion tendency have good values for both biomaterials;
- titanium ion release is very low and cannot be considered dangerous for the human body;
- surface roughness values increased in time and in the presence of the fluoride ions, denoting some increase in the anodic activity; no form of the local corrosion was put in evidence.

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