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Monitoring of titanium base alloys–biofluids interface

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Abstract

Monitoring of the titanium, Ti–5Al–4V, Ti–6Al–4Fe implant materials — Ringer 1 and Ringer 2 solutions (of different pH values) interface for long term was studied in this work. In Ringer 1 solution (with high chloride ion content) all biomaterials present self-passivation. On Ti–6Al–4Fe alloy, the breakdown of the passive film was registered but at high pitting potential; pitting protection potential is very noble and can not be reached in human fluids. In Ringer 2 solution was obtained more electropositive corrosion potential values than in Ringer 1 solution; pitting corrosion of Ti–6Al–4Fe alloy is characterised by nobler breakdown and pitting protection potential values, therefore a better pitting corrosion resistance and tendency. Ion release increases in time, for the first 400–600 immersion hours and then tend to a constant level with very low values, non-dangerous for human body. All open circuit potentials oscillate around some electropositive values. The potential gradients calculated for extreme pH values have low values during 20 000 exposure hours and can not accelerate the corrosion. Atomic Force Microscopy images obtained after different exposure periods in Ringer 1 solution revealed that the roughness increased in time, suggesting a dynamic process at biomaterial–biofluid interface. X-ray Photoelectron spectra obtained after 2880 immersion hours in Ringer 2 solution show the existence of protective titanium dioxide TiO_2 and TiO and Ti_2O_3 oxides both for titanium and Ti–5Al–4V alloy. Also, Al_2O_3 oxide was detected.

Keywords: Long-term behaviour; Ion release; Potential gradients; Surface topography; Passive film composition

1. Introduction

Titanium and its alloys are used in implantology for their high corrosion and mechanical resistance in biofluids. The behaviour of these metals and alloys is usually a combination of the electrochemical, physiological and mechanical effects [1–5]. Electrochemically, was proved that titanium and its alloys are very resistant as a result of their very stable oxide films formed by titanium dioxide (TiO_2), the most stable oxide of titanium and some suboxides [6–9]. The surface analysis proved data about the composition of the passive layer on titanium and Ti–6Al–4V alloy. All papers confirmed the predominantely presence of TiO_2 with small quantities of suboxides TiO and Ti_2O_3 [9–13]. For Ti–6Al–4V alloy, at the inner metal-oxide interface, TiO_2, TiO and Ti_2O_3 were determined and at outer oxide-solution interface, the layer was enriched with Al_2O_3 [9]. The presence of Al in the passive film was observed by few authors: Ask et al. [10], Sundararajan et al. [11] Maeusli et al. [14]. Also, the presence of vanadium was reported by Sodhi et al. [15], Okazaki et al. [12], etc. The presence of vanadium is relatively ambiguous, because this element could not be detected by XPS and AES methods but only with SIMS method; this fact was attributed to its low concentration, under the detection limits of the first and second methods [15]. The oxidation state of Al was Al^{3+}, i.e. Al_2O_3, whereas that of V was V^{3+} and V^{5+}, i. e. V_2O_3 or V_2O_5 [10,15]. It was concluded that these two metals can be presented either as Al_2O_3 and V_2O_5 respectively or as ions at interstitial or substitutional sites in the TiO_2 matrix [10]. The passive film is compound of a inner layer of n-type semiconductivity and an outer layer of p-type semiconductivity [9,16].

The physiological and electrochemical properties of the titanium dioxide film and its long-term stability in biofluids play

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an important role for the biocompatibility of titanium and its implant alloys [17–24]. These materials can release ions into the surrounding tissues and can produce some reactions. Titanium and aluminum ions can affect the cell function and proliferation in vivo. Titanium, aluminum and vanadium ions can inhibit the apatite formation in vivo and consequently, the mineralisation process at the bone-implant interface [25–30]. Sometimes, the infections can increase the corrosion due to the high temperature, metabolic products and pH modification [31,32].

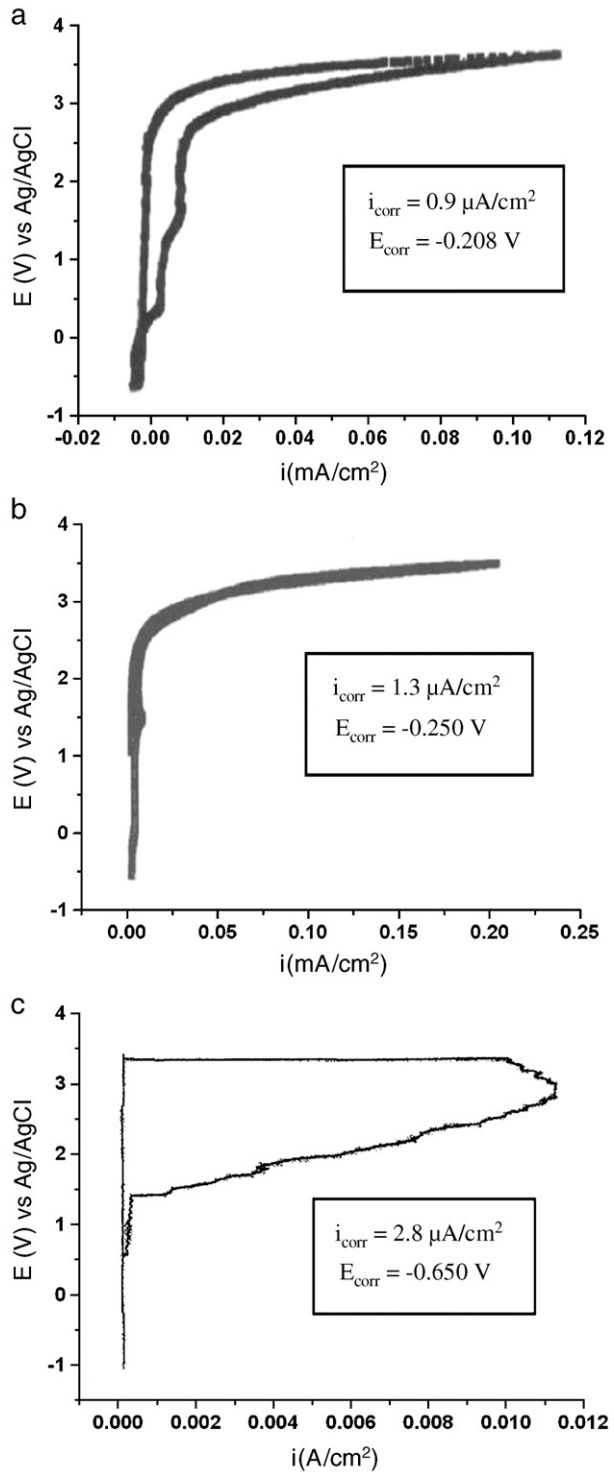

Fig. 1. Cyclic anodic curves in Ringer 1 solution at 37 °C for: a) Ti; b) Ti–5Al–4V; c) Ti–6Al–4Fe.

Table 1
Electrochemical parameters for Ti, Ti–5Al–4V and Ti–6Al–4Fe in Ringer1 and Ringer 2 solutions at 37 °C

Parameter	Ti		Ti–5Al–4V		Ti–6Al–4Fe	
	Ringer 1	Ringer 2	Ringer 1	Ringer 2	Ringer 1	Ringer 2
E_{oc} (V)	−0.208	−0.160	−0.250	−0.180	−0.650	−0.208
E_{cp} (V)	−0.208	−0.160	−0.250	−0.180	−0.650	−0.208
E_T (V)	+2.6	+2.8	+2.6	+2.8	–	–
E_b (V)	–	–	–	–	+3.158	+3.612
E_{pp} (V)	–	–	–	–	+1.644	+1.918
ΔE_p (V)	2.8	2.96	2.85	2.98	–	–
$E_b - E_{pp}$ (V)	–	–	–	–	1.514	1.494
$E_{oc} - E_b$ (V)	–	–	–	–	3.366	3.817

In condition of long-term service of the implants, it is possible to take place the hydrolysis of different passive film components in contact with physiological electrolytes. Therefore, important pH changes on some zones of the implant can appear and can generate potential and current gradients [21–24]. These gradients can initiate galvanic cells and can produce local corrosion.

There are new Romanian Ti–5Al–4V and Ti–6Al–4Fe alloys and their electrochemical behaviour and corrosion resistance for long term was published in Electrocimica Acta [21]. In this paper, the monitoring of the titanium, Ti–5Al–4V, Ti–6Al–4Fe implant materials — Ringer 1 and Ringer 2 solutions interface for very long term (20 000 exposure hours) was continued. Film composition was determined by X-ray photoelectron spectroscopy (XPS). Also, the variation in time of the surface topography was studied.

2. Experimental

Titanium and its new alloys Ti–5Al–4V and Ti–6Al–4Fe were obtained by vacuum melting in experimental charges at Institute for Non-Ferrous and Rare Metals, Bucharest, Romania. The composition and mechanical properties were given in another paper [21]. The ingots were processed into cylindrical electrodes; these samples were abraded with emery paper, fixed in Stern–Makrides mount system, rinsed with distilled water, degreased in boiling benzene and dried.

The electrochemical cell contained a central inlet for the electrode assembly, a cylindrical platinum grid as counter electrode, a Luggin probe connected with a saturated calomel reference electrode (SCE) or Ag/AgCl reference electrode.

For experiments, two type of physiological solutions were chosen: Ringer 1 with a high concentration of NaCl for to study the resistance of these new alloys in a very aggressive biofluid, and Ringer 2 solution with a more complete content. Ringer 2 solution was used with three different pH values (2.5; 4.35; 6.98) for to simulate the “in situ” conditions that can appear in the life service of the implants. Their composition was:

– Ringer 1 (g/L); NaCl — 8.6; $CaCl_2$ — 0.33; KCl — 0.3;

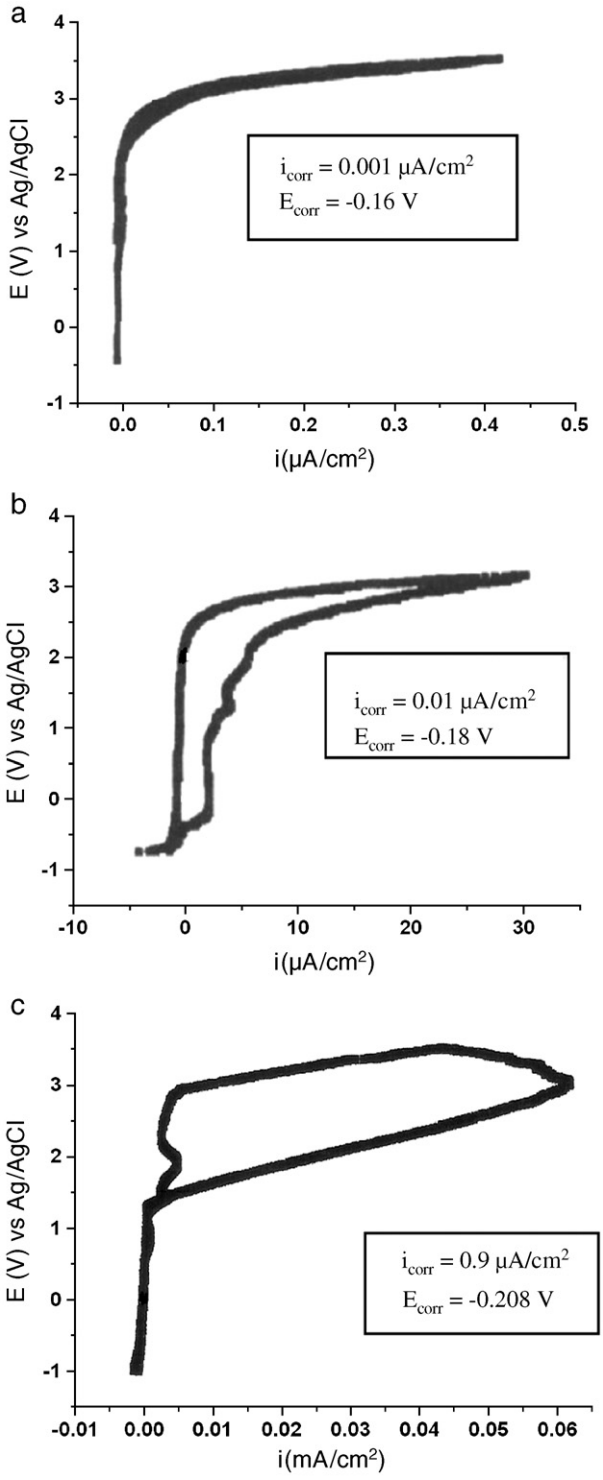

Fig. 2. Cyclic anodic curves in Ringer 2 solution at 37 °C for: a) Ti; b) Ti–5Al–4V; c) Ti–6Al–4Fe.

– Ringer 2 of different pH values (2.5; 4.35; 6.98; acid pH was obtained by HCl addition) (g/L): NaCl — 6.8; KCl — 0.4; $CaCl_2$ — 0.2; $MgSO_4.7H_2O$ — 0.2048; $NaH_2PO_4.H_2O$ — 0.143; $NaHCO_3$ — 2.2; glucose — 1.

The following techniques were used: cyclic potentiodynamic and linear polarisation, monitoring of the open circuit potentials, atomic absorption spectroscopy (AAS), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

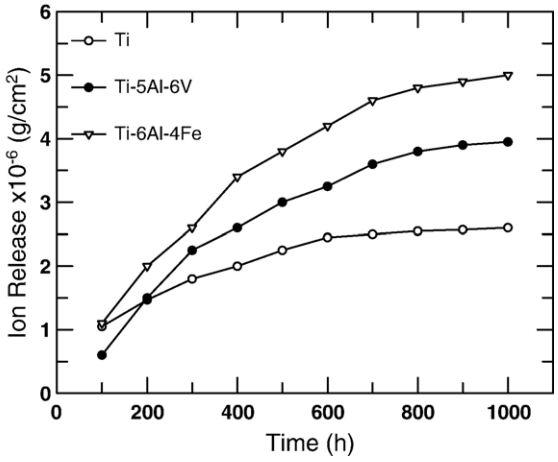

Fig. 3. Tanium ion release vs. time in Ringer 1 solution at 37 °C for 1000 exposure hours.

Potentiodynamic polarisation was performed starting from −0.8 V to +4.0 V with a scan rate of 2 mV/s. using a Voltalab 21 system with analysis corrosion VoltaMaster program. The main electrochemical parameters were determined: E_{oc} — open circuit (corrosion) potential; E_{cp} — complete passivation potential, at which the current density is constant; E_b — breakdown (pitting) potential when the current density increases; E_{pp} — pitting protection potential at which the current density on the negative sweep equals the passive current density; E_T — transpassive potential; ΔE_p — passive potential range of constant current; $E_b - E_{pp}$ difference represents pitting corrosion resistance; $E_{oc} - E_b$ difference characterises tendency to pitting corrosion; i_p — passive current density.

The linear polarisation was applied for ±10 mV around the open circuit potential and corrosion current density $i_{corr} = k(dE/di)_{Ecorr}$ was obtained with Stern formula considering $k = 26$ mV; then, the corrosion rates were calculated. The electrochemical

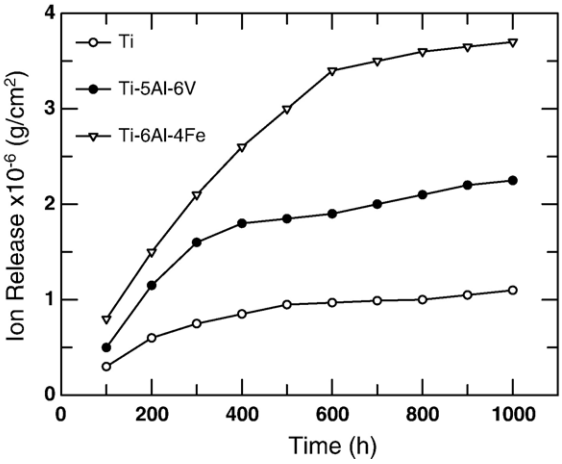

Fig. 4. Titanium ion release vs. time in Ringer 2 solution at 37 °C for 1000 exposure hours.

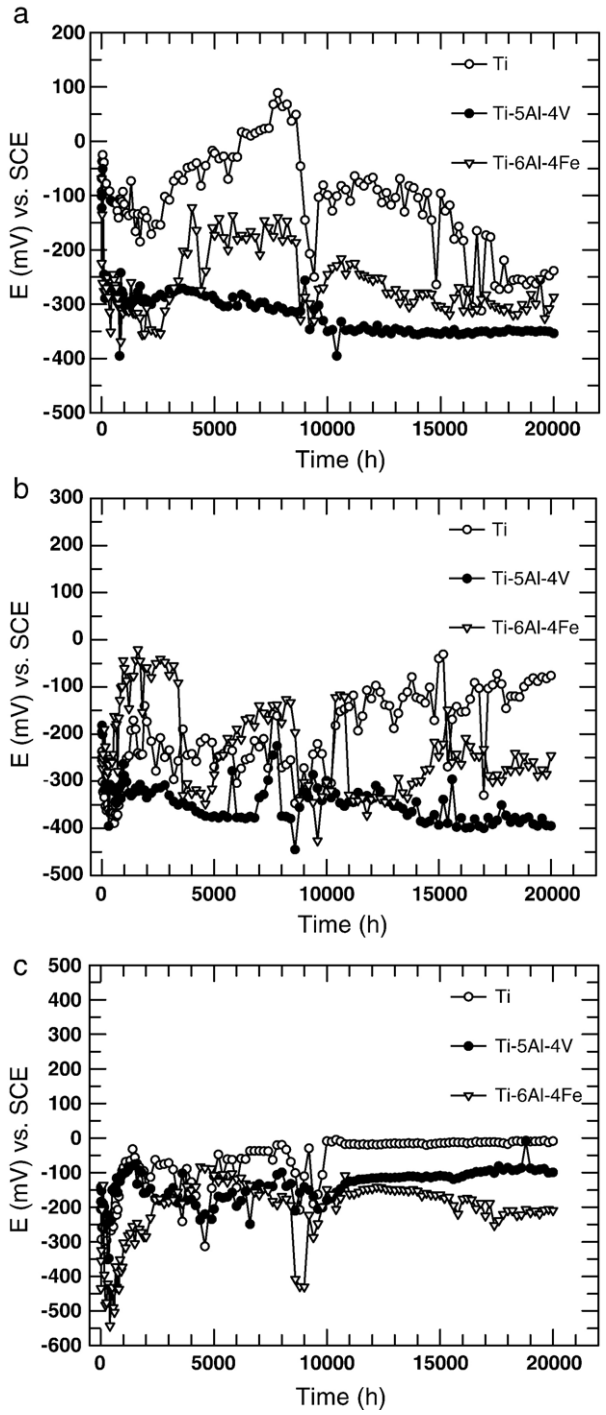

Fig. 5. Monitoring (20000 exposure hours) of the open circuit potential in Ringer 2 solution (at 37 °C) of: a) pH=2.5; b) pH=4.35; c) pH=6.98.

set-up consisted of a pulse generator (AT type) and an XY recorder (Endim 62002 type).

Monitoring of the open circuit potential, E_{oc} was made after different periods during 20000 immersion hours. A performance Hewlett–Packard instrument was used. Biostatistical treatment of these potential values was performed with Medcalc. program and provided histograms, scatter diagrams with corresponding regression equations which can supply a prognosis. If the determination coefficient (D) has values from 0.7 to 1, the credibility of the prognosis is very good.

Atomic absorption spectroscopy (AAS) has analysed the quantity of the titanium ion release and its variations for 1000 exposure hours. An atomic absorption flame spectrophotometer type Zeiss AIS L3 with graphite atomiser furnace was used.

Atomic force microscopy (AFM), operating in contact mode was applied (using a non-conventional model developed at Twente University, Nederlands) in order to perform surface analysis. A simple document Interface was used for the topography characterization with AFM Images Analysis Program, which provided 2D and 3D images and roughness (R_a) and root mean square roughness (R_{rms}) were determined.

X-ray photoelectron spectroscopy (XPS) used an electron spectrometer type ESCALAB MKII with an interface for X-ray photoelectron microscopy; a bank data in VGS-5000 program existed to process the spectra. This spectrometer used non-monochromatised Al K_α radiation (1486.6 eV) from a twin Mg/Al anode operating at 300 W. The hemispherical energy analyser was operated in constant analyser transmission with a constant pass energy of 20 eV. The calibration of the energy scale was performed according to the standard procedure [33].

3. Results and discussions

3.1. Passive film evolution from anodic cyclic curves

Anodic cyclic curves for titanium and its Ti–5Al–4V and Ti–6Al–4Fe alloys reveal many resemblances and some differences.

3.1.1. Ringer 1 solution

In Ringer 1 solution all biomaterials (Fig. 1) present self-passivation, very large passive potential range and very low passive current densities (Table 1) showing a good corrosion resistance.

For Ti and Ti–5Al–4V alloy, pitting corrosion was not registered. M. A. Khan at al [30] have determined this type of local corrosion on Ti–6Al–4V alloy in phosphate buffer solution of pH=7.4. Also, A. Choubey et al. [16] observed pitting corrosion on Ti–6Al–4V alloy in Hank's solution at about +1280 mV÷+1290 mV (vs. SCE). These facts show the superior resistance to pitting corrosion of our new Ti–5Al–4V alloy probably due to its different composition and structure. The zero current potential, E_{oc} in our Table 1 has closed values with of [30,16].

On Ti–6Al–4Fe alloy, pitting corrosion was registered but at a very electropositive breakdown (+3.158 V) potential (E_b); pitting protection potential (E_{pp}) is very noble (+1.644 V) and can not be reached in human fluids; below this potential, no pit can be initiated; pitting corrosion resistance ($E_b - E_{pp}$) present low values (1.514 V), namely a high ability to re-passivation; also, the difference $E_{oc} - E_b$ is very large (3.366 V), revealing a very low pitting corrosion tendency (Table 1). Therefore, is not possible to appear pitting corrosion on this alloy even in long-term service conditions. A. Choubey [16] reported pitting corrosion on Ti–6Al–4Fe alloy in Hank's solution at a more

Table 2
Regression equations and determination coefficients (D) in Ringer 2 solution

Metal	pH	Regression equation	D
Ti	2.5	$Y=-202.81+0.0231x-6.980x^2$	0.610
Ti–5Al–4V	2.5	$Y=-193.66+0.0587x-2.1086\cdot10^{-5}x^2+2.761\cdot10^{-9}x^3-1.479\cdot10^{-13}x^4+2.805\cdot10^{-18}x^5$	0.591
Ti–6Al–4Fe	2.5	$Y=-439.69+0.136x-2.222\cdot10^{-5}x^2+1.4324\cdot10^{-9}x^3-3.1986\cdot10^{-14}x^4$	0.706
Ti	4.35	$Y=-369.66+0.1308x-4.102\cdot10^{-5}x^2+5.197\cdot10^{-9}x^3-2.77\cdot10^{-13}x^4$	0.783
Ti–5Al–4V	4.35	$Y=-276.179-0.0446x+8.5806\cdot10^{-6}x^2-6.104\cdot10^{-10}x^3+1.401\cdot10^{-14}x^4$	0.599
Ti–6Al–4Fe	4.35	$Y=-293.06-0.0183x+1.926\cdot10^{-6}x^2-6.535\cdot10^{-11}x^3$	0.587
Ti	6.98	$Y=-238.54+0.117x-3.645\cdot10^{-5}x^2+3.929\cdot10^{-9}x^3-1.8063\cdot10^{-13}x^4+3.027\cdot10^{-18}x^5$	0.665
Ti–5Al–4V	6.98	$Y=-127.911+0.0299x-2.739\cdot10^{-6}x^2+4.143\cdot10^{-11}x^3$	0.785
Ti–6Al–4Fe	6.98	$Y=-234.67-0.0306x-5.031\cdot10^{-6}x^2-3.1816\cdot10^{10}x^3+9.752\cdot10^{-15}x^4$	0.765

active potential (about +1130 mV÷+1150 mV vs. SCE). This difference of behaviour can be attributed to the difference of the solution composition, but also to the more favourable structure of our Ti–6Al–4Fe alloy, that was treated by forging after casting.

All electrochemical parameters indicate compact, stable, passive films on all studied materials.

3.1.2. Ringer 2 solution

In Ringer 2 solution (Fig. 2), the following behaviour was observed: same typical passive metal behaviour, more electropositive corrosion potential values (Table 1) than in Ringer 1 solution because of reduced aggressivity of Ringer 2 solution; lower passive current densities than in Ringer 1. Pitting corrosion of Ti–6Al–4Fe alloy is characterised by nobler breakdown (+3.612 V) and pitting protection (+1.918 V) potential values, therefore a better pitting corrosion resistance (1.494 V) and tendency (3.817 V) and no probability to appear this form of local corrosion in long service conditions. In consequence, it results a very stable and resistant passive film.

Both in Ringer 1 and Ringer 2 solutions, titanium and Ti–5Al–4V alloy exhibited an increase of the anodic current densities at higher potentials of +1.5 V (vs. SCE), which was attributed to oxygen evolution by S.Y. Yu and J.R. Scully [34]. It is reasonable to assume that the same processes take place on our new Ti–5Al–4V alloy surface.

3.2. Ion release for short term

Titanium ion release (Figs. 3 and 4) increased in time, for the first 400–600 immersion hours and then tend to a constant level, due to absorption processes from solution [20,27,28,35]. It is possible to be absorbed hydroxil (OH^-) and calcium ions in Ringer 1 solution and phosphorus ions in addition, in Ringer 2 solution. On the biomaterial surface will be a thicker passive layer, a barrier against the ion transport through the passive film. The very low values obtained both in Ringer 1 and Ringer 2 solutions can not be dangerous for human body.

3.3. Monitoring of the open circuit potentials

Monitoring of the open circuit potentials (Fig. 5) for 20 000 exposure hours in Ringer 2 solution of different pH values (2.5; 4.35; 6.98) show the following behaviour.

All open circuit potentials oscillate around some electropositive values placed in the passive domain of titanium on Pourbaix diagram [36], denoting very good stability for long term. Ti–5Al–4V and Ti–6Al–4Fe alloys have more electronegative but more stable values than the base metal. The fluctuations in time of the open circuit potential values can be explained by an increase of the anodic activity of the biomaterials, probably due to some processes of thinning or thickening, remodeling or adsorption of $H_2PO_4^-$ ions [21,27,28,37,38].

The computing of the scatter diagrams permits to obtain regression equations and corresponding determination coefficient (D). From Table 2 resulted a good percent of credibility (0.6–0.8 value). So, it is possible to calculate the open circuit potential values for longer time than the experimental. But such predictions must need more precautions because of the human body complexity and of some unexpected phenomena which could take place in time.

In conditions of long-term service of the implants, can appear local acidification of the surrounding environment due to the hydrolysis of the passive layer compounds or in the distress

Table 3
Open circuit potential gradients ΔE_{oc}(pH) in Ringer 2 solution at 37 °C

Biomaterial	Time (h)	ΔE_{oc1} (V)	ΔE_{oc2} (V)	ΔE_{oc3} (V)
Titanium	15 000	−0.082	−0.050	−0.026
	20 000	−0.230	−0.163	−0.067
Ti–5Al–4V	15 000	−0.246	−0.191	−0.284
	20 000	−0.255	0.041	−0.296
Ti–6Al–4Fe	15 000	−0.140	−0.057	−0.083
	20 000	−0.081	−0.041	−0.040

Table 4
Corrosion rates (mm/yr) in Ringer 2 solution at 37 °C

Biomaterial	Time (h)	V (mm/yr)		
		pH=2.5	pH=4.35	pH=6.98
Titanium	15 000	6.89×10^{-3}	6.75×10^{-3}	6.69×10^{-3}
	20 000	7.12×10^{-3}	7.08×10^{-3}	7.02×10^{-3}
Ti–5Al–4V	15 000	6.24×10^{-3}	5.92×10^{-3}	5.83×10^{-3}
	20 000	6.98×10^{-3}	6.83×10^{-3}	6.77×10^{-3}
Ti–6Al–4Fe	15 000	6.64×10^{-3}	6.53×10^{-3}	6.49×10^{-3}
	20 000	7.09×10^{-3}	7.10×10^{-3}	6.99×10^{-3}

periods of the body. So, the non-uniformity of the pH values along the implant surface can generate open circuit potential gradients $\Delta E_{oc}(pH)$. In this paper were simulated three different situations:

$$\Delta E_{oc1}(pH) = E_{oc}^{pH=2.5} - E_{oc}^{pH=6.98} \quad (1)$$

$$\Delta E_{oc2}(pH) = E_{oc}^{pH=2.5} - E_{oc}^{pH=4.35} \quad (2)$$

$$\Delta E_{oc3}(pH) = E_{oc}^{pH=4.35} - E_{oc}^{pH=6.98}. \quad (3)$$

The potential gradients calculated for extreme pH values (Table 3) have low absolute values during 20 000 exposure hours, about 0.23 V for titanium and 0.296 V and respectively 0.140 V for its alloys (values for short and medium term were published in [21]). These values can not generate galvanic cells (only differences over 0.6 V can form these cells) and local corrosion [39–41].

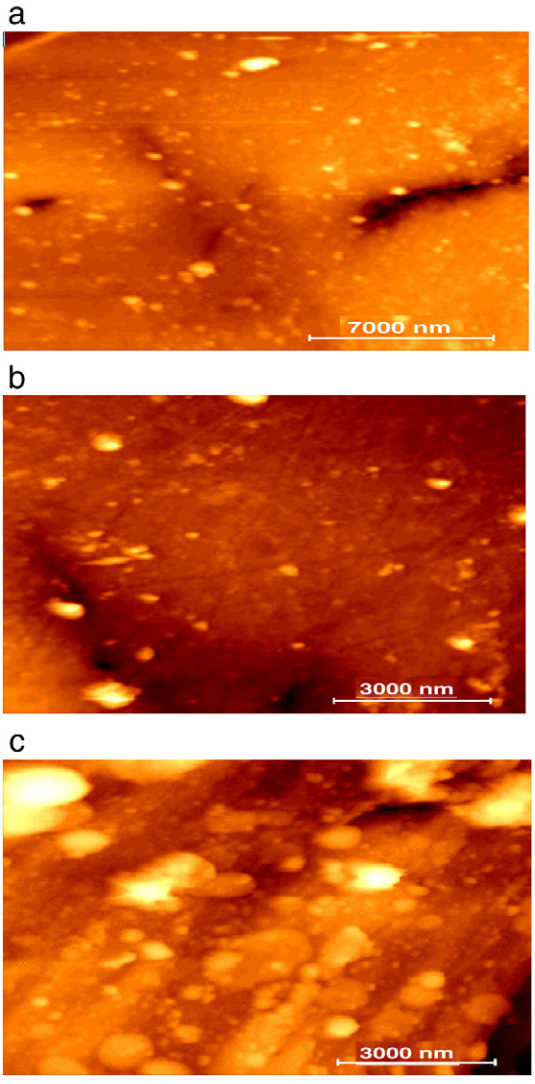

Fig. 6. AFM images (2D form) in Ringer 1 solution (at 37 °C) after 2400 hours for: a) Ti; b) Ti–5Al–4V; c) Ti–6Al–4Fe.

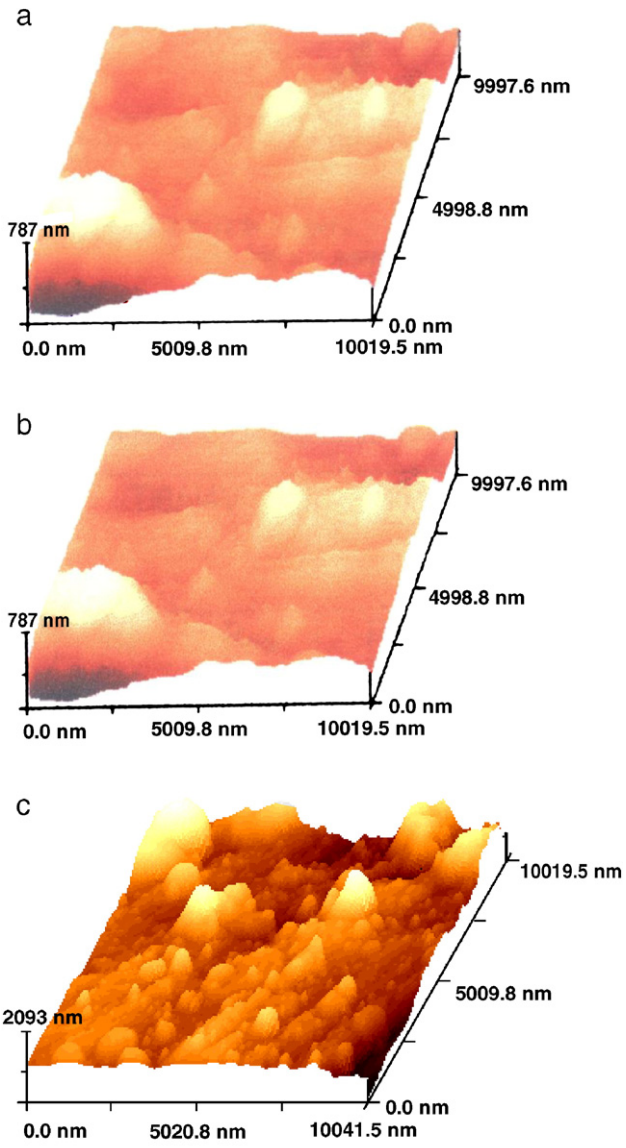

Fig. 7. AFM images (3D form) in Ringer 1 solution (at 37 °C) after 2400 hours for: a) Ti; b) Ti–5Al–4V; c) Ti–6Al–4Fe.

Table 5
Average roughness (R_a) and root mean square roughness (R_{rms}) in Ringer 1 and Ringer 2 solutions

Time (h)	Solution	Ti		Ti–5Al–4V		Ti–6Al–4Fe	
		R_a (nm)	R_{rms} (nm)	R_a (nm)	R_{rms} (nm)	R_a (nm)	R_{rms} (nm)
24	Ringer 1	97.86	294.25	202.48	260.82	481.25	448.57
2400		102.40	258.54	298.20	380.43	462.32	521.85
4800		248.44	340.43	388.27	482.05	510.98	670.25
24	Ringer 2	54.67	71.43	194.96	272.35	62.35	87.23
2400		38.42	55.48	125.42	204.89	50.01	78.03
4800		27.96	39.98	99.35	139.09	55.88	78.87

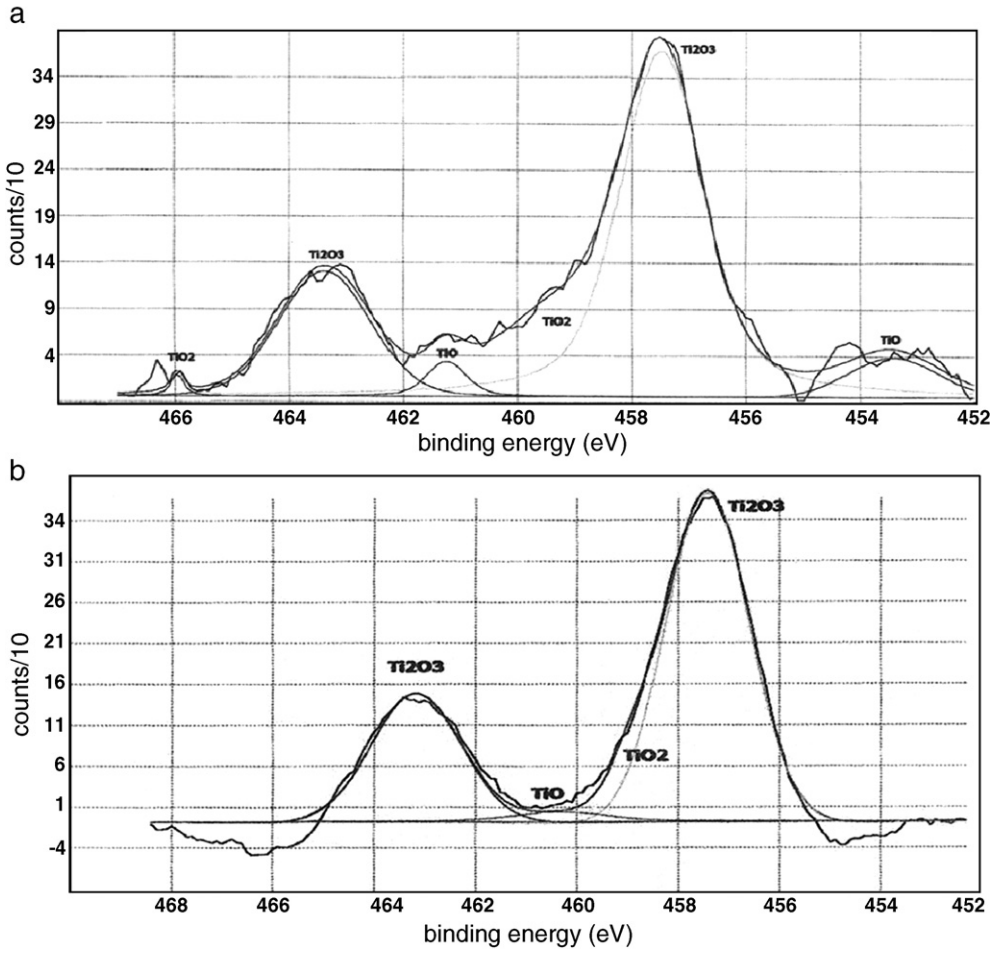

Fig. 8. XP Spectra obtained after 2880 exposure hours in Ringer 2 solution (at 37 °C) for: a) Ti; b) Ti–5Al–4V alloy.

3.4. Monitoring of the corrosion rates

The corrosion rates were monitored after different periods (100, 200, 500, 1000, 2000, 3000, 4000, 5000, 8000, 10 000, 15 000, 20 000 hours; corrosion rates for the periods till 10 000 hours were given in paper [21]) by the linear polarisation method. From Table 4 it can be seen that the alloys Ti–5Al–4V and Ti–6Al–4Fe have lower corrosion rates than titanium. All biomaterials present "very good" corrosion resistance in Ringer 2 solution at 37 °C for 20 000 hours. The corrosion rates obtained by [16] are a little lower than those from Table 4: 1.21 μm/yr. for Ti–6Al–4V and 1.18 μm/yr. for Ti–6Al–4Fe. The explication is the very long exposure time in our experiments and the slight difference between of alloy content and solution composition. The slight increase of the corrosion rates in time denotes (like the variations of the open circuit potentials in time) some disolution or remodeling processes.

3.5. Surface topography by AFM

The surface topography is an important factor in the increase of the corrosion resistance of the implant materials. Also, the surface roughness influences the biomaterials–biomolecules interactions allowing the tissue growth into porous, adsorbing molecules, therefore contributing to the osseointegration process and the increase of the biocompatibility [31].

AFM images in 2D form (Fig. 6) and 3D form (Fig. 7) obtained after different exposure periods in Ringer 1 solution revealed that the roughness like corrosion rates increased in time (Table 5), suggesting a dynamic process at biomaterial–

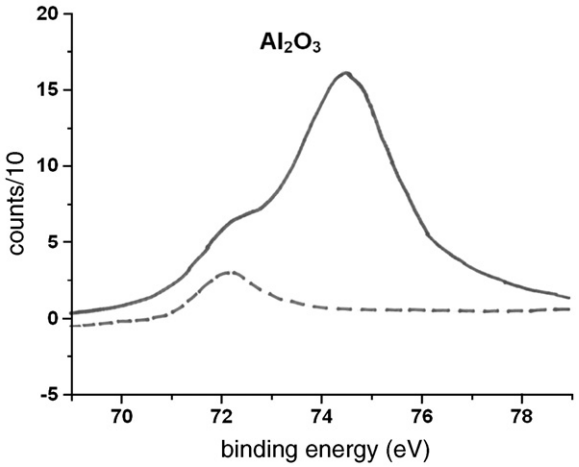

Fig. 9. XP Spectra obtained after 2880 exposure hours in Ringer 2 solution (at 37 °C) for Ti–6Al–4V alloy; peak for Al_2O_3 oxide.

biofluid interface. M.A. Khan et al. [30] show (the same fact) that the surface roughness on Ti–6Al–4V alloy varied following corrosion rates at different level of pH of phosphate buffer saline solution.

3.6. Passive film composition from XPS

Spectra obtained after 2880 immersion hours (about 120 days) in Ringer 2 solution show the existence of protective titanium dioxide TiO_2 and TiO and Ti_2O_3 oxides both for titanium (Fig. 8a) and Ti–5Al–4V alloy (Fig. 8b). Vanadium was not detected by XPS method because of its very low concentration. D. Zaffe et al. [42] were not able to detect vanadium by EDS method due to the fact that the vanadium Kα emission (4.95 keV) is covered by titanium Kβ emission (4.93 keV). But, Maeusli and co-workers [14] put in evidence vanadium by SIMS method. Aluminum presents a peak at 74.2 eV (binding energy) characterising its Al_2O_3 oxide (Fig. 9) and can be easily determined.

4. Conclusions

1. In Ringer 1 solution (with high chloride ion content) all biomaterials present self-passivation and very large passive potential range. On Ti–6Al–4Fe alloy, pitting corrosion was registered but at a very electropositive breakdown potential; pitting protection potential is very noble and can not be reached in human fluids.
2. In Ringer 2 solution were obtained more favourable electrochemical properties than in Ringer 1 solution because of its reduced aggressivity; pitting corrosion of Ti–6Al–4Fe alloy is characterised by better values of its parameters, therefore, no probability to appear this form of local corrosion in long service conditions.
3. Titanium ion release increased in time, for the first 400–600 immersion hours and then tend to a constant level and presented very low values, non-dangerous for human body.
4. All open circuit potentials oscillate around some electropositive values. The fluctuations in time can be explained by some processes of thinning or thickening, remodeling or adsorption of ions.
5. The potential gradients calculated for extreme pH values have low values during 20 000 exposure hours and can not accelerate the corrosion.
6. All biomaterials present “very good” corrosion resistance in Ringer 2 solution at 37 °C for 20 000 hours.
7. AFM images revealed that the roughness increased in time, suggesting a dynamic process at biomaterial–biofluid interface.
8. XP spectra show the existence of titanium dioxide TiO_2 and TiO and Ti_2O_3 oxides both for titanium and Ti–5Al–4V alloy. Also, Al_2O_3 oxide was detected.

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