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Long Term Stability of a New Implant Alloy in Biological Environment

Ecaterina Vasilescu, Paula Drob, Daniela Ionita, Steliana Ivanescu and Cora Vasilescu

***Abstract*— This paper studies the long term (3000 exposure hours) behaviour of a new titanium base Ti-6Al-4V-1Zr alloy un-covered and covered with hydroxyapatite (HA) or bovine serum albumin/hydroxyapatite (BSA/HA) in Ringer solution of different pH values for to reproduce the complex conditions from the human body. Electrochemical cyclic voltammetry and linear polarization methods were used. Also, open circuit potentials and gradients were monitored for 3000 immersion hours in Ringer solution of different pH values. Bare Ti-6Al-4V-1Zr alloy presented more electropositive corrosion potentials, lower values of the tendency to passivation and passive current densities indicating an easier passivation and a very resistant passive film than of Ti. Covered BSA/HA/Ti-6Al-4V-1Zr alloy exhibited lower values of the tendency to passivation and lower passive current densities than the covered HA/Ti-6Al-4V-1Zr alloy and bare alloy due to the more stable coating. The corrosion rates have lower values for bare Ti-6Al-4V-1Zr alloy than Ti. Comparing with the un-covered alloy, lower corrosion rates were obtained for covered alloy, proving the very good protective properties both of HA and BSA/HA coating.**

***Index Terms*—new Ti-6Al-4V-1Zr alloy; long term behaviour; open circuit potentials and gradients.**

I. Introduction

The corrosion resistance of titanium can be improved by alloying with resistant metals. Zirconium [1-3] is a good alloying material for various applications because has excellent resistance in many severe corrosive environments. Zr and Ti have several properties in common: both are transition metals with similar outer shell valence electron structure; they are normally covered by thin, chemical stable TiO_2 and ZrO_2 surface oxides [2]. Zirconium is considered immune for human body and has a positive effect on the tissue-material interactions and a good response with the bone [3].

Only few alloys of Ti with Zr were elaborated for implant use [1-3]. M. Karthega et al. [1] showed that Ti-29Nb-13Ta-4.6Zr alloy has a noble behaviour compared to Ti-Mo alloys. D. Caceras et al. [2] observed that the oxides formed by reaction with air at 760^0C on surface of Ti-13Nb-13Zr, Ti-15Zr-4Nb and Ti-7Nb-6Al alloys increased their hardness and Young's modulus.

Knowing that, in surgical applications, the pH can decrease from 5 till 2-3, since the hydrogen concentration increases in the traumatised tissue and also an inflammatory response can appear increasing the pH value till 9 [4-7], a Ringer solution with different pH values (3.36, 6.42, 8.91) was used in order to simulate these severe functional conditions.

This paper studies the long term (3000 exposure hours) behaviour of a new implant Ti-6Al-4V-1Zr alloy un-covered and covered with hydroxyapatite (HA) or bovine serum albumin/hydroxyapatite (BSA/HA) in Ringer solution of different pH values for to reproduce the complex conditions from the human body.

II. Procedures

Titanium and the new Ti-6Al-4V-1Zr alloy were obtained by vacuum melting. The new Ti-6Al-4V-1Zr alloy principally contains 7.12% aluminium, 3.92% vanadium, 1.07% zirconium and balance titanium.

These materials were studied as bare material and covered with layers of electrodeposited hydroxyapatite (HA) or bovine serum albumin/hydroxyapatite (BSA/HA).

The bare electrodes were polished, fixed in a Stern - Makrides mount system, washed with bi-distilled water, degreased in boiling benzene and dried in air.

The solutions used in experiments were Ringer of different pH values (2.5; 6.9; 8.9) for to reproduce the complex conditions from the human body. The composition was ($g.l^{-1}$): NaCl - 6.8; KCl - 0.4; $CaCl_2$ - 0.2; $MgSO_4.7H_2O$ - 0.2048; $NaH_2PO_4.H_2O$ - 0.1438; $NaHCO_3$ - 1; glucose - 1; pH = 6.9 (normal); pH = 2.5 (obtained by HCl addition); pH = 8.9 (obtained by KOH addition). Temperature was kept at $37^0C \pm 1^0C$.

The electrochemical glass cell was provided with inlets for working electrode, auxiliary platinum electrode and for Haber-Luggin capillary connected with reference saturated calomel electrode (SCE).

The cyclic potentiodynamic polarization measurements were applied starting from -0.8 V to +4.0 V (vs. SCE) using a scan rate of $10mV.sec^{-1}$. Voltalab 80 equipment with its

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E. Vasilescu is with the Institute of Physical Chemistry "Ilie Murgulescu", Spl. Independentei 202, Bucharest, 060021 Romania (corresponding author phone: 4021 3121147; fax: 4021 3121147; e-mail: ec_vasilescu@ yahoo.com).

P. Drob is with the Institute of Physical Chemistry "Ilie Murgulescu", Spl. Independentei 202, Bucharest, 060021 Romania (e-mail: paula_drob@ yahoo.com).

D. Ionita is with the Politehnica University, Spl. Independentei 313, Bucharest, 060042 Romania (e-mail: md_ionita@yahoo.com).

S. Ivanescu is with SC R&D Consulting and Services, Str. M. Ghiculeasa 45, Bucharest, 023761 Romania (e-mail: sivanescu@yahoo.com).

C. Vasilescu is with the Institute of Physical Chemistry "Ilie Murgulescu", Spl. Independentei 202, Bucharest, 060021 Romania (e-mail: cora_vasilescu@ yahoo.com).

VoltaMaster 4 program was used. From voltammograms, the main electrochemical parameters were determined: E_{corr} - corrosion potential, like zero current potential, E_p –passivation potential, at which the current density is constant; $|E_{corr} - E_p|$ difference shows the tendency to passivation (low values meaning an easy passivation); ΔE_p – passive potential range of the constant current; i_p – passive current density. If the reverse curve presents lower currents than the direct curve, it results a very stable passive state.

The linear polarization measurements (Tafel extrapolation) were carried out with the purpose to obtain the polarisation resistance (R_p), the corrosion current densities (i_{corr}), and the corrosion rates (V_{corr}) using the same Voltalab 80 equipment with its VoltaMaster 4 program. Ion release rate (in $ng.cm^{-2}$) was calculated [8] by the following formula:

$$\text{ion release rate} = 1{,}016.V_{corr}.10^5 \quad (1)$$

where V_{corr} is the corrosion rate in mm/year.

The Standard resistance classes correspond to the following limits of corrosion rates [9]:

Perfectly stable: $<1x10^{-3}$ mm/year;

Very stable: $1x10^{-3}$ - $1x10^{-2}$ mm/year;

Stable: $1x10^{-2}$ - $1x10^{-1}$ mm/year;

Relatively stable: $x10^{-1}$ - 1 mm/year;

Less stable: 1 – 10 mm/year;

Unstable: > 10 mm/year.

The open circuit potentials E_{oc} (vs. SCE) were monitored with the exposure time (3 000 immersion hours till present). The possible open circuit potential gradients, $\Delta E_{oc}(pH)$ that can appear due to the pH non-uniformity along the implant surface [10-12] were simulated and calculated:

$$\Delta E_{oc1}(pH) = E_{oc}^{pH=2.5} - E_{oc}^{pH=6.9} \quad (2)$$

$$\Delta E_{oc2}(pH) = E_{oc}^{pH=2.5} - E_{oc}^{pH=8.9} \quad (3)$$

$$\Delta E_{oc3}(pH) = E_{oc}^{pH=6.9} - E_{oc}^{pH=8.9} \quad (4)$$

III. Results

A. *Cyclic voltammetry in Ringer solutions*

Cyclic voltammetry in Ringer solutions for the bare Ti-6Al-4V-1Zr alloy

In Ringer solution of pH = 2.5, the cyclic polarisation curves (Fig. 1a) show a better behaviour of the alloy than of base metal, as follows:

- corrosion potential (E_{corr}) of Ti-6Al-4V-1Zr alloy has more electropositive value than of Ti (Table I) due to the galvanic couple effect of the alloying elements that shift this potential to nobler values;
- passivation potential (E_p) of Ti-6Al-4V-1Zr alloy is moved in electronegative direction and the tendency to passivation ($|E_{corr} - E_p|$) is lower than of Ti, revealing an easier passivation for alloy due to the participation of the alloying elements with their protective oxides (TiO_2) to the formation of the passive layer [13,14];
- the dissolution current density in the passive state (i_p) (Table I) is lower for Ti-6Al-4V-1Zr alloy than Ti, denoting a more resistant passive film as result of the beneficial influence of the alloying elements.

In neutral Ringer solution of pH = 6.9 (Fig. 1b), the following behaviour was observed:

- both Ti and Ti-6Al-4V-1Zr alloy present self passivation, good behaviour with very large passive potential range (ΔE_p), higher of +4 V (Table I), limit value in our experiments;
- Ti-6Al-4V-1Zr alloy exhibited nobler corrosion (E_{corr}) being the noblest value obtained in the studied Ringer solutions and more active passivation potentials (E_p) than base metal (Table I), due to the same favourable contributions of the alloying elements;
- tendency to passivation ($|E_{corr} - E_p|$) and passive current densities (i_p) have lower values for alloy than for Ti (Table I), showing the formation of a more compact, resistant, stable passive film on the alloy surface.

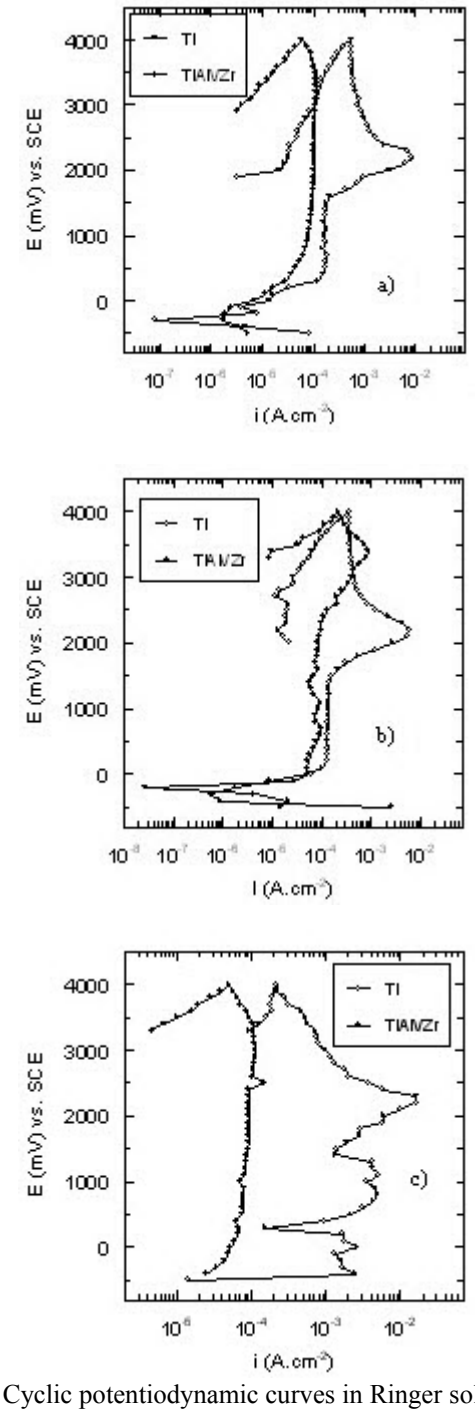

Fig. 1. Cyclic potentiodynamic curves in Ringer solution of:

a) pH = 2.5; b) pH = 6.9; c) pH = 8.9

Table I Main electrochemical parameters for Ti and Ti-6Al-4V-1Zr alloy in Ringer solutions at 37^0C

pH	Material	E_{corr} (V)	E_p (V)	$\|E_{corr} - E_p\|$ (V)	ΔE_p (V)	i_p ($\mu A.cm^{-1}$)
2.5	Ti	-0.66	+0.27	0.93	>4	127
	TiAlVZr	-0.54	+0.25	0.79	>4	50
6.9	Ti	-0.48	+0.08	0.56	>4	86
	TiAlVZr	-0.46	-0.02	0.48	>4	40
8.9	Ti	-0.72	+0.09	0.81	>4	218
	TiAlVZr	-0.67	+0.02	0.71	>4	50
6.9	HA/TiAlVZr	-305	-300	0.005	3.3	12.5
	BSA/HA/TiAlVZr	-195	-190	0.004	> 4	2.1

covered Ti6Al4V1Zr alloy in Ringer solution of pH=6.9

In alkaline Ringer solution of pH = 8.9, cyclic polarisation curves (Fig. 1c) revealed the superior behaviour of Ti-6Al-4V-1Zr alloy than of Ti:
- more electropositive corrosion (E_{corr}) potentials and more electronegative passivation (E_p) potentials (Table I) due to the positive, favourable action of the alloying constituent elements;
- lower values of the tendency to passivation ($E_{corr} - E_p$) and passive current densities (i_p) indicating an easier passivation and a very resistant passive film for alloy (Table I).

At all studied pH values, the reverse curves show lower current densities than the direct curves, proving a stable oxide film; also, the electrochemical parameters had better values for alloy than for the base metal demonstrating the beneficial effect of the alloying with Al, V and Zr.

Cyclic voltammetry in Ringer solutions for the Ti-6Al-4V-1Zr alloy covered with hydroxyapatite (HA) or bovine serum albumin/hydroxyapatite (BSA/HA)

Typical potentiodynamic polarization curves for Ti-6Al-4V-1Zr alloy covered with HA or BSA/HA in neutral Ringer solution (pH=6.9) are shown in Fig. 2. It can be seen that the polarization curve for Ti-6Al-4V-1Zr alloy covered with BSA/HA had a higher corrosion potential (-195 mV) than for samples covered with HA (-305 mV). Also, samples covered with BSA/HA exhibited a lower tendency to passivation ($|E_{corr} - E_p|$) and passive current densities (i_p) than the samples covered with HA due to the more stable coating (Table I). Both curves were characterized by very similar trend.

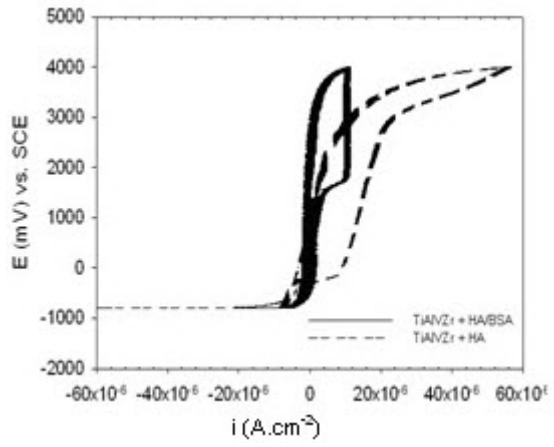

Fig. 2. Cyclic potentiodynamic curves for HA and BSA/HA

B Corrosion rates and ion release rates in Ringer solutions

Corrosion rates and ion release rates in Ringer solutions for the bare Ti-6Al-4V-1Zr alloy

The corrosion current densities (i_{corr}), corrosion rates (V_{corr}) and polarization resistances (R_p) of specimens, were determined from the polarization curves using Tafel extrapolation method.

The corrosion rates (V_{corr}) have lower values for Ti-6Al-4V-1Zr alloy than Ti in the "Perfect Stable" and "Very Stable" resistance class (Table II) with the mention that the lowest value was registered in neutral Ringer solution, in which the alloy will work the most part of time. Correspondingly, the total quantity of ions released in the physiological solutions is very low for the new alloy. Polarisation resistance (R_p) is higher for Ti-6Al-4V-1Zr alloy than for base metal, revealing a more resistant passive film.

Corrosion rates and ion release rates in neutral Ringer solution for the Ti-6Al-4V-1Zr alloy covered with hydroxyapatite (HA) or bovine serum albumin/hydroxyapatite (BSA/HA)

The alloy covered with BSA/HA exhibited lower corrosion rates than the alloy covered with HA, denoting the better efficiency of the BSA/HA coating (Table II) in neutral Ringer solution.

The obtained polarization resistance (R_p) can be used to determine the porosity [15,16]. According to the resulting R_p value, it is marked that the advantageous effect of the porosity reduction occurred in the BSA/HA/Ti-6Al-4V-1Zr alloy samples. This was because BSA reduced the layer defect, forming a dense coating that possesses higher corrosion resistance.

Comparing with the un-covered alloy, lower corrosion rates were obtained for covered alloy, proving the very good protective properties both for HA and BSA/HA coatings.

C. Monitoring of the open circuit potentials (E_{oc}) in Ringer solutions

Monitoring of E_{oc} for bare alloy in Ringer solutions

In Ringer solution of pH = 2.5, the open circuit potentials both for Ti and bare Ti-6Al-4V-1Zr alloy (Fig. 3a) presented some oscillations at the beginning, probably that the passive layer gets disrupted and re-formed [17].

Table II Corrosion and ion release rates for Ti and Ti-6Al-4V-1Zr alloy in Ringer solutions at 37^0C

pH	Material	R_p (kΩ.cm^{-2})	i_{corr} (μA.cm^{-2})	V_{corr} (μm.yr^{-1})	Class	Ion release (ng.cm^{-2})
2.5	Ti	11.35	0.746	8.63	VS	876.81
	TiAlVZr	36.88	0.220	2.45	VS	248.92
6.9	Ti	20.47	0.822	9.50	VS	965.20
	TiAlVZr	219.36	0.071	0.803	PS	81.58
8.9	Ti	13.91	1.190	13.76	S	1398.02
	TiAlVZr	85.12	0.153	1.74	VS	176.78
6.9	HA/TiAlVZr	552.71	0.2	0.67	PS	68.1
	BSA/HA/TiAlVZr	986.86	0.1	0.22	PS	22.4

PS – Perfect Stable; VS – Very Stable; S - Stable

The general tendency is to ennoble, due to the increase of the passive film thickness [17]; correspondingly, the corrosion rate decreased. For 1 000 exposure hours, the open circuit potentials for the new Ti-6Al-4V-1Zr alloy have more electropositive values than of Ti and then titanium has nobler open circuit potential values than the new alloy. But, both biomaterials present electropositive values (-0.1 V for alloy; -0.02 V for Ti), that denote a stable passive state. Also, more stable values of E_{oc} it resulted after 1000 immersion hours, showing an improvement of the passive state.

In neutral Ringer solution of pH = 6.9, the open circuit potential values for bare Ti-6Al-4V-1Zr alloy (Fig. 3b) are more electropositive than of base metal due to the beneficial contribution of the alloying elements with their resistant oxides to the formation of the passive layer. In this pH and potential range, all constituent elements of the alloy are placed in the passive potential range on the Pourbaix diagrams [18] improving the resistance of the passive layer and proving a very good passive state for long term (3000 hours). After 1000 immersion hours, the open circuit potential values are very constant, stable, denoting a tenacious, stable, compact, barrier passive layer [17].

The oscillations that appeared in the first 1000 exposure hours denote some dissolution and repassivation processes.

In alkaline Ringer solution of pH = 8.9 (Fig. 3c), the positions of Ti, Zr and V on Pourbaix diagrams [18] are in passive domain and of Al in corrosion state. Yet, the open circuit potential values for bare alloy (about -0.18 V) are nobler than for Ti (about -0.32 V) probably due to the higher positive influence of Ti, Zr and V and to the lower unfavourable influence of Al. For 1000–1500 immersion hours, the open circuit potentials show some variations, due to the same processes of disruption and reformation of their passive layer. After 1500 exposure hours, the open circuit potential values tend to a constant level, denoting a stabilization of alloy passive state [17].

Monitoring of E_{oc} for covered alloy with HA and BSA/HA in neutral Ringer solution

The open circuit potential (E_{oc}) of samples covered with HA shifted toward active direction and reached a potential of -128 mV after 75 immersion minutes in neutral Ringer solution. This could be due to the dissolution of coating [15].

Comparing with the HA/Ti-6Al-4V-1Zr alloy, the samples coated with BSA/HA showed an initial E_{oc} of -25 mV, reached a steady state after 30 min and attained nobler potential of +52 mV, indicating a better passive state, a better corrosion behaviour and resistance than HA/Ti-6Al-4V-1Zr samples.

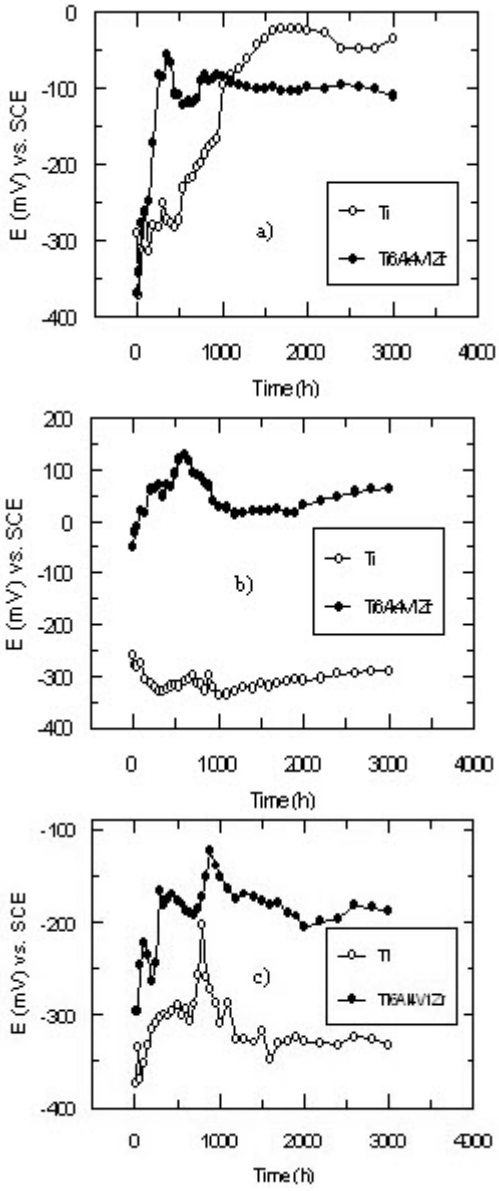

Fig. 3. Monitoring of open circuit potential in Ringer solution of a) pH = 2.5; b) pH = 6.9; c) pH = 8.9

Monitoring of open circuit potential gradients (ΔE_{oc}) for bare alloy in Ringer solutions

Immediately after the surgical application, the implant is surrounded by exudates containing fibrine and chloride ions

of relative low pH (5 or lower, till 3), because hydrogen concentration increases in the traumatized tissues [6]. Moreover, an inflammatory response can appear producing the increase of the pH value till 9 [7]. Also, differential aeration electrochemical cells can be formed and their function is controlled by the diffusion processes [6].

The implant alloys are used for long term (more 20 years) and in this period, it is possible that the value of pH to change along the implant surface [8]; the local acidity (till pH ≈ 2) can be produced by the hydrolysis of the different oxides from passive film (TiO_2, Al_2O_3, V_2O_3, V_2O_5, ZrO_2); local alkalinity (till pH ≈ 9) appears in the case of inflammations or in distress periods of the body. So, open circuit potentials will have various values on different zones of the implant, producing potential gradients ΔE_{oc}. These potential gradients can generate galvanic corrosion and can accelerate the corrosion process [11,12].

Open circuit potential gradients due to the pH non-uniformities ΔE_{oc}(pH) were monitored for 3000 exposure hours (Table III). These gradients presented low values, from 0.014 V to 0.305 V for Ti and from 0.018 V to 0.244 V for the new Ti-6Al-4V-1Zr alloy. These values cannot generate galvanic or local corrosion, because, only differences of 0.6 V – 0.7 V can initiate and maintain such kinds of local corrosion [19,20].

Table III. Open circuit potential gradients ΔE_{oc}(pH) in Ringer solution

Biomaterials	Time (h)	ΔE_{oc1} (V)	ΔE_{oc2} (V)	ΔE_{oc3} (V)
Ti	100	-0.014	+0.077	+0.091
	500	-0.044	-0.028	+0.016
	1 000	-0.241	-0.029	+0.212
	2 000	-0.284	+0.021	+0.305
	3 000	-0.245	+0.043	+0.298
Ti6Al4V1Zr	100	+0.244	+0.202	-0.042
	500	+0.018	+0.086	+0.068
	1 000	+0.059	+0.123	+0.065
	2 000	+0.069	+0.175	+0.106
	3 000	+0.047	+0.125	+0.078

IV. Conclusion

1. Bare Ti-6Al-4V-1Zr alloy presented more electropositive corrosion potentials, lower values of the tendency to passivation and passive current densities indicating an easier passivation and a very resistant passive film than of Ti in Ringer solutions of different pH values. Covered BSA/HA/Ti-6Al-4V-1Zr alloy exhibited lower values of the tendency to passivation and lower passive current densities than the HA/Ti-6Al-4V-1Zr alloy and bare alloy due to the more stable coating.

2. The corrosion rates in Ringer solutions have lower values for bare Ti-6Al-4V-1Zr alloy than Ti. Comparing with the un-covered alloy, lower corrosion rates were obtained for covered alloy, proving the very good protective properties both for HA and BSA/HA coatings.

3. The open circuit potential values are very constant, stable, denoting a tenacious, stable, compact, barrier passive layer for un-covered alloy. Covered BSA/HA/Ti-6Al-4V-1Zr alloy attained nobler potentials, indicating a better corrosion resistance than of HA/Ti-6Al-4V-1Zr and bare alloy.

4. Open circuit potential gradients due to the pH non-uniformity of Ringer solutions presented low values that cannot generate galvanic or local corrosion.

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