Artigo

CORROSION RESISTANCE IMPROVEMENT OF TITANIUM BASE ALLOYS

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The corrosion resistance of the new Ti-6Al-4V-1Zr alloy in comparison with ternary Ti-6Al-4V alloy in Ringer-Brown solution and artificial Carter-Brugirard saliva of different pH values was studied. In Ringer-Brown solution, the new alloy presented an improvement of all electrochemical parameters due to the alloying with Zr; also, impedance spectra revealed better protective properties of its passive layer. In Carter-Brugirard artificial saliva, an increase of the passive film thickness was proved. Fluoride ions had a slight negative influence on the corrosion and ion release rates, without to affect the very good stability of the new Ti-6Al-4V-1Zr alloy.

Keywords: corrosion rates; EIS; Ti6Al4V1Zr alloy.

INTRODUCTION

Titanium and its Ti-6Al-4V alloy were used as implant material for many years.[1-6] These materials have very good corrosion resistance and biocompatibility. In the last years, important problems have been raised over their long-term performance. Several cases of extensive metallosis and necrosis in periprosthetic tissues of failed cemented Ti-6Al-4V prostheses were registered.[7,8] In recent years, attempts were made to develop titanium alloys with biomechanical compatibility, low modulus and biochemical compatibility by the using of non-toxic alloying elements as: Ti, Nb, Zr.[9-11] These elements are chemically very stable and highly corrosion resistant in biological fluids and are considered immune for human body.[12,13]

Zirconium has excellent corrosion resistance to many types of corrosive media including strong acids and basses. Zirconium has acceptable mechanical strength and good biocompatibility.[14,15] Zirconium implants exhibit good osseointegration and the degree of bone-implant contact is higher for Zr than for Ti.[16-19] Only few alloys with zirconium were elaborated for implant use: Ti-2.2Al-2.6Zr,[11] Ti-13Nb-13Zr,[20,21] Ti-15Zr-4Nb-4Ta,[10] Ti-15Zr-4Nb-4Ta-0.2Pd,[22] Ti-50Zr and Zr-25Nb.[14]

The new Romanian Ti-6Al-4V-1Zr alloy was elaborated for to combine the very good mechanical properties of Ti-6Al-4V alloy with the good biocompatibility of zirconium. Its corrosion resistance in Ringer-Brown solution and Carter-Brugirard artificial saliva of different pH values was studied in this paper.

EXPERIMENTAL

The alloy synthesis was performed by melting in vacuum. The obtained composition for main constituents in wt% is: Al – 6.12; V – 3.92; Zr – 1.07; balance – Ti. The electrodes for experiments were prepared from ingots in casting state.

All measurements were carried out in Ringer-Brown solution and artificial Carter-Brugirard saliva at 37 ± 1 °C. Ringer-Brown solution of pH = 7.0 had the following composition (g/L): NaCl – 6; KCl – 0.4; $CaCl_2.2H_2O$ – 0.2; natrium lactate – 3.05; pH = 7. Carter-Brugirard saliva of pH = 2.54; 5.52; 8.21; 8.91 had the following composition (g/L): KCl -1.2; NaCl – 0.7; KH_2PO_4 – 0.26; KSCN – 0.33; Na_2HPO_4 – 0.19; urea – 0.13; $NaHCO_3$ – 1.5; neutral saliva was doped with 0.05M NaF for to reproduce the F^- concentration from the dental hygiene products.

The following experimental techniques were used: potentiodynamic and linear polarization, electrochemical impedance spectroscopy (EIS) and monitoring of the open circuit potentials, E_{oc} and of the open circuit potential gradients, due to the pH, ΔE_{oc}(pH) and content, ΔE_{oc}(c) non-uniformities of the artificial Carter-Brugirard saliva, versus exposure time (3000 h).

The cyclic potentiodynamic polarization was applied beginning from -0.5 to +4.0 V (vs. SCE) using a scan rate of 10 mV/sec. Voltalab 80 equipment with its VoltaMaster 4 program were used. From the 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 represents the tendency to passivation (low values characterise a good, easy passivation); ΔE_p – passive potential range of the constant current; i_p – passive current density.

The linear polarization measurements (Tafel) were carried out for a range of ± 200 mV around the open circuit potential, with a scan rate of 10 mV/sec. The same Voltalab 80 equipment with its VoltaMaster 4 program that delivered the values of the corrosion current densities (i_{corr}) and rates (V_{corr}) obtained from Tafel curves was used.

The total quantity of the ions (ng/cm^2) released in the solution was determined:

$$\text{ion release rate} = 1.016.V_{corr}.10^5 \quad (1)$$

where: V_{corr} = corrosion rate in mm/year.

The electrochemical impedance spectroscopy (EIS) was performed at open circuit potential (E_{oc}) and at +0.4 V (a potential from passive domain) using a PAR 263A potentiostat connected with a PAR 5210 lock-in amplifier. The amplitude of the AC potential was 10 mV and single sine wave measurements at frequencies between 10^{-1} and 10^5 Hz were performed.

The open circuit potentials E_{oc} were registered with the exposure time (3000 h till present) using a performing Hewlett-Packard

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multimeter. Three potential gradients due to the pH non-uniformity, ΔE_{oc}(pH) of Carter-Brugirard saliva (relations 2-4) and one potential gradient (relation 5) due to the composition non-uniformity, ΔE_{oc}(c) of Carter-Brugirard saliva were monitored:

$$\Delta E_{oc1}(pH) = E_{oc}^{pH=2.54} - E_{oc}^{pH=5.52} \quad (2)$$

$$\Delta E_{oc2}(pH) = E_{oc}^{pH=2.54} - E_{oc}^{pH=8.21} \quad (3)$$

$$\Delta E_{oc3}(pH) = E_{oc}^{pH=5.52} - E_{oc}^{pH=8.21} \quad (4)$$

$$\Delta E_{oc4}(c) = E_{oc}^{pH=8.21} - E_{oc}^{NaF} \quad (5)$$

RESULTS AND DISCUSSION

Improvement of corrosion resistance in Ringer-Brown solution

Improvement of corrosion resistance from polarization curves

Potentiodynamic polarization curves for the new Ti-6Al-4V-1Zr alloy exhibited self-passivation, stable, very constant passive current density and a corrosion potential placed in the passive potential range of Ti, Al, V, Zr on the Pourbaix[23] diagrams. Comparing with Ti-6Al-4V alloy (Table 1) it results an improvement of all electrochemical parameters, due to the favorable influence of zirconium.

Table 1. Main electrochemical parameters in Ringer-Brown solution

Alloy	E_{corr} (V)	E_p (V)	$\|E_{corr}-E_p\|$ (V)	ΔE_p (V)	i_p ($\mu A/cm^2$)
Ti6Al4V	-0.560	+0.100	0.660	> 4	14
Ti6Al4V1Zr	-0.403	-0.100	0.300	> 4	1.5

The alloy with Zr exhibited more electropositive corrosion potentials than the comparison Ti-6A-l4V alloy due to the galvanic couple effect of zirconium. The tendency to passivation $|E_{corr} - E_p|$ is lower (better) for Ti-6Al-4V-1Zr alloy showing that, this alloy can be easier passivated as result of the favorable influence of Zr that participates with its passive oxide (ZrO_2)[10,22] to the formation of the passive film. This layer is more compact, more stable than of the comparison alloy, as it results from the lower values of the passive current densities, i_p.

Also, the corrosion current density, corrosion and ion release rates (Table 2) presented lower values for Ti-6Al-4V-1Zr alloy than for Ti-6Al-4V alloy showing the benefic influence of Zr.

Improvement of corrosion resistance from electrochemical impedance spectra

The behavior of the new Ti-6Al-4V-1Zr alloy was studied from Bode spectra that permit to determine the presence of a compact passive film if the phase angle is close to -90° over wide frequency range of the spectrum, if the Bode form of log Zmod – log f has a linear portion with the slope about -1 at intermediate frequency and if the parameter n is about 1.[24,25]

Table 2. Corrosion current density, corrosion and ion release rates in Ringer-Brown solution

Alloy	R_p ($k\Omega/cm^2$)	i_{corr} ($\mu A/cm^2$)	V_{corr} ($\mu m/yr.$)	Resistance class	Ion release rate (ng/cm^2)
Ti6Al4V	42.13	0.82	7.13	Very Stable	724.41
Ti6Al4V1Zr	65.19	0.42	3.65	Very Stable	370.84

In Figure 1, the Bode spectrum obtained for the new quaternary Ti-6Al-4V-1Zr alloy at open circuit potential exhibited a phase angle of ≈ -80° and a linear portion with a slope ≈-1. Similar results obtained S. Piazza *et al*.;[26] an electric equivalent circuit with two time constants (Figure 2) was modeled: one constant is for the inner, thin, barrier, compact, passive film illustrated by the compact layer resistance, R_1 and capacitance CPE_1 (a constant phase element to describe the deviation from an ideal capacitor due to the certain heterogeneity of the surface);[25] the second time constant is for the outer, porous layer and is represented by the porous layer resistance, R_2 and capacitance CPE_2.

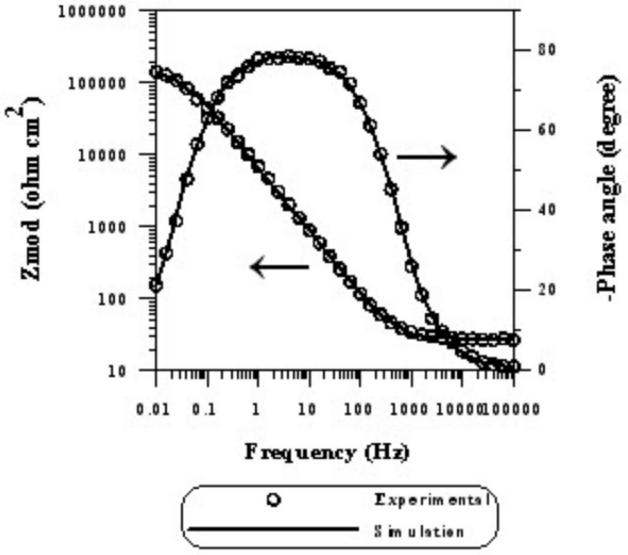

Figure 1. *Bode spectra in Ringer-Brown solution at open circuit potential for Ti-6Al-4V-1Zr alloy*

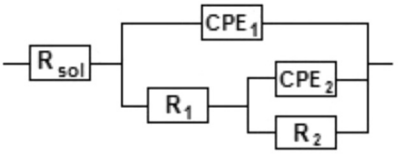

Figure 2. *Electric equivalent circuit with two time constants*

For ternary Ti-6Al-4V alloy, Bode plot (Figure 3) at E_{oc} exhibited two phase angles at -70° and -80° corresponding with three time constants: the third time constant is for diffusion processes through

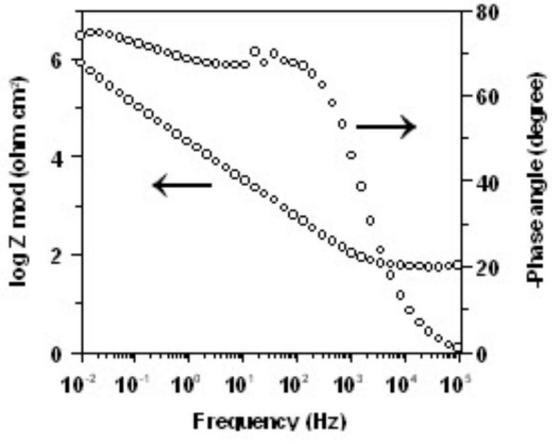

Figure 3. *Bode spectra in Ringer-Brown solution at open circuit potential for Ti-6Al-4V alloy*

Table 3. Parameters for equivalent electric circuit at E_{oc}

Potential	Alloy	R_1 (Ω cm^2)	CPE_1 (S s^n cm^{-2})	n_1	R_2 (Ω cm^2)	CPE_2 (S s^n cm^{-2})	n_2	R_3 (Ω cm^2)	W (S s^n cm^{-2})	n_3
E_{oc}	Ti6Al4V	$9.2x10^4$	$2.3x10^{-5}$	0.87	$1.7x10^3$	$6.1x10^{-5}$	0.84	$6.8x10^2$	$2.1x10^{-4}$	0.51
	Ti6Al4V1Zr	$1.6x10^5$	$2.9x10^{-6}$	0.98	$5.3x10^3$	$3.1x10^{-5}$	0.91	-	-	-
+0.4 V	Ti6Al4V	$9.3x10^5$	$1.3x10^{-6}$	0.89	-	-	-	-	-	-
	Ti6Al4V1Zr	$7.9x10^6$	$1.1x10^{-6}$	0.99	-	-	-	-	-	-

the passive film[27] and is shown by the diffusion Warburg impedance, W and diffusion resistance R_3 (Figure 4).

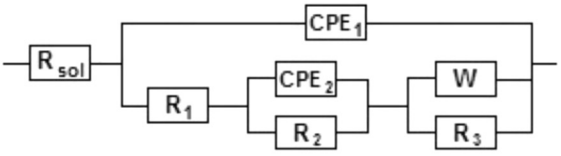

Figure 4. *Electric equivalent circuit with three time constants*

Fitting parameters for Ti-6Al-4V-1Zr alloy (Table 3) show that the resistance of the porous layer, R_2 is lower than the resistance of the barrier layer, R_1, denoting a more protective barrier layer.[28] Capacitance of the porous layer, CPE_2 is higher than the capacitance of the barrier layer, CPE_1 supporting the idea that the corrosion resistance is mainly due to the barrier layer.

Higher value of resistance R_1 of the quaternary Ti-6Al-4V-1Zr alloy than of the ternary Ti-6Al-4V alloy were registered; this fact denotes better protective properties of the passive layer on the new Ti-6Al-4V-1Zr alloy. The frequency independent parameter n_3 = 0.51 for ternary Ti-6Al-4V alloy indicates diffusion processes; the diffusion resistance R_3 has lower value than R_1 or R_2, showing reduced diffusion processes through the passive layer.

In the passive potential range, at +0.4 V, Bode spectra both for Ti-6Al-4V-1Zr and Ti-6Al-4V alloys (Figure 5) presented a phase angle of ≈ -80° over the wide frequency range, a slope of -1 and $n_1 \approx 0.90$, showing the same passive, compact film (Table 3). No reactions to this protective layer were detected and the electric equivalent circuit for the fitting of the impedance data contains one time constant (Figure 6).

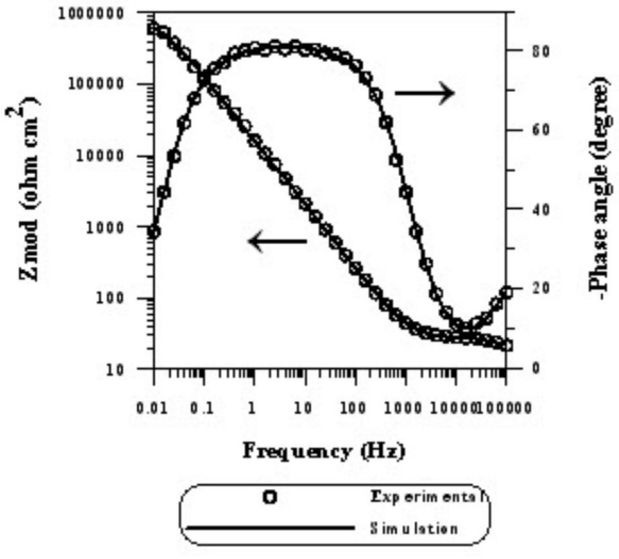

Figure 5. *Bode spectra in Ringer-Brown solution at +0.4 V for Ti-6Al-4V-1Zr alloy*

The EIS data are in agreement with the results obtained from the cyclic polarization curves.

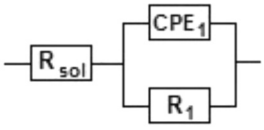

Figure 6. *Electric equivalent circuit with one time constant*

Improvement of corrosion resistance in artificial Carter-Brugirard saliva

Improvement of corrosion resistance from polarization curves

In artificial Carter-Brugirard saliva, the new Ti-6Al-4V-1Zr alloy is self-passivated both in acid, neutral and alkaline saliva. The most electropositive corrosion potential and lowest passive current density were registered in neutral saliva of pH = 8.21 (Table 4) showing that the passive film is the most stable and the alloy has the best resistance in this saliva. The difference between the corrosion potential, E_{corr} and passivation potential, E_p that provide an indication of the ease of passivation has the lowest value in neutral saliva, proving that the best passivation of the alloy appeared in this saliva.[29] The fluoride ion has a slow negative influence on the electrochemical parameters due its higher corrosivity.[24,30,31]

Table 4. Main electrochemical parameters in Carter-Brugirard saliva

pH	Alloy	E_{corr} (V)	E_p (V)	$\lvert E_{corr}-E_p \rvert$ (V)	ΔE_p (V)	i_p (μA/cm^2)
2.54	Ti6Al4V	-0.560	-0.335	0.225	> 4	2.00
	Ti6Al4V1Zr	-0.403	-0.295	0.106	> 4	1.80
5.52	Ti6Al4V	-0.410	-0.220	0.190	> 4	1.90
	Ti6Al4V1Zr	-0.320	-0.210	0.110	> 4	1.65
8.21	Ti6Al4V	-0.300	-0.190	0.110	> 4	1.90
	Ti6Al4V1Zr	-0.280	-0.180	0.100	> 4	1.32
8.91	Ti6Al4V	-0.540	-0.420	0.140	> 4	1.80
	Ti6Al4V1Zr	-0.520	-0.400	0.120	> 4	1.60
8.21+NaF	Ti6Al4V	-0.480	-0.370	0.120	> 4	1.90
	Ti6Al4V1Zr	-0.401	-0.290	0.111	> 4	1.75

In comparison with Ti-6Al-4V alloy, from Table 4 it resulted more favorable values of all electrochemical parameters for Ti-6Al-4V-1Zr alloy, revealing the beneficial effect of Zr.

Improvement of corrosion resistance from in time variations of the open circuit potentials

From Figure 7 it can be seen that the open circuit potential values of the new quaternary alloy have shown an overall increase for about

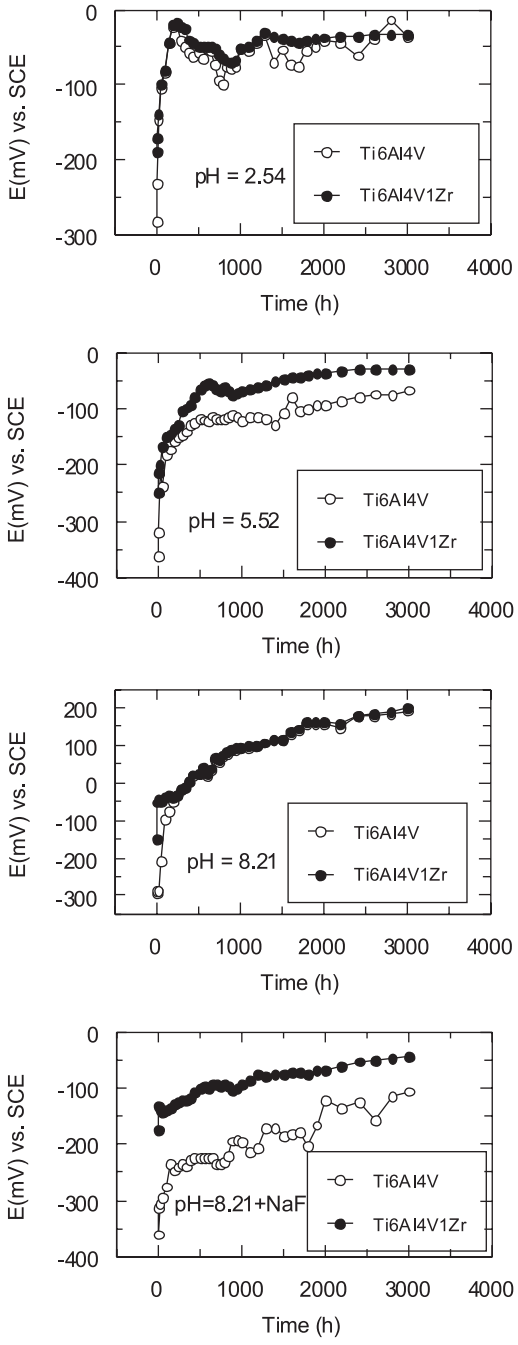

Figure 7. *In time variations of open circuit potential in artificial Carter-Brugirard saliva*

500 immersion hours and than slowly tended to more electropositive values; for Carter-Brugirard saliva of pH = 2.54, the open circuit potential values tended to a constant level after 500 immersion hours. According to Blackwood,[32] the shift of E_{oc} to positive values shows an increase of the passive film thickness and correspondingly, a decrease of the corrosion rate. Therefore, the new Ti-6Al-4V-1Zr alloy improved its passive state and corrosion resistance.

The more electronegative values of E_{oc} registered at pH = 2.54 are due to the fact that, at this pH value, only Ti is in the passive state on the Pourbaix diagrams,[23] while Al, V and Zr are placed in the active state and so, some dissolution and repassivation processes take place, conducting to the variations of E_{oc} for about 500 exposure hours.

At pH = 5.52, only V is in the corrosion state, Ti, Al and Zr are passive; so, a more stable values of the open circuit potentials can be observed because of more compact passive layer that contains the resistant Al_2O_3 and ZrO_2 oxides.[10,22]

In neutral saliva of pH = 8.21, the open circuit potentials of Ti-6Al-4V-1Zr alloy stabilized at very electropositive values (about +0.2 V) after 3000 immersion hours, showing a very resistant, compact passive layer; at this pH value, all constituent elements (Ti, Al, V, Zr) are placed in the passivation state on the Pourbaix diagrams,[23] contributing with their insoluble oxides to the formation of the passive layer.

Ternary Ti-6Al-4V alloy presented some oscillations of E_{oc} values (Figure 7) suggesting some dissolution and repassivation processes of the passive layer.[29,32-34] Also, all E_{oc} values of ternary Ti-6Al-4V alloy have more electronegative values than of quaternary Ti-6Al-4V-1Zr alloy, pointing out a more stable passive state for the new alloy, due to the passive ZrO_2 oxide[10,22] that is presented in the passive layer.

In the presence of fluoride ions, open circuit potential changed to more electronegative values due to the negative effect of F^- ion;[24,30,35] the same tendency to stabilize and to ennoble was registered, showing a good, resistant passive layer.

Improvement of corrosion resistance from in time variations of the open circuit potential gradients

From Table 5 can be observed that, till present (3000 exposure hours), the open circuit potential gradients have low values (between 0.001 and 0.228 V) which cannot generate galvanic or local corrosion; because only differences of 0.6 – 0.7 V can initiate and keep galvanic cells.[24,27]

Table 5. Open circuit potential gradients in Carter-Brugirard saliva

Time (h)	Alloy	ΔE_{oc1} (V)	ΔE_{oc2} (V)	ΔE_{oc3} (V)	ΔE_{oc4} (V)
100	Ti6Al4V	+0.112	+0.042	-0.070	+0.058
	Ti6Al4V1Zr	+0.085	-0.060	+0.085	-0.095
500	Ti6Al4V	+0.038	+0.075	-0.017	+0.053
	Ti6Al4V1Zr	+0.045	-0.013	+0.048	-0.101
1000	Ti6Al4V	+0.164	+0.146	-0.018	+0.044
	Ti6Al4V1Zr	-0.126	-0.089	-0.126	-0.008
2000	Ti6Al4V	+0.198	+0.199	+0.001	+0.033
	Ti6Al4V1Zr	-0.187	-0.104	-0.083	-0.062
3000	Ti6Al4V	+0.228	+0.231	+0.003	+0.014
	Ti6Al4V1Zr	-0.199	-0.221	-0.079	+0.079

Improvement of corrosion and ion release rates from Tafel curves

From Tafel curves, the corrosion current densities and corrosion rates were obtained (Table 6); also ion release rates were calculated. The new Ti-6Al-4V-1Zr alloy has a very good anticorrosive resistance, being classified as "Perfect Stable" and "Very Stable". The ternary Ti-6Al-4V alloy presented slow higher corrosion rates than quaternary Ti-6Al-4V-1Zr alloy, situated in the "Very Stable" category.[27]

CONCLUSIONS

The corrosion resistance improvement of the new Ti-6Al-4V-1Zr alloy in comparison with ternary Ti-6Al-4V alloy in Ringer-Brown solution was proved by the more electropositive corrosion potentials, lower passive current densities and better tendency to passivation, resulting from the beneficial influence of Zr. Impedance spectra revealed better protective properties of the passive layer on the surface of the new alloy.

Table 6. Corrosion current density, corrosion and ion release rates in Carter-Brugirard saliva

pH	Alloy	i_{corr} ($\mu A/cm^2$)	V_{corr} ($\mu m/yr.$)	Resistance class	Ion release rate (ng/cm^2)
2.54	Ti6Al4V	0.140	1.601	VS	162.66
	Ti6Al4V1Zr	0.092	1.054	VS	411.89
5.52	Ti6Al4V	0.135	1.534	VS	155.85
	Ti6Al4V1Zr	0.137	0.984	PS	99.97
8.21	Ti6Al4V	0.125	1.421	VS	144.37
	Ti6Al4V1Zr	0.082	0.944	PS	95.91
8.91	Ti6Al4V	0.153	1.742	VS	176.98
	Ti6Al4V1Zr	0.090	1.028	VS	104.46
8.21+NaF	Ti6Al4V	0.161	1.832	VS	196.13
	Ti6Al4V1Zr	0.133	1.511	VS	153.81

PS – Perfect Stable; VS – Very Stable

In Carter-Brugirard artificial saliva it resulted the same more favorable values of all electrochemical parameters for Ti-6Al-4V-1Zr alloy. Open circuit potentials tend to more electropositive values, denoting an increase of the passive film thickness. Fluoride ions had a slight negative influence on the corrosion and ion release rates, without to affect the very good stability of the new Ti-6Al-4V-1Zr alloy.

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