

Corrosion Resistance of a New Titanium Base Implant Alloy in Simulated Human Biofluid

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A new Ti-10Zr-5Ta-5Nb alloy that contains only non-toxic elements was obtained and its anticorrosive resistance was studied in simulated physiological fluids (Ringer solution), in extreme functional conditions, namely acid, neutral and alkaline pH. The electrochemical techniques of potentiodynamic and linear polarization were used to characterize this behaviour. The open circuit potentials and the possible open circuit potential gradients that could appear due to the non-uniformity of Ringer solution pH were simulated, calculated and monitored for 750 h. Ti and Ti-10Zr-5Ta-5Nb alloy are both self-passivated in Ringer solutions. All electrochemical parameters are better for the alloy than for Ti, proving the beneficial effects of the alloying elements. Corrosion rates and ion release have lower values than those of Ti, describing the alloy as very stable. Open circuit potentials revealed more stable and more electropositive values for alloy than for base metal.

Keywords: Ti-Zr-Ta-Nb alloy; non-toxic elements; corrosion rates; open circuit potential gradients

Materials used as permanent implants must possess corrosion resistance, biocompatibility, vitality and elasticity. Titanium base materials partly realize these conditions. Titanium and its Ti-6Al-4V alloy were frequently used in orthopaedic applications. But, it was proved that vanadium is a toxic material both as element and as oxide V_2O_5 [1]. Now, new titanium base alloys without vanadium are developed [2-9].

Several metallic elements can be used as β stabilizer for titanium alloys: Fe, V, Ta, Nb, Mo, Ni, Cr, etc.; α stabilizer can be: Al, O and Zr [10,11].

Protective oxides on the alloy surface are in contact with human cells and fluids and by friction, wear and corrosion can release their component ions in surrounding tissues. Therefore, is very important to analyse the biocompatibility of the individual elements [1,12]. In this way was proved that only Nb, Ta, Ti and Zr are biologically inert and may be used as alloying metals for long term implants [1].

There is a number of alloys used for biomedical applications such as: Ti-15Mo-5Zr-3Al [13-15], Ti-12Mo-6Zr-2Fe [16], Ti-30Nb, Ti-30Ta [17,18], Ti-6Al-7Nb, Ti-13Nb-13Zr [19-23].

In recent times it was proved that the following titanium base alloys may be used as implants: Ti-15Zr-4Nb-4Ta [24,25], Ti-15Zr-4Nb [26,27], Ti-5Al-2Nb-1Ta [28], Ti-23Ta [29]. These alloys contain only non-toxic elements, have a good resistance to corrosion, a good biocompatibility and mechanical resistance, observing the necessary conditions for an implant, but they have a very high cost that cannot be made accessible to patients with low or middle incomes.

A new Romanian, cheaper alloy that contains only non-toxic elements Ti-10Zr-5Ta-5Nb was obtained. Anti-corrosive resistance of this new alloy was studied in simulated physiological fluids, Ringer solution, in extreme functional conditions, namely acidic, neutral and alkaline pH. Acidic pH appears after surgery (because the hydrogen ions concentration increases in the traumatic tissues) and by the hydrolysis in time of the protective oxides [30,31]; alkaline pH forms rarely, in the illness periods of the human body [32].

Experimental part

Ti-10Zr-5Ta-5Nb alloy was obtained by vacuum melting. An electron beam furnace type EMO 80, with an installed power of 80 kW was used. The alloy synthesis was performed in two steps under vacuum, consisting in melting and re-melting both with cooling stages inside furnace. The chemical composition, in weight % was: Zr – 9.12; Nb – 4.09; Ta – 4.16; Fe – 0.036; O₂ – 0.195; N₂ – 0.004; H₂ – 0.0016; Ti – up to the balance.

The electrodes were grinded with emery paper and aluminium paste to mirror surface, fixed in a Stern-Makrides mount system, rinsed with distilled water, degreased in boiling benzene and dried.

All measurements were carried out in Ringer solution of pH = 2.33 (obtained by HCl addition), pH = 7.1 (normal pH) and pH = 9.12 (obtained by KOH addition). Solution composition as (g/L) is: NaCl – 6.8; KCl – 0.4; CaCl₂ – 0.2; MgSO₄·7H₂O – 0.2048; NaH₂PO₄·H₂O – 0.1438; NaHCO₃ – 1.1; glucose – 1. Temperature was 37^o ± 1^oC and was constantly maintained by a thermostated bath for short-term experiments and by a drying oven for long-term experiments.

An electrochemical glass cell with three electrodes provided with a central inlet for the electrode assembly, a cylindrical platinum grid counter electrode, a Luggin probe connected with a saturated calomel electrode (SCE) was used.

The electrochemical techniques of potentiodynamic and linear polarization were used. Cyclic potentiodynamic measurements were applied starting from -0.5 V to +4.0 V (versus SCE) using a scan rate of 10 mV/s. Voltalab 80 equipment with a VoltaMaster 4 software was used for data processing. From the voltammograms, the main electrochemical parameters were determined: E_{corr} – corrosion potential, like the zero current potential; E_p – passivation potential; E_{cp} – complete passivation potential; ΔE_p – passive potential range; i_p – passive current density. If the reverse curve of cyclic voltammogram presents lower current densities than the current densities from the direct curve it results that the studied material has a passive, stable behaviour. If the reverse curve shows the higher

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lower current densities than the current densities from the direct curve it results that the pitting corrosion exists [33]. Linear polarization measurements (Tafel curves) were carried out for ± 300 mV range around the open circuit potential (E_{oc}) with a scan rate of 10 mV/sec. The corrosion current densities i_{corr} and rates V_{corr} were obtained. The total amount of ions released in biofluid in ng/cm^2 was determined:

$$\text{Ion} \cdot \text{release} = -1.016 \cdot V_{corr} \cdot 10^5 \quad (1)$$

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

The open circuit potentials were monitored in time (750 exposure hours) and with pH values. The possible open circuit potential gradients that could appear due to the non-uniformity of Ringer solution pH, $\Delta E_{oc}(pH)$ were simulated, calculated and monitored for 750 h. Values of the following differences were discussed:

$$\Delta E_{oc1}(pH) = E_{oc}^{pH=2.33} - E_{oc}^{pH=7.1} \quad (2)$$

$$\Delta E_{oc2}(pH) = E_{oc}^{pH=2.33} - E_{oc}^{pH=9.12} \quad (3)$$

$$\Delta E_{oc3}(pH) = E_{oc}^{pH=7.1} - E_{oc}^{pH=9.12} \quad (4)$$

Results and discussions

Corrosion resistance in Ringer solution of pH = 2.33

From figure 1 it results that the Ti-10Zr-5Ta-5Nb alloy has a self-passivated metal behaviour, without active – passive dissolution potential range and with a large passive potential range >4 V (table 1). The corrosion potential for Ti-10Zr-5Ta-5Nb alloy located at -0.247 V (table 1) is more electropositive than that of Ti and is placed on the Pourbaix diagrams [34] in the passive potential range of titanium, tantalum and niobium and in the corrosion potential range of zirconium. However, taking into account that in the human body can not be reached potentials higher than $+0.5$ V [35], the corrosion of zirconium can not take place and the alloy is in the passive stable state with a relative low passive current density of $120 \mu\text{A}/\text{cm}^2$ (table 2).

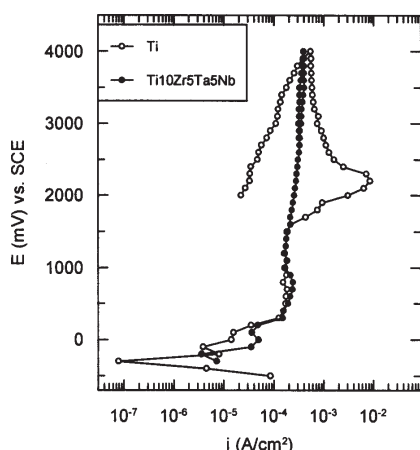


Fig. 1 Cyclic potentiodynamic curve in Ringer solution of pH = 2.33 at 37°C for Ti and Ti-10Zr-5Ta-5Nb alloy

From Tafel curve (fig. 2) of linear polarization, a relative higher corrosion rate and total quantity of ions released in the physiological environment than of titanium resulted, the Ti-10Zr-5Ta-5Nb alloy being placed in “Stable” resistance class and titanium in “Very Stable” resistance class (table 2). Taking into account that, this pH = 2.33 appears very rarely in the human body and considering the fact that the alloy would continually work for 20 years in a physiological environment that all the time would have pH = 2.33, the alloy would corrode with 0.2 mm in all this

period. It results that the implant would resist very good for 20 years even in these extreme conditions of very high acidity.

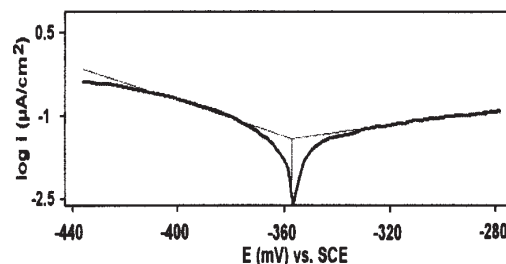


Fig. 2 Tafel curve in Ringer solution of pH=2.33 at 37°C for Ti-10Zr-5Ta-5Nb alloy

Corrosion resistance in Ringer solution of pH = 7.1

In normal Ringer solution of pH = 7.1, that exists in human body the most part of the time, both titanium and Ti-10Zr-5Ta-5Nb alloy are self-passivation (fig. 3) and have a large passive potential range, >4 V and reduced passive current densities of $86 \mu\text{A}/\text{cm}^2$ and respectively $30 \mu\text{A}/\text{cm}^2$ (table 1). The corrosion potential of alloy of -0.507 V is very closed to that of -0.47 V for Ti, and shows that all constituent elements are in the passive state on the Pourbaix diagrams [34]; so, the alloy is passive and resists both to uniform and pitting corrosion.

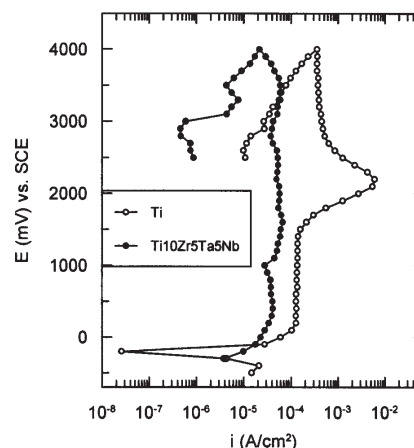


Fig. 3 Cyclic potentiodynamic curve in Ringer solution of pH = 7.1 at 37°C for Ti and Ti-10Zr-5Ta-5Nb alloy

The corrosion rates and “ion release” data (table 2) for alloy have lower values than those for titanium, describing the alloy as “Very Stable”.

Corrosion resistance in Ringer solution of pH = 9.12

In alkaline Ringer solution of pH = 9.12, that accidentally can appear in the human body, titanium and Ti-10Zr-5Ta-5Nb alloy also presented self-passivation behaviour (fig. 4), having a large passive potential range (>4 V) and reduced passive current densities (table 1). All electrochemical parameters (table 1) are more favourable for the alloy than for titanium, proving the beneficial effects of the alloying elements.

Taking into consideration the value of the corrosion potentials of Ti and Ti-Zr-Ta-Nb alloy from the Pourbaix diagrams [34], it results that both Ti and all alloying elements Zr, Ta and Nb are in the passive state, so, the alloy also is in the passive, stable, resistant state.

From Tafel curve it resulted low values for corrosion rate and “ion release” in the “Very Stable” class (table 2) for Ti-10Zr-5Ta-5Nb alloy and in “Stable” class for Ti.

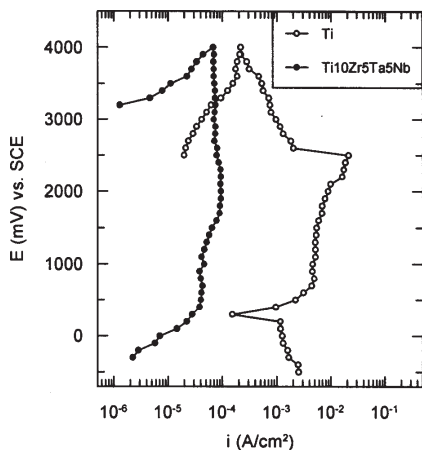


Fig. 4 Cyclic potentiodynamic curve in Ringer solution of $pH = 9.12$ at $37^{\circ}C$ for Ti and Ti-10Zr-5Ta-5Nb alloy

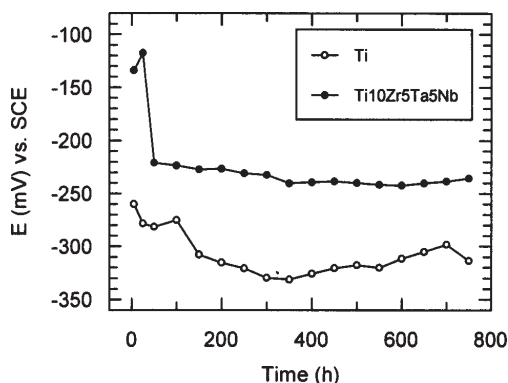


Fig. 5. Monitoring of open circuit potentials for Ti and Ti-10Zr-5Ta-5Nb alloy in Ringer solution of $pH = 2.33$ at $37^{\circ}C$

Monitoring of open circuit potentials

In acid Ringer solution of $pH = 2.33$ (fig. 5), the alloy revealed more stable and more electropositive open circuit potential values than of base metal. These values are placed on Pourbaix diagrams in the passive potential range of Ti, Ta and Nb and in the corrosion potential range of Zr; so, the favourable influence of Ta and Nb product the ennobled of the open circuit potential of the alloy.

In neutral Ringer solution of $pH = 7.1$ (fig. 6), the open circuit potentials of the alloy are nobler than that of titanium

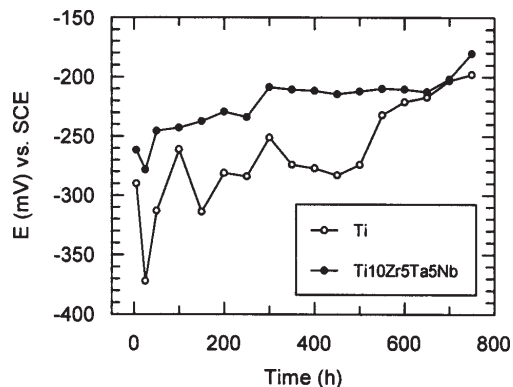


Fig. 6. Monitoring of open circuit potentials for Ti and Ti-10Zr-5Ta-5Nb alloy in Ringer solution of $pH = 7.1$ at $37^{\circ}C$

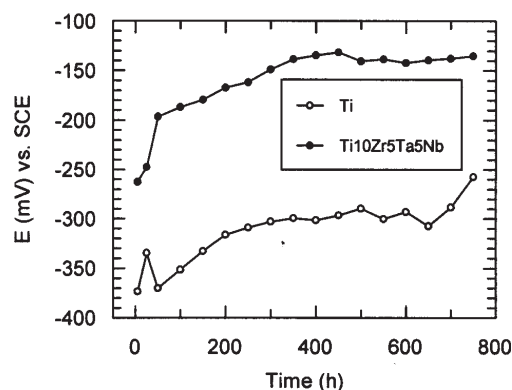


Fig. 7. Monitoring of open circuit potentials for Ti and Ti-10Zr-5Ta-5Nb alloy in Ringer solution of $pH = 9.12$ at $37^{\circ}C$

and tend to reach value of about -200 mV, that characterizes a passive state for all alloying elements in the Pourbaix diagrams. This behaviour shows that the passive films became more stable and resistant.

In alkaline Ringer solution of $pH = 9.12$ (fig. 7), the open circuit potentials for Ti-10Zr-5Ta-5Nb alloy are more electropositive than of Ti showing that the passive films formed on the alloy surface are non-reactive and more resistant than those formed on the titanium surface. The

Table 1
MAIN ELECTROCHEMICAL PARAMETERS FOR Ti AND Ti-10Zr-5Ta-5Nb ALLOY IN RINGER SOLUTION OF DEFFERENT pH VALUES, AT $37^{\circ}C$

pH	Biomaterial	E_{corr} (V)	E_p (V)	ΔE_p (V)	i_p ($\mu A/cm^2$)
2.33	Ti	-0.66	-0.66	>4	127
	Ti-10Zr-5Ta-5Nb	-0,257	-0,257	>4	120
7.1	Ti	-0.48	-0.48	>4	86
	Ti-10Zr-5Ta-5Nb	-0,507	-0,507	>4	30
9.12	Ti	-0.72	-0.72	>4	218
	Ti-10Zr-5Ta-5Nb	-0,373	-0,373	>4	32

Table 2
CORROSION RATES AND ION RELEASE FOR Ti AND Ti-10 Zr-5Ta-5Nb ALLOY IN RINGER SOLUTION OF DEFFERENT pH VALUES, AT $37^{\circ}C$

pH	Biomaterial	i_{corr} ($\mu A/cm^2$)	V_{corr} ($\mu m/an$)	Resistance class	Ion release (ng/cm^2)
2.33	Ti	0.746	8.36	Very Stable	876.81
	Ti-10Zr-5Ta-5Nb	0.940	10.96	Stable	1113.5
7.1	Ti	0.822	9.5	Very Stable	969.2
	Ti-10Zr-5Ta-5Nb	0.231	2.70	Very Stable	274.3
9.12	Ti	1.19	13.76	Stable	1398.02
	Ti-10Zr-5Ta-5Nb	0.146	1.70	Very Stable	172.7

tendency to reach a stable state in time proves a very good stability of these passive layers.

Monitoring of open circuit potential gradients

From table 3 can be observed that the highest value of the open circuit potential gradients for Ti is (in absolute value) 0.089 V and for Ti-10Zr-5Ta-5Nb alloy is 0.100 V. It was shown that, only differences of 0.6 V – 0.7 V can initiate and maintain galvanic cells [36,37]. Therefore, the open circuit potential gradients determined for Ti and Ti-10Zr-5Ta-5Nb alloy cannot generate galvanic or local corrosion, even in the extreme case of a very large pH difference of 2.33 and 9.12.

Table 3
OPEN CIRCUIT POTENTIAL GRADIENTS FOR Ti
AND Ti-10 Zr-5Ta-5Nb ALLOY IN RINGER SOLUTION

Biomaterial	Time (h)	ΔE_{oc1} (V)	ΔE_{oc2} (V)	ΔE_{oc3} (V)
Ti	50	+0.032	+0.089	+0.057
	250	-0.037	-0.012	+0.025
	500	-0.044	-0.028	+0.016
	750	-0.116	-0.056	+0.060
TiZrTaNb	50	+0.025	-0.024	-0.049
	250	+0.003	-0.69	-0.072
	500	-0.028	-0.099	-0.072
	750	-0.055	-0.100	-0.045

Conclusions

The corrosion behaviour and main electrochemical parameters that characterize the behaviour of the new implant alloy Ti-10Zr-5Ta-5Nb in Ringer solution of acid, neutral and alkaline pH values simulating the normal and extreme functional conditions of an implant was studied.

In Ringer solution of acid pH < 3, corrosion rate shows behaviour in the "Stable" category and the main electrochemical parameters characterize the alloy as being passive and resistant.

In Ringer solution of normal pH = 7.1, the Ti-10Zr-5Ta-5Nb is "Very Stable", is self-passivated and all electrochemical parameters have values favourable for a good stability and resistance to corrosion.

In Ringer solution of alkaline pH > 9, the Ti-10Zr-5Ta-5Nb alloy also presented a good resistance to corrosion and a stable passive state.

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