The Corrosion Behavior of TiMoZrTa Alloys Used for Medical Applications

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Titanium alloys are widely used as biomaterials for their excellent properties. In the last years, low modulus β-type Ti-based alloys are being developed. The aim of this paper is developing two original Ti-based alloys improved with non-toxic elements and to evaluate the electrochemical response of this alloys. The alloys electrochemical corrosion resistance using cyclic voltammetry was determined in Ringer solution, at 37°C. An important factor in biocompatibility is stability of implant materials and the changes parameters of experimental electrochemical data are discussed.

Keywords: biomaterials, corrosion, voltammetry , TiMoZrTa alloys

Biomaterials used for medical applications include various applications and must exhibit specific properties. The most important property of materials used for fabricating implants is biocompatibility, followed by corrosion resistance. The main metallic biomaterials are stainless steels, cobalt alloys and titanium alloys [1-5].

Ti-based alloys are used as biomaterials due to their excellent mechanical properties and good biocompatibility. Pure titanium and Ti-6Al-4V are still the most widely used ones for biomedical applications. The development of β-type titanium alloys are increasing to reduce the modulus of the implants to the level equivalent to that of human bone. A higher elastic modulus and strength of alloys than of the human bone, may result the stress shielding phenomena and failure of implants [6, 7].

The development of new Ti-based alloys containing non-toxic elements for biomedical application is highly required. The alloying elements which are considered non-toxic and non-allergenic through the reported data of cell viability for pure metals, polarization resistance and tissue compatibility, are: Nb, Ta, Zr, Sn, Mo, Fe and Hf [8, 9].

The corrosion resistance of an implant can influences the functional performance and durability. The purpose of this work was to study the electrochemical behavior of two origin alloys: Ti15Mo7Zr5Ta(Ti15MZT) and Ti20Mo7Zr5Ta(Ti20MZT) in Ringer solution, with possible medical application. Electrochemical principles are very useful to understanding the factors affecting corrosion resistance of alloys studied [10, 11].

Experimental part

The alloy was obtained from the melting of the pure elements (Ti, Mo, Zr and Ta) in arc melting furnace MRF vacuum ABJ 900. The ingot experimentally obtained were remelted six times in order to homogenize chemically the alloy.

The chemical composition of the alloy was analysis with VegaTescan LMH scanning electron microscope manufactured by the TESCAN Co., the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by the BRUKER/ROENTEC Co., Germany.

The metallographic structure was investigated using optical microscopy Leica 5000DMI. Metallographic structure of alloy was shown after the attack surface with a chemical solution having the following composition: 10 mL HF, 5 mL HNO_3, 85 mL H_2O immersed in 5-30s.

For phase analysis, XRD analysis was carried out using a X'Pert Pro MPD diffractometer. Parameters used for sample analysis are: a range of angle θ-2 θ between 20° - 80°; continuous scanning; step size 0.0131303; time per step 60 s; scan speed 0.054710 (°/s); number of steps 6093; use a copper X-ray tube.

Measurements of electrochemical stability were conducted with an Volta Lab 21 Economical Potentiostat. To evaluate the TMZT alloy stability, potentiodynamic and cyclic polarization measurements were recorded in Ringer's solution: Na 3.38 g/L, K 0.16 g/L, Ca 0.09 g/L, Cl 5.52g/L. The temperature of electrolyte was 23 ± 1°C. Potentiodynamic polarization curves were carried out with a scan rate of 1mV/s in the range from -500 to 1500 mV and cyclic polariation curves with a scan rate of 10 mV/s in the range from -1500 to 1500 mV.

Results and discussions

The chemical analyses (EDX) of the alloys studied were performed in many different points. The chemical composition are shown in table 1. EDX mapping showed a uniform distribution of elements and a homogeneous alloy.

The phase constitution of the TMZT alloys was identified by metallographic analysis and X-ray diffraction analysis. Optical microstructure of experimental alloys studied present acicular (dendritic) structure with irregular grain boundaries (fig. 1). The microstructure of TiMoZrTa alloy is a specific β-type [12-15].

XRD analysis was carried out to identify the constituient phases of the sample at room temperature. As presented in figure 2, in alloy studied were found two phases: α" with orthorhombic structure and β with a body-centered cubic structure. The β phase consists majority in the sample while α" is minor phase.

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Table 1
CHEMICAL COMPOSITION OF THE TMZT SAMPLE AFTER MELTING

Element	Mo	Zr	Ta	Ti
wt.(%)	14.56	6.34	4.63	Balance
	18.49	6.45	5.17	Balance

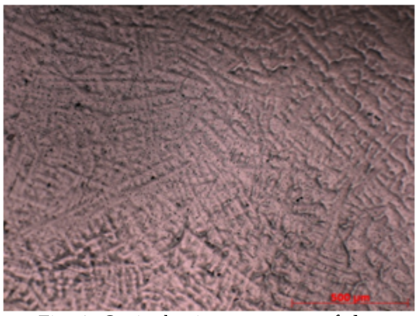

Fig. 1. Optical microstructure of the reprezentative T15MZT alloy

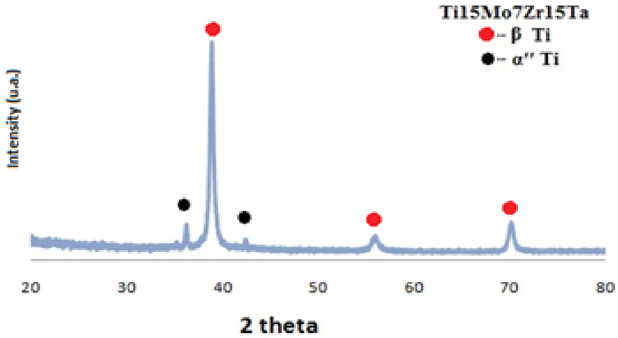

Fig. 2. Reprezentative XRD patterns of T15MZT

Table 2
THE ELECTRO-CHEMICAL DATA OBTAINED FOR THE ALLOY

Sample	E_0 [µV]	b_a [µV]	b_c [µV]	R_p [kΩ/m²]	J_{cor} [µA/cm²]	V_{cor} [nm/an]
Ti15MZT	-461.2	117.9	-39.5	22.00	1.0834	12.67
Ti20MZT	-331.1	161.3	-143.0	0.47	40.0429	468.3

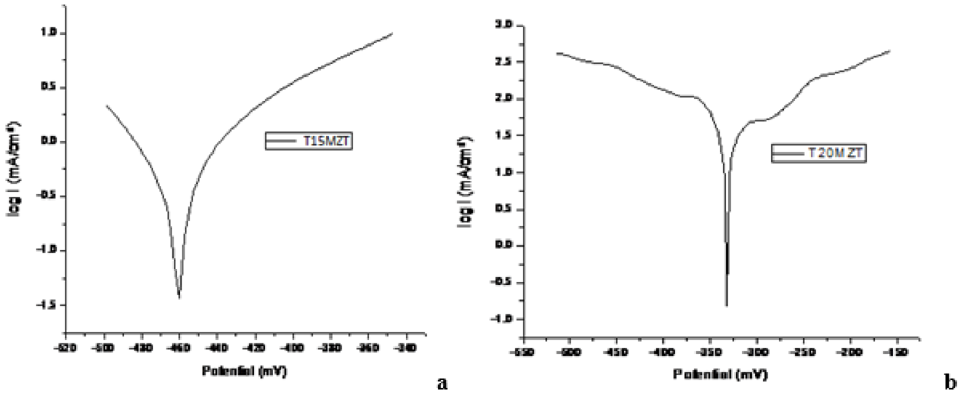

Fig. 3. Potentiodynamic polarization curves for the experimental alloys: a) T15MZT; b)T20MZT

In figures 3 and 4 are shown the potentiodynamic and cyclic polarization curves for the experimental alloys. From the Tafel linear curve was extracted the key process parameters (table 2), showing a very good behavior at corrosion of alloys and a small corrosion speed than 12.67 µm / Y for sample Ti15MZT.

Tafel slopes (fig. 3) are determined by adjustment an empirical curve with experimental curve in ± 100 mV domain around E_0 value. Branch anodic polarization curve provides information on the rate of anodic dissolution, of transition active-passive, of potentials and areas passivation. The polarization resistance was determined from the tangent to the polarization curve in point (E_{cor}, J = 0). The polarization resistance is directly proportional to the corrosion resistance, since the resistance is the larger with that much the material is more resistant to corrosion [16].

In figure 4 is presented the curve cyclic of corrosion process which do not show the character of pitting. In the cathode active branch (curve return) almost overlaps the anode branch, both being practically linear, in this area corrosion current is directly proportional to alloy pottential. Cyclic polarization curve shape is characteristic

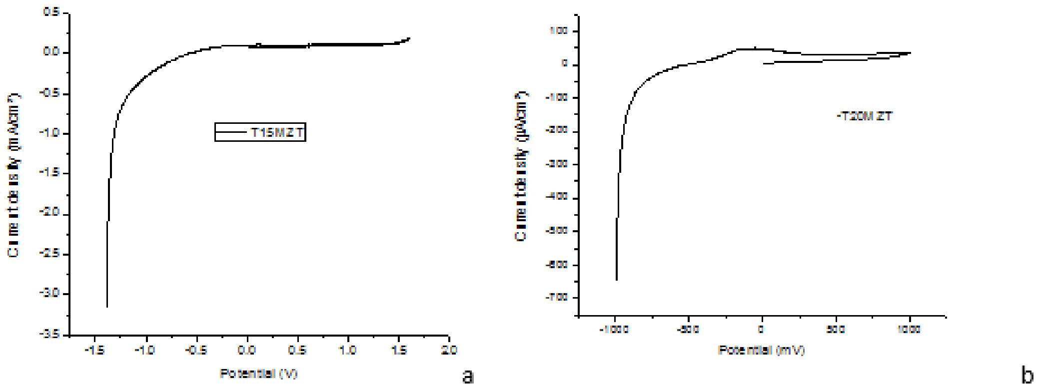

Fig. 4. Cyclic polarization curves for the experimental alloys: a) T15MZT; b)T20MZT

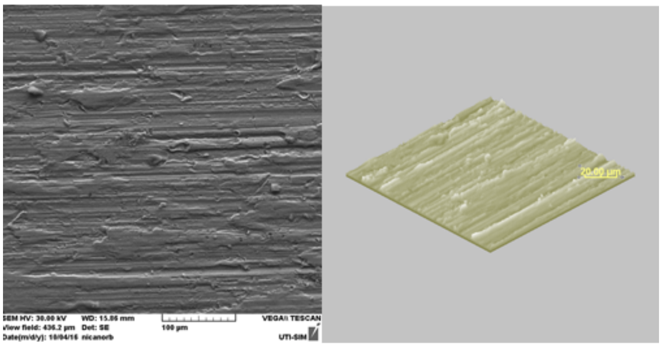

Fig. 5. SEM images for T15MZT alloy immersed in Ringer solution
a) 500 x; b) 3D morphology

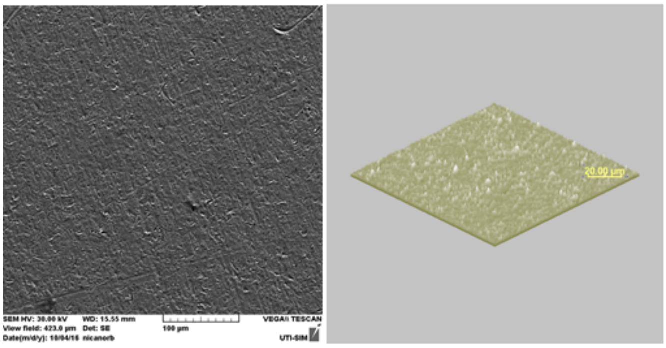

Fig. 6. SEM images for T20MZT alloy immersed in Ringer solution
a) 500 x; b) 3D morphology

generalized corrosion showing a passive-active transition preceded by an area where the current is practically independent of potential and completed with a region of significant increase in current density. It may be noted that the material is highly resistant to corrosion in a wide potential range [17-18].

Figures 5 and 6 showing the SEM surface of the experimental alloys after the corrosion test in Ringer solution and 3D morphology of the surface. Noticing the SEM images it reveals a rather uniform topography and the observable defects corespond to small scrathes remaining from the prior polishing of the surface.

In another paper was studied the electrochemical behaviour of TiMoNb alloys used in implantology [19].

Conclusions

Ti-based alloys display a variety of properties which depend to chemical composition. It is very important to know the phase transformation of a metallic biomaterial, like Ti and its alloys, to control the mechanical properties and corrosion resistance.

The two alloys of TMZT were obtained in arc melting furnace. The metallographic analysis and X-ray diffraction analysis shows that have dual phases with β phase consists majority while α" is minor phase. The experimental alloys have a good corrosion behavior after testing in Ringer solution. Although the Ti15MoZrTa showed to be more resistant to corrosion in physiological human fluids.

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