Electrochemical Behaviour of Ti-Mo Alloys for Medical Application in Biological Solution

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Abstract. Nowadays, primordial concern represent population health with all materials that are used in medical applications. It were obtained three alloys of titanium with addition of elements like molybdenum, zirconium and tantalum, in a vacuum arc melting furnace (VAR), in argon atmosphere. These alloys were investigated in biological solution, similar with to the human body by electrochemical study method (linear and cyclic polarization). Results revealed that it possesses a good behaviour which does not influence the human body, with future applications in medical field.

1. Introduction
Metallic materials are used of a few thousand years ago for the reconstruction of tissues in the human body but important progress they have achieved in the last century [1-3]. Applications of the biomaterials are found in applications such as orthopedics, cardiovascular surgery, ophthalmology, dentistry, urology, aesthetic surgery, neurology etc. Titanium-based alloys are commonly found in medical applications for properties close to the tissue that prostheses it like mechanical properties, biocompatibility and corrosion resistance. The most used titanium alloy is the Ti4Al6V alloy, which has remarkable physico-mechanical, chemical and biocompatibility characteristics. However, vanadium being expensive and toxic, began to be replaced with various biocompatible elements: Fe, Si, Ta, Zr, Mo etc., [4-7].

As implant materials are also used precious and semi-precious metals, or alloys thereof, based on silver, platinum, zirconium or niobium, but which currently have too high a cost price and are therefore far from common use in the realization of implants.

Three TiMoZrTa (TMZT) alloys for medical applications have been designed based on the literature. Alloying elements such as Mo, Zr and Ta alloyed with titanium, have very good characteristics, close to human bone. All elements are biocompatible with human tissue, which means that the proposed alloys can be used successfully in medical applications [8-9].

This work highlights corrosion behavior of Ti15Mo7ZrXTa (where x = 5, 10, 15 wt%) alloys. Corrosion monitoring is the practice of qualitative assessment and quantitative measurement of the corrosion of an environment on a metal or alloy immersed in this environment. Monitoring tests can be performed using mechanical, electrical, electrochemical or chemical methods. Corrosion processes
depend on the nature of the metal and the corrosive environment, the conditions of pressure and temperature, the static or dynamic conditions of the corrosive environment [10-15].

2. Experimental procedure

Three alloys were prepared by arc remelting method with MRF ABJ 900 equipment. The raw materials used: titanium (99.8%), molybdenum (99.8%), zirconium (99.8%), tantalum (99.5%), supplied by Alfa Aesar by Thermo Fisher Scientific. After elaboration, alloys were cut to specific dimensions without being thermally influenced.

The corrosion behavior of three alloys of TiMoZrTa with various compositions was studied. Alloys composition are presented in Table 1.

| Alloy       | Ti [wt. %] | Mo [wt. %] | Zr [wt. %] | Ta [wt. %] |
|-------------|------------|------------|------------|------------|
| Ti15Mo7Zr5Ta| 75.46      | 13.56      | 6.34       | 4.64       |
| Ti15Mo7Zr10Ta| 73.63      | 12.33      | 6.80       | 7.24       |
| Ti15Mo7Zr15Ta| 66.00      | 12.56      | 6.99       | 14.45      |

The study of corrosion behavior was done by electrochemical methods (Linear Potentiodynamic Polarization and Cyclic Potentiodynamic Polarization) in artificial (simulated) physiological environment.

Was prepared one of simulated physiological solutions, currently used in the literature for the study of alloys corrosion, respectively: Ringer's solution. This solution have the following compositions:

Ringer solution: NaCl – 9.00 g/L; NaHCO$_3$ – 0.20 g/L; CaCl$_2$6H$_2$O – 0.40 g/L; KCl – 0.43g/L; pH = 6.8.

The measurements were performed at 25°C, the solution being naturally aerated, the metal surface being freshly polished. The electrochemical corrosion studies and the characterization of the corroded surfaces were performed with The VoltaLab PGP 201 Potentiostat.

The VoltaLab PGP 201 Potentiostat (VolataLab 21) (Radiometer Analytical SAS - France) is a compact potentiostat / galvanostat that can be operated either manually, when programmed from the instrument panel, or with Voltamaster 4 acquisition and processing software. When operated manually the maximum potential scanning speed is 2.5 mV / s, and when operated with Voltamaster 4 the maximum scanning speed is 10 mV / s. The device, together with the operating system, allows the evaluation of the polarization resistance, the corrosion potential over long periods of time, the torque potential and tests to highlight the corrosion in points. Under these conditions the device is ideal for electrochemical corrosion studies.

VolataLab 21 was used for: obtaining anodic polarization curves, at low scanning speeds of the electrode potential, curves then used to evaluate the polarization resistance, the instantaneous corrosion current and the instantaneous corrosion rate; obtaining cyclic polarization curves, at scanning potential speeds of 10 mV/s based on which the type of corrosion was assessed and the corrosion rate under load was evaluated (when the alloy is polarized at potentials far from the corrosion potential); obtaining and processing potential dynamic data, both for the evaluation of the corrosion speed and for the analysis of the influence of the sweep speed on the electrochemical behavior.

A cell with three electrodes, horizontal, was used for the potentiodynamic measurements. The surface of samples exposed to corrosion media was in all cases equal to 0.283 cm$^2$. The samples were polished on SiC paper, degreased and washed with distilled water. A platinum electrode was used as an auxiliary electrode and a saturated calomel electrode as a reference.

3. Results and discussions

To obtain the electrochemical parameters that characterize the corrosion resistance of the developed TMZT alloys, the electrochemical study method by linear (Figure 1) and cyclic polarization (Figure 2) was used. These methods can directly and quantitatively determine the corrosion rate.
Corrosion represents the physical-chemical, spontaneous, irreversible and undesirable destruction of metals and alloys under the chemical, electrochemical or biological action of the environment.

The behavior of TMZT alloys during the electrochemical corrosion test at linear polarization is represented in Figure 1 by Tafel diagrams.

![Tafel diagrams of alloys investigated by corrosion test in Ringer's solution](image)

**Figure 1.** Tafel diagrams of alloys investigated by corrosion test in Ringer's solution: (a) Ti15Mo7Zr5Ta alloy, (b) Ti15Mo7Zr10Ta alloy, (c) Ti15Mo7Zr15Ta alloy.

The values of the electrochemical parameters for the TMZT alloys immersed in Ringer's solution are presented in Table 2.

**Table 2.** The main parameters of the corrosion process for TMZT alloys in Ringer's solution.

| Alloy          | $E_0$ [mV] | $\beta_a$ [mV] | $\beta_c$ [mV] | $R_p$ [k$\Omega$/cm$^2$] | $J_{cor}$ [$\mu$A/cm$^2$] | $V_{cor}$ [$\mu$m/year] |
|---------------|------------|---------------|---------------|-----------------|----------------|--------------------------|
| Ti15Mo7Zr5Ta  | -461.20    | 117.90        | -39.50        | 22.00           | 1.08           | 12.67                    |
| Ti15Mo7Zr10Ta | -400.10    | 92.10         | -91.20        | 46.22           | 0.37           | 4.31                     |
| Ti15Mo7Zr15Ta | -365.40    | 88.30         | -115.00       | 38.78           | 0.47           | 5.49                     |

![Cyclical diagrams of alloys investigated by corrosion test in Ringer's solution](image)

**Figure 2.** Cyclical diagrams of alloys investigated by corrosion test in Ringer's solution: (a) Ti15Mo7Zr5Ta alloy, (b) Ti15Mo7Zr10Ta alloy, (c) Ti15Mo7Zr15Ta alloy.

The corrosion potential ($E_0$) has values close to -400 [mV] for all TMZT samples. The best alloy, which has a much delayed corrosion priming is Ti15Mo7Zr15Ta having $E_0 = -365.4$ [mV], which suggests that it has a very high surface passivation chemical stability. The alloy with the most oxidation sensitive corrosion potential is Ti20Mo7Zr5Ta, having $E_0 = -461.20$ [mV].

Table 1 shows that the samples with very good corrosion resistance are Ti15Mo7Zr10Ta ($R_p = 46.22$ [k$\Omega$/cm$^2$]).

For all samples the process that takes place on the surface is the oxidation of titanium with the formation of an oxide adhering to the surface, which in fact produces the passivation of the alloy.
Corrosion rates (actually passivation rates) are of the same order of magnitude, relatively small for all alloys.

Figure 3. Surface area of the sample analysed after corrosion testing for: (a), (b) Ti15Mo7Zr5Ta alloy; (c), (d) Ti15Mo7Zr10Ta alloy; (e), (f) Ti15Mo7Zr15Ta.

Passivation of these alloys can be influenced by the presence of alloying elements as well as the presence of impurities in the material. Although titanium, in the context of the electrochemical series, is a metal that should corrode strongly, but due to the formation of an oxide layer, it remains passive in the human body, which makes it very useful in medical applications [10-13].

After investigating the alloys by linear and cyclic polarization, it is found that the elaborated TMZT alloys have surfaces slightly affected by corrosion, without traces of pitting corrosion.
SEM micrographs and surface chemical compositions highlight the formation of chemical compounds from the Ringer's solution on the surface of the alloy.

Analyzing the surface of the samples subjected to electrocorrosion in a simulated biological environment, slight unevenness is observed that follow the surface imperfections (non-formalities due to processing and deepened after corrosion), Figure 3.

4. Conclusions
The electrochemical behavior of TMZT alloys was investigated by the electrochemical study method (linear and cyclic polarization), and the selected corrosion medium was the Ringer's solution. The value of tantalum concentrations in the studied alloys is important in the case of corrosion studies. The higher percentage of tantalum show a better corrosion resistance (12.67 [µm/yr] for 5%Ta, 4.31 [µm/yr] for 10%Ta and 5.49 [µm/yr] for 15%Ta). The aspect of the corroded samples indicate that the passive oxide film formed on TMZT alloys is compact, has a uniform aspect with isolated corrosion compounds, specific feature of titanium alloys that resulting a good corrosion resistance.

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