EVALUATION OF THE CORROSION RESISTANCE OF Ti-Mo-W ALLOYS IN SIMULATED BODY FLUID (SBF)

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Titanium and its alloys due to their high strength-to-density ratio, excellent corrosion resistance and biocompatibility have an increasing use in the medical field and especially for implantology applications. The aim of this study is to investigate the influence of different contents of tungsten on the corrosion behavior of Ti-Mo-W alloys (where Mo = 15 wt.% and W = 5, 7, 9 and 11 wt.%) in simulated body fluid (SBF). The corrosion behavior in SBF of Ti-Mo-W alloys was studied by means of linear polarization technique by measuring the open circuit potential (EOC), for a period of 6 hours and plotting the Tafel curves from -200 mV (vs OCP) to +200 mV (vs OCP), with a scan rate of 0.167 mV / s. The tests were performed in SBF solution with a pH of 7.4 at the human body temperature (37±0.5°C). Based on the polarization curves the electrochemical parameters of oxidation for the investigated alloys were determined.

Keywords: titanium alloys; corrosion resistance; Tafel plots; SBF solution.

1. Introduction

Metals have been used as dental materials for over 100 years. Since the 1960, commercially pure titanium – cp Ti and some of its alloys become a popular metalic biomaterial and it is gaining more and more ground [1]. The choice of a material for dental applications depends on a number of factors: mechanical properties (especially the modulus of elasticity), corrosion behavior, biocompatibility, cost, etc. [2] but not all Ti alloys meet the requirements for biomedical applications and especially for implantology [3, 4].

Of the widely used metals, which meet these criteria, pure titanium (CP Ti) and Ti-6Al-4V alloy have been the most successful to date. But, as it turned out, the latter alloy presents some problems in use due to the release of Al and V ions into the human body which causes long-term health problems. Research of new titanium-based alloys to meet all these requirements, without affecting in one way or another the human body becomes necessary [5].

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Lately, the development of titanium-based alloys has gained momentum, with the formation of the beta phase, using non-toxic elements for the body and which have a good biocompatibility: Niobium, Tantalum, Ziconium, Molybdenum, Tungsten. Ti-Nb and Ti-Zr-based alloys were recently placed on the market to overcome the toxicity associated with Ti-6Al-4V alloys.

Current researches aims at developing implants that will serve for a longer period of time, without loss or revision operation, implants made of suitable materials without cytotoxicity, superior corrosion resistance in biological environment, excellently combined with high mechanical strength, low elasticity, high resistance to fatigue and wear, high ductility, excellent biological and mechanical compatibility, respectively [6, 7].

In the studies carried out up to now [8-13], the authors designed and developed alloys in the Ti-Mo-W system, and after several investigations and analyzes it was shown that they have good structural, mechanical and tribological properties, Even more recently attention was paid to the corrosion resistance behabior. In this paper we investigate the influence of different contents of tungsten on the corrosion behavior of Ti-Mo-W alloys in simulated body fluid (SBF) by means of linear polarization technique.

2. Materials, methods and experimental

2.1. Elaboration of alloys

For melting, alloying and homogenization remelting, a vacuum arc melting furnace model ABD MRF 900 (RAV) was used, which reaches a maximum temperature of 3700^{o}C and allows the melting of refractory metals with high melting temperatures (Ti-1668^{o}C, Mo-2896^{o}C, W-3695^{o}C). The ABD MRF 900 furnace ensures the possibility of melting the metal samples in vacuum (10^{-6} bar) or under protective atmosphere by means of a non-consumable mobile electrode made of tungsten-thorium. Samples can be obtained in small cylinders form (of different shapes and sizes) in a water-cooled copper base plate (max. 50^{o}C temperature).

The elaboration of Ti-Mo-W alloys (where Mo = 15 wt.% and W = 5, 7, 9 and 11 wt.%) did not raise special problems because Mo and W dissolve easily in titanium and the melting and re-melting ensures a good homogeneity, due to the intense stirring. At the same time, the removal of impurities by evaporation took place, due to the advanced vacuum (10^{-6} bar). Due to the very short cooling time, a single-phase structure β is obtained, which is a stable structure above 850^{o}C, and does not need for a solution or stress relief treatment.

After the first melting, alloys with a non-uniform structure and unmelted - undissolved metal inclusions were obtained (both molybdenum and undissolved tungsten inclusions were found). By remelting this problem has been solved (only one remelting is required).

Samples were obtained from each type of alloy in the form of small cylinders with a diameter of 30 mm, to be subjected to the corrosion test in simulated body fluid (SBF), starting from the basic alloy Ti-15Mo in which different tungsten contents were added (tungsten was added to reduce the modulus of elasticity). At the same time, the Ti6Al4V alloy was considered as control sample for the comparison. In Table 1 are presented the chemical composition of the alloys investigated in terms of corrosion resistance in SBF media.

Table 1

Chemical composition of alloys subjected to corrosion test

Code	**Alloy type**	**Chemical composition, wt. %**				
		W	Mo	Al	V	Ti
1	Ti15Mo11W	11.08	13.78	-	-	75.14
2	Ti15Mo9W	9.21	15.15	-	-	75.64
3	Ti15Mo7W	7.29	14.97	-	-	77.74
4	Ti15Mo5W	5.75	15.67	-	-	78.58
5	Ti6Al4V alloy	-	-	5.92	4.27	89.81

The results of the chemical composition (in wt.%) of alloys subjected to corrosion test were obtained using an EDS spectrometer (Quanta Inspect F50 microscope - Thermo Fisher Scientific Inc).

2.2. Corrosion testing

Corrosion resistance was determined in the Laboratory of Electrochemistry and Surface Functionalization, SIM, by linear polarization technique. This technique consists of the following steps:

- measuring the open circuit potential (E_{OC}), for a period of 6 hours.
- plotting the Tafel curves from -200 mV (vs OCP) to +200 mV (vs OCP), with a scanning rate of 0.167 mV / s.

Corrosion resistance tests were performed using a Potentiostat / Galvanostat (model PARSTAT 4000, manufacturer Princeton Applied Research, USA) to which a low current module was coupled (VersaSTAT LC, manufacturer Princeton Applied Research), and the potential dynamics curves (Tafel) were recorded using VersaStudio software. Electrochemical tests using the linear polarization technique were performed according to ASTM G5–94 (2011).

The corrosion tests were conducted in typical three-electrode electrochemical cell (Fig. 1), which consists of a saturated calomel electrode (SCE) (as reference electrode), a platinum electrode (as a counter electrode) and the working electrode which consisted of the investigated experimental samples. The electrochemical cell was introduced, during the corrosion tests, in a Faraday cage to eliminate the interferences due to the electromagnetic fields.

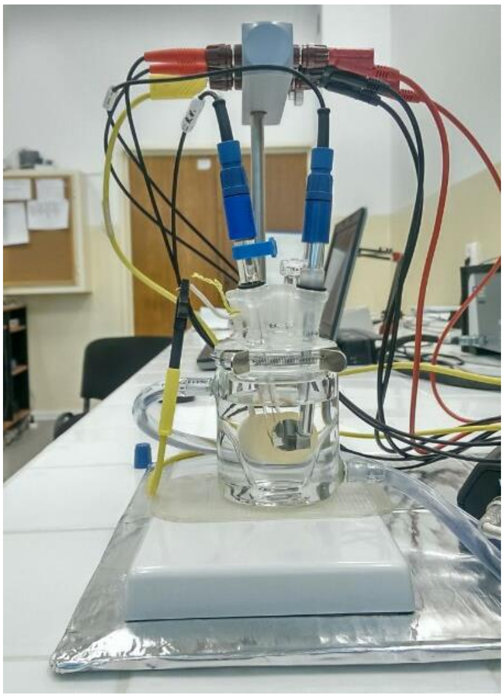

Fig.1. The electrochemical cell set-up used in the corrosion tests

The tests were performed at human body temperature (37 ± 0.5°C) with a heating and recirculation bath model CW-05G produced by Jeio Tech.

The tests were performed in simulated body fluid (SBF) (composition: 7.996 g / L NaCl, 0.350 g / L $NaHCO_3$, 0.224 g / L KCl, 0.228 g / L $K_2HPO_4 \cdot 3H_2O$, 0.305 g / L $MgCl_2 \cdot 6H_2O$, 40 mL 1 M-HCl, 0.278 g / L $CaCl_2$, 0.071 g / L Na_2SO_4, 6.057 g / L (CH_2OH) $3CNH_2$)) at pH = 7.4.

3. Results and discussion

To evaluate the corrosion behavior of the investigated Ti-Mo-W alloys, the samples were exposed to SBF media, and the main electrochemical parameters were extracted. To assess the corrosion rate for the Ti-Mo-W alloys, the polarization resistance method was used, through which the corrosion current density and the corrosion potential can be obtained. The current that occurs at the interface when the alloy is immersed in the solution represents the instantaneous corrosion current.

The Tafel plots corresponding to the tested samples are presented in Figs. 2-6. Based on the extracted parameters from the Tafel plots the polarization resistance (Eq. 1) and the corrosion rate (Eq. 2) were calculated.

The polarization resistance was calculated according to ASTM G59-97 (2014) [14] using the equation:

$$R_p = \frac{1}{2.3} \frac{\beta_a |\beta_c|}{\beta_a + |\beta_c|} \frac{1}{i_{corr}} \quad (1)$$

where: β_a – anodic Tafel slope; β_c – cathodic Tafel slope; i_{corr} – corrosion current density.

The corrosion rate was calculated according to ASTM G102-89 (2015) [15] using the equation:

$$CR = K_i \frac{i_{corr}}{\rho} EW \quad (2)$$

where: CR – corrosion rate; K_i – constant which defines the units of corrosion rate (3.27×10^{-3}); ρ – density; i_{corr} – corrosion current density; EW – equivalent weight.

For a good comparison of the results, the Tafel curves were superimposed in a single graph (Fig. 7).From the point of view of the corrosion potential (E_{cor}), it is considered that a more electropositive value of the E_{cor} corrosion potential indicates a better corrosion behavior. From this point of view, it is observed that Ti15Mo9W has the most electropositive value (51.8 mV) and thus it has a better corrosion behavior compared to the other alloys in the electrolyte used - SBF.

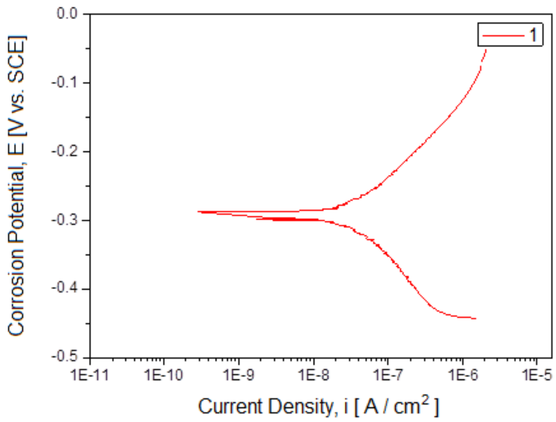

Fig. 2. Tafel curve of the Ti15Mo11W alloy

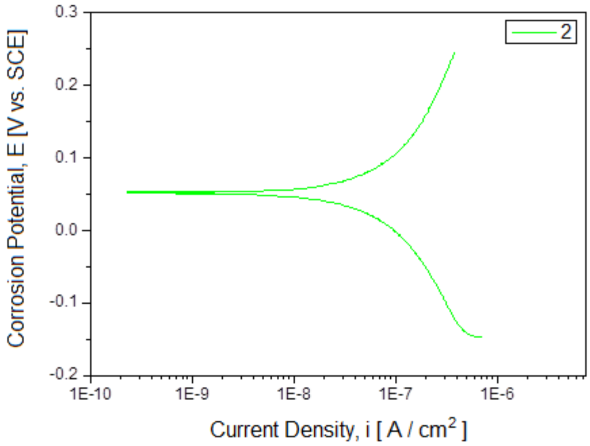

Fig. 3. Tafel curve of the Ti15Mo9W alloy

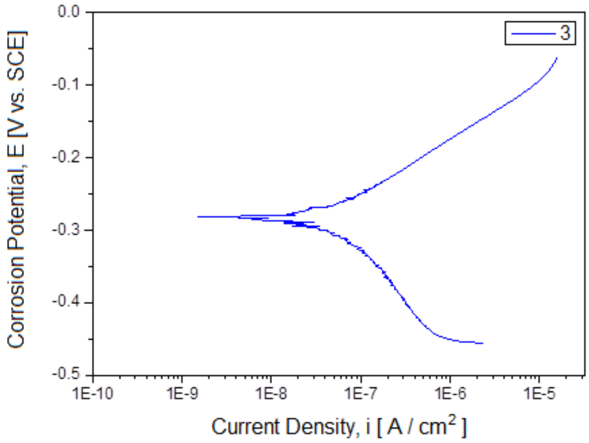

Fig. 4. Tafel curve of the Ti15Mo7W alloy

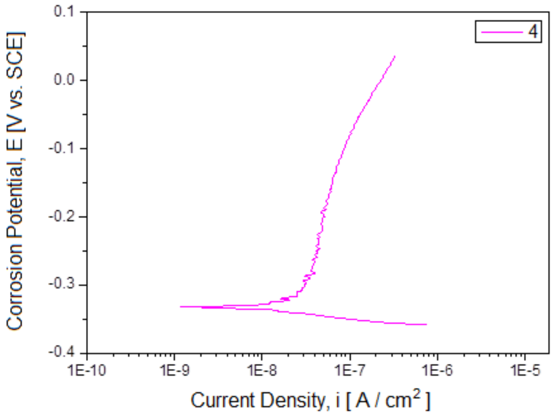

Fig. 5. Tafel curve of the Ti15Mo5W alloy

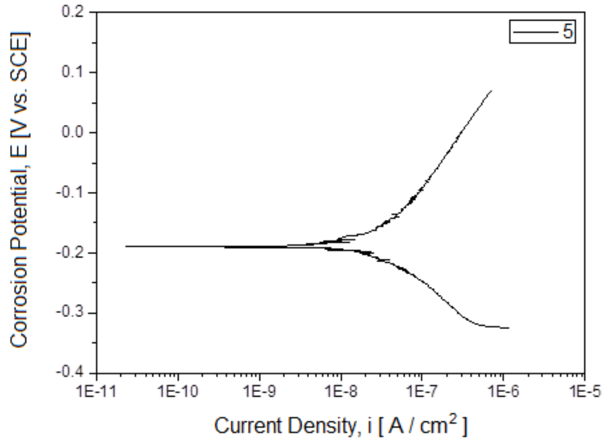

Fig. 6. Tafel curve of the Ti6Al4V alloy

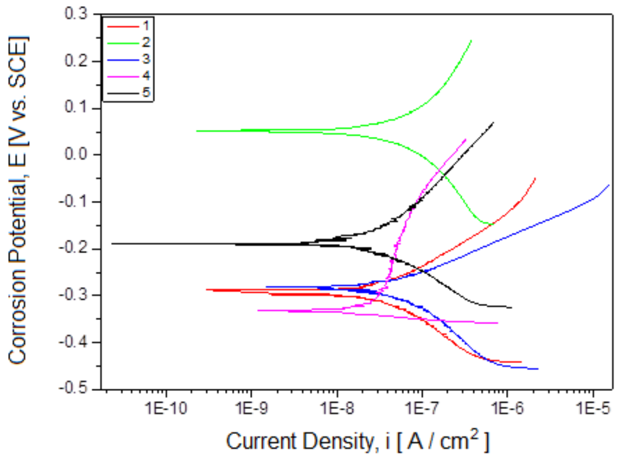

Fig. 7. Tafel curves of all investigated alloys

It is known that a small corrosion current density (i_{cor}) indicates a good corrosion resistance. Thus, if we consider this criterion, it is observed that Ti15Mo5W alloy has registered the smallest value (28.862 nA/cm^2) demonstrating that it has a better corrosion resistance compared to the other alloys investigated, while the highest value was obtained for Ti15Mo9W (105.649 nA/cm^2). Nevertheless, it can be observed that compared to the reference alloy Ti6Al4V, which have registered a corrosion current density of 35.415 nA/cm^2, the values for Ti15Mo11W (52.919 nA/cm^2) and Ti15Mo7W (54.955 nA/cm^2) one are very close, with a difference of 17 and 19 nA/cm^2, respectively. It can be observed that at a difference of 17-19 nA/cm^2 compared to the Ti6Al4V alloy are the current densities of Ti15Mo11W and Ti15Mo7W alloys with the values of 52.919 nA/cm^2 and 54.955 nA/cm^2, respectively.

Table 2 presents the main electrochemical parameters obtained from the corrosion tests performed in SBF.

Table 2

The main electrochemical parameters of the corrosion process

Code	Sample	E_{cor} (mV)	i_{cor} (nA/cm^2)	β_c (mV)	β_a (mV)	R_p (kΩxcm^2)	CR (μm/year)
1.	Ti15Mo11W	-293.2	52.919	155.72	141.74	609.645	0.542
2.	Ti15Mo9W	51.8	105.649	258.10	273.12	546.109	1.093
3.	Ti15Mo7W	-282.6	54.955	148.51	85.37	428.885	0.537
4.	Ti15Mo5W	-333.1	28.862	28.55	541.99	408.642	0.296
5.	Ti6Al4V	-186.2	35.415	120.98	199.62	924.836	0.321

It is known that a high polarization resistance (R_p) highlights a good corrosion behavior of a material, while a low value of this parameter indicates a poor corrosion behavior. Thus, it can be observed that all the Ti-Mo-W alloys have values smaller than the ones obtained for the reference alloy. Regarding the polarization resistance the Ti15Mo11W alloy stands out with a value 609.64 kΩxcm^2. In terms of corrosion resistance, it can be observed that the smallest value was obtained for Ti15Mo5W (0.296 μm/year), followed by reference alloy - Ti6Al4V (0.321 μm/year).

Thus, based on the obtained main electrochemical parameters, it can be said the best corrosion behavior was obtained for Ti15Mo5W, which have registered the lowest corrosion current density and the smallest corrosion rate.

4. Conclusions

Titanium and its alloys represent the material of choice for designing biomedical implants. Still, detailed studies are necessary to understand the corrosion behavior in simulated body fluid which resemblance the human body environment. To obtain the electrochemical parameters for characterizing the corrosion resistance of Ti-Mo-W alloys, the electrochemical tests of linear polarization were used to directly and quantitatively determine the corrosion rate. Among others, the corrosion resistance of Ti alloys depends on their composition. By comparing the values of the main electrochemical parameters corresponding to the investigated alloys in terms of corrosion resistance in SBF it can be concluded that Ti15Mo5W alloy can be considered a potential candidate for medical applications; the alloy with this chemical composition shows the smallest values for the corrosion rate and polarization resistance.

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