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ELECTROCHEMICAL BEHAVIOR OF $TiMo_xNb_y$ ALLOYS IN SIMULATED BIOLOGICAL FLUID

BY

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Abstract. The present study explores the electrochemical behavior of Ti-Mo-Nb alloys with: open-circuit potential, potential-dynamic polarization and electrochemical impedance spectroscopy in SBF solution. The paper presents a deep analysis of the processes that take place on the surface of the alloy/electrolyte interface on the electrochemical behavior of the samples under investigation. The measurements were performed in simulated biological fluid (SBF) for one hour of immersion. The EIS results showed that TiMoNb alloys exhibit passivity for open circuit potential.

Keywords: Ti-Mo-Nb alloys; corrosion resistance; SBF solution; biomaterial application.

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1. Introduction

Titanium and its alloys have been widely used in medical implants due to their excellent biocompatibility and corrosion resistance (Shi, 2006).

Metals such as Zr, Mo, Ni, Nb, Ta and Pt are elements that may be present in titanium alloys because they exhibit excellent biocompatibility and belong to the group of non-toxic metals in their interaction with living tissue (Vișan *et al.*, 2002). According to the theoretical studies carried out by Song *et al.* (1999), the elements Nb, Zr, Mo and Ta are the most suitable alloying elements that can be used to reduce the elasticity of the alloy, without compromising its hardness.

The influence of the molybdenum content on the corrosion resistance of Ti-Mo alloys was studied by Capela *et al.* (2008), using electrochemical methods in 0.9% NaCl solutions that simulate the environment of the human body. The results of the research concluded that with the increase of Mo content in Ti-Mo alloys the susceptibility of alloys to corrosion in aggressive environments decreases.

Other electrochemical tests in various simulated physiological environments have shown the improvement of the behaviour of the titanium alloys in the composition as Mo alloying element. (Oliveira and Guastaldi, 2008; Oliveira and Guastaldi, 2009; Oliveira *et al*., 2007; Zhou and Luo, 2011; Zhao *et al*., 2011).

A study on the same TiMoNb alloys was conducted by Chelariu R. *et al.* (2014). The corrosion resistance (potentiodynamic polarization and electrochemical impedance spectroscopy) of the alloys was determined in 0.9% saline at 25°C. They concluded that a significant improvement of the corrosion resistance of the materials in the saline solution is obtained by adding niobium to the Ti-Mo alloys.

As an alloying element, niobium is known to be very good at resisting corrosion in the simulated body fluid and has excellent biocompatibility (Okazaki *et al*., 1998; Matsuno *et al*., 2001).

A recent concern of the researchers is to find ways to optimize the properties of these alloys with applications in medicine. In this way, studies are focused on finding an optimal surface of the alloy that has excellent qualities which can allow it to withstand longer the exposure of the aggressive environment of the environment organism.

Ti-based alloys remain some of the most commonly used biomaterials.

2. Experimental

Samples from 5 alloys symbolized as follows were used in this study: Ti12Mo, Ti10Mo8Nb, Ti8Mo16Nb, Ti6Mo24Nb and Ti4Mo32Nb which were tested at room temperature and a pH of 7.4.

Experiments were performed using the SBF solution (1L solution of SBF solution: NaCl 7.996 g, $NaHCO_3$ 0.350 g, KCl 0.224 g, $K_2HPO_4 \cdot 3H_2O$ 0.228 g, $MgCl_2 \cdot 6H_2O$ 0.305 g, HCl1M 40 mL, $CaCl_2$ 0.278 g, Na_2SO_4 0.071 g, $(HOCH_2)_3CNH_2$ 6.057 g).

The surfaces of the samples that were subjected to electrochemical tests were 0.25, 0.27 and 0.28 cm^2.

For conducting the electrochemical tests, a glass electrochemical cell was used, with a simple wall and a potentiostatic assembly consisting of a working electrode, a reference electrode and a platinum auxiliary electrode. The potentiostat used was PGZ-301, which was connected to a computer. The experimental data was processed with the Voltamaster4 program.

Solatron equipment was used to perform electrochemical impedance spectroscopy (EIS) and experimental data are recorded using the Voltamester4 program and processed using the Zsimwiew program.

Before each test, the electrochemical surface of the alloys was sanded with SiC 1000, 2000, AND 4000 grains of paper, then rinsed with distilled water and placed in the ultrasonic bath.

The aim of this research was to study the electrochemical behaviour of TiMoNb alloys using the following methods:

– open circuit potential (OCP);
– potentiodynamic polarization;
– electrochemical impedance spectroscopy.

3. Results and Discussion

Potential open circuit monitoring

The alloys were immersed in SBF solution and subjected to an open circuit potential. Variation of open circuit potential in SBF solution for the studied systems are shown in Fig. 1.

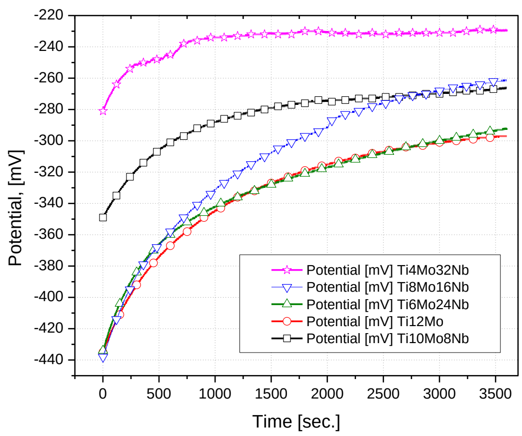

Fig. 1 − Variation of open circuit potential in SBF solution.

Reaching the noblest values by the OCP indicates an increase in the thickness of the protective layer on the surface of the alloy, thus the corrosion rate decreases.

Analysis of electrochemical behaviour by potentiodynamic curves

Fig. 2 shows the potentiodynamic curves for the Ti, Mo and Nb alloys, having about the same alloy, the differences being very small.

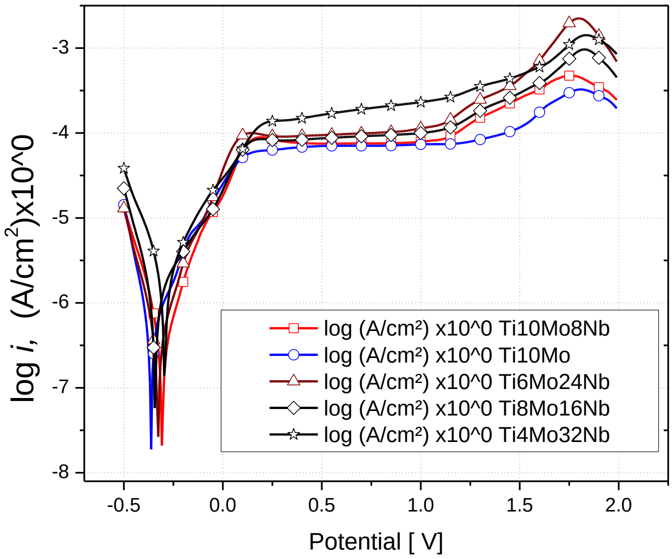

Fig. 2 − Potentially dynamic polarization curves for samples immersed in SBF solution.

In all cases, TiMoNb alloys have a large passivation zone indicating a stable metal passivity in the electrolyte environment. With the increase of the Nb content, the corrosion process is also favoured by increasing the corrosion current values and the corrosion potential (Table 1):

Table 1

The Electrochemical Parameters of TiMoNb Alloys in SBF Solution

Sample	E(i=0), mV	i_{corr}, μA/cm²	R_p, kohm·cm²
Ti12Mo	–355.5	1.3373	53.88
Ti10Mo8Nb	–320.3	0.6514	77.08
Ti8Mo16Nb	–298.2	0.6112	28.45
Ti6Mo24Nb	–285.3	0.4787	66.62
Ti4Mo32Nb	–253.2	0.4312	16.86

Analysis of electrochemical behaviour using electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was performed under the potential conditions in the open circuit. The results were represented as the Bode diagram, Fig. 3. The maximum phase angle was reached at 90° values.

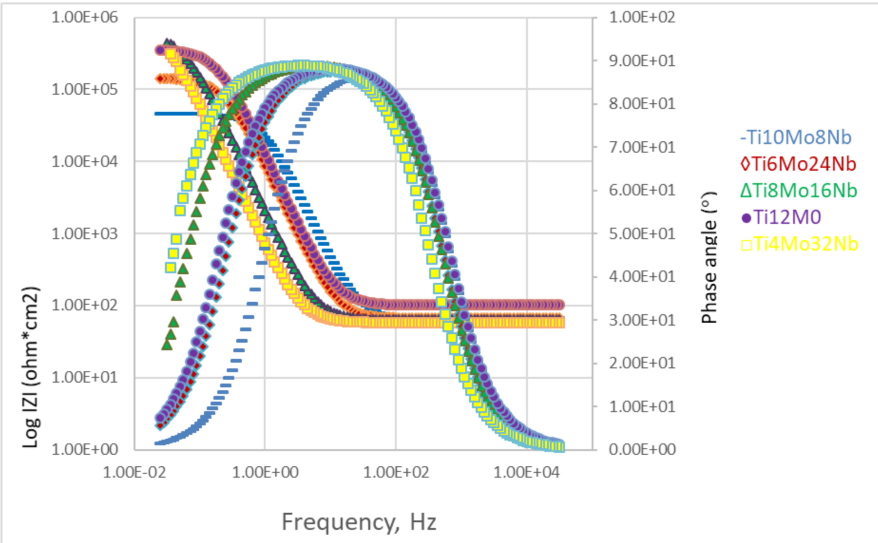

Fig. 3 − Bode diagram for TiMoNb alloys in SBF solution.

For the correct interpretation of the electrochemical behaviour of the TiMoNb alloys, the same equivalent electric circuit model was chosen. The resistance of the solution decreases as the content of Nb increases. The data adjusted using this circuit are presented in Table 2.

Table 2

Electrical Parameter Values for TiMoNb Alloys

Sample	R_s [ohm·cm^2]	CPE [S·sec^n/cm^2]	n	R [ohm·cm^2]	X^2
Ti12Mo	57.9	$1.01\cdot10^{-5}$	0.821	$2.14\cdot10^{6}$	0.00254
Ti10Mo8Nb	47.34	$1.77\cdot10^{-5}$	0.865	$3.65\cdot10^{4}$	0.00324
Ti8Mo16Nb	42.33	$1.78\cdot10^{-5}$	0.7598	$3.05\cdot10^{5}$	0.00875
Ti6MO24Nb	43.64	$1.32\cdot10^{-5}$	0.824	$2.77\cdot10^{6}$	0.00325
Ti4Mo32Nb	41.83	$1.757\cdot10^{-5}$	0.7443	$6.33\cdot10^{4}$	0.00127

3. Conclusions

In this paper was presented the electrochemical study to which titanium, molybdenum and niobium alloys were subjected in order to investigate the electrochemical stability and the corrosion resistance of the alloys in the SBF solution.

Electrochemical studies on TiMoNb alloys demonstrate that a significant improvement in corrosion resistance of materials in SBF solution is achieved by the addition of niobium to Ti-Mo alloys. The values of the corrosion potential (E_{cor}) and the density of the corrosion current (i_{cor}) of the materials were determined by Tafel analysis of the anodic and cathodic branches of the polarization curves. All curves show active-passive behaviour of samples immersed in SBF solution.

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COMPORTAMENTUL ELECTROCHIMIC AL ALIAJELOR $TiMo_xNb_y$
ÎN FLUID BIOLOGIC SIMULAT

(Rezumat)

Studiul de față explorează comportamentul electrochimic al aliajelor Ti-Mo-Nb cu: potențial de circuit deschis, polarizare potențial-dinamică și spectroscopie cu impedanță electrochimică în soluție SBF. Lucrarea prezintă o analiză profundă a proceselor care au loc pe suprafața interfeței aliaj/electrolit pe comportamentul electrochimic al eșantioanelor cercetate. Experimentele, adică măsurătorile au fost efectuate în lichid biologic simulat pentru o oră de imersiune. Rezultatele EIS au arătat că aliajele TiMoNb prezintă pasivitate pentru potențialul circuitului deschis.