# Electrochemical Behaviour of TiMoNb Alloys in Hanks Balanced Salt Solution with Addition of Aminoacids Infusion Solution

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In the last decade, new titanium alloys were developed for use in implantology. TiMoNb alloys were synthesized by the cold crucible levitation melting technique, and their compositions were adjusted to keep the molybdenum equivalency close to 12 wt% Mo<sub>eq</sub>. The aim of this study was to compare two different composition TiMoNb based alloys, regarding the corrosion resistance in Hanks Balance Salt Solution (HBSS) with and without aminoacids. The electrochemical impedance spectroscopy (EIS) studies showed high impedance values for both samples, and increased with immersion times in HBSS with and without aminoacids, at 37 °C. The passivation properties were comparable for both samples. The EIS spectra were best fitted using an equivalent circuit (EC), which is consistent with the model for the passive film.

Keywords: TiMoNb alloys, HBSS, aminoacids, corrosion, microscopy

The corrosion process is one of the essential phenomena that determine the biocompatibility of implant alloys. Due to their many advantageous properties, the applications of commercially pure titanium and titanium alloys in the medical fields have increased over the last few decades.

Commercial titanium and titanium alloys are used on a large scale as implant alloy due to their advantages as compared with other similar materials: chemical inertia, low specific gravity, adequate mechanical properties, toxicity absence and good biocompatibility. Corrosion resistance is determined by the formation of an adherent titanium oxide layer, with reduced thickness, on the titanium or titanium alloys surface. This film contains as a major compound  $\text{TiO}_2$  with anionic gaps, which confer the semiconductor character [1, 2]. This film functions as a barrier versus the metal tendency to interact with the corrosion medium. The film formation is enhanced by the alloying with transitional metals having d unsaturated orbitals, when solid solutions with Cu, Mo, W, Nb or intermetallic compounds with Pt, Ni may appear. The increase of the oxide film thickness conducts to the formation both of a crystalline layer and of another porous layer containing hydrated oxides with 30% water content.

Casting titanium is quite difficult due to it's high melting point value (around 1680°C) and high tendency of contamination (induced by it's increased reactivity). In order to lower these drawbackse, titanium is alloyed with various elements. Titanium alloys having biphasic structure ( $\alpha$ + $\beta$ ) are used on a large scale. Among the alloying elements, Al is  $\alpha$ -stabilizer and it dissolves in the  $\alpha$ -phase increasing the stability domain of this phase. Mo, V, Nb, Ta are  $\beta$ -stabilizers elements which decrease the temperature of allotropic transformation, forming continuous series of solid solutions with  $\beta$ -Ti but their solubility in  $\alpha$ -Ti is limited. Corrosion of metal implants is critical because it can adversely affect biocompatibility and mechanical integrity. Ideally, a biomaterial should not cause any biological reaction in the body, remaining stable and retaining its functional properties.

The standard Ti6Al4V was one of the first titanium biomaterial introduced in implantable components and devices (particularly for orthopaedic and osteosynthesis applications). Although this alloy is still widely used in medicine, some concern has been recently expressed over its use, since it appears that small amounts of vanadium released in the human body, may induce possible cytotoxic effect. Thus, the potential toxicity of conventional Ti6Al4V alloy has required the development of a new titanium alloys with non-toxic elements (Nb, Zr, Ta, and Mo).

The first objective of this study was to elaborate and to characterize new alloy compositions in the ternary Ti-Mo-Nb system with the objective to design new biomedical metastable  $\beta$  Ti-based alloys with improved corrosion resistance. The effects of  $\beta$ -stabilizer elements on the martensite transus temperature [3] and stability of the  $\beta$ -phase [4, 5] is often expressed [3,6] using the so-called molybdenum equivalent [Mo\_g], where the new alloying elements (in wt.%), such as Nb in this system, are expressed in terms of the equivalent weight ratio of molybdenum on the basis of the irrelative atomic weights. In this work, two

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new Ti-Mo-Nb alloy compositions with the molybdenum equivalency fixed around 12 wt.% Mo<sub>en</sub> were produced.

The electrochemical techniques most commonly used for corrosion studies have their own specific advantages for addressing effectively to certain aspects of the electrochemical performance of implant materials [7]. Direct current (DC) electrochemical methods are commonly used to evaluate corrosion, but also, the alternative current (AC) impedance method may be particularly useful when monitoring some electrochemical behaviour changes as a function of time, being a nondestructive technique [8-17]. Also, the implant alloys properties variation can be determined with rapid electrochemical tests [18-22], by considering that a qualitative criterion of estimation it's the corrosion resistance,

The second objective of this study was to evaluate the corrosion resistance of the TiMoNb alloys with electrochemical techniques during their exposure to Hanks Balance Salt Solution modified with 10% infusion of Aminoven Infant.

#### **Experimental part**

In this study, two alloy (Ti10Mo8Nb, and Ti4Mo32Nb) compositions (wt.%) were synthesized by the cold cold crucible levitation melting (CCLM) technique in an induction furnace (Fives Celes, Lautenbach, France) under a pure Ar atmosphere. The ingots were cold rolled to 90% in thickness and machined to obtain tensile test specimens and corrosion test samples. After this mechanical treatment, both samples were solution treated at 850 °C for 30 min and water quenched to restore a fully recrystallized.

The structure of the both alloys was characterized by Xray diffraction (XRD) at ambient temperature using a Philips PW 1830/00 (Eindhoven, The Netherlands) diffractometer (CuK $\alpha_1$  radiation, 1.5406 A wavelength). The microstructures of the alloys were characterized by optical microscopy using a Leica DM RM system (Wetzlar, Germany). Prior to optical imaging, the samples were first mechanically abraded using a sequence of silicon carbide abrasive papers followed by a final polishing step with a colloidal silica suspension (particle size: 50 nm). Samples were observed under polarized light to enhance the phase contrast. The microstructures were revealed by etching in 10%HF + 5% HNO<sub>3</sub> solutions for 3-5 s at room temperature. Also, the microhardness was measured on an electronic AFFRI Micro Hardness Tester, using a force of 200 g for 15 s. The microhardness measurements were performed tangentially with a Vickers indenter applied at every 0.5 mm along the diameter of the sample.

Hanks Balance Salt Solution (HBSS) was used as corrosion medium [23], with and without Aminoven Infant 10% addition (Frenius Kabi AB, Rapsgatan, Uppsala, Sweden), an infusion solution containing 100 g/100 mL essential, semiessential or undispensable aminoacids like L-izoleucine, L-leuicine, L-lysine, L-methionine, L-phenilalanine, L-threonine, L-tryptophan, L-valine, L-histidine, Lcysteine, L-arginine, L-proline, L-serine, L-tyrozine, etc.

Electrochemical measurements were carried out at room temperature and began after different immersion times in HBSS with and without Aminoven Infant, in order to allow the formation of the the passive film as a result of electrochemical reactions. The working electrodes, processed in cylindrical shape and mounted in a tetrafluoro-ethylene support, presented a one-dimensional circular area exposed to corrosion and measure.

Before experimental tests the samples were mechanically polished with SiC abrasive paper up to a 2096

granulation number of 4000, than polished using 1 mm alumina suspension and cleaned in ethyl-alcohol.

The electrochemical techniques used for the corrosion behaviour study were the potential measurements, polarization curves and electrochemical impedance spectroscopy (EIS).

The measurement was managed by a PARSTAT 4000 potentiostat controlled by a personal computer with dedicate software (Power Corr, Princeton Applied Research, Princeton, NJ, USA). A saturated calomel electrode (SCE) was used as reference and platinum as auxiliary electrode. All potential values given in this article are referred to SCE.

Électrochemical impedance spectroscopy (EIS) measurements were carried out in an open circuit potential  $(E_{oc})$  in aerated solutions. A frequencies range from  $10^{-2}$  to 10<sup>9</sup>Hz was used and the amplitude of AC potential was 10 mV with a single shine wave measurements.

Linear polarization was conducted at a small scan rate of the potential electrode (dE/dt = 0.5 mV/s) in a potential range closed to zero current potential (ZCP  $\pm$  250 mV). The corrosion current density (jcorr) was calculated as the slope of the potential vs. zero current potential, ZCP (in the range from -100 to +100 mV vs ZCP). These corrosion current densities are a test to characterize the corrosion behaviour of a metal and evaluate how effectively a passive film protects a metal from corrosion.

In the electrochemical estimations, the polarisation data were converted into instantaneous corrosion rate values ,) by means of the well known Stern-Geary equation (j\_\_\_) [24]:

$$\dot{j}_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \cdot \frac{1}{R_p} = \frac{B}{R_p}$$

where **R**<sub>n</sub> is defined by:

$$\mathbf{R}_{p} = \left(\frac{\Delta \mathbf{E}}{\Delta \mathbf{j}}\right)_{\Delta \mathbf{E} \to 0}$$

 $\beta_{a}$  and  $\beta_{c}$  are the Tafel slopes for the partial anodic and cathodic processes, respectively, and  $\mathbf{B} = \text{constant}$ .

# **Results and discussions**

Microstructural characterization

Both TiMoNb alloys were found to be (body-centred cubic structure) by X-ray diffraction as shown in figure 1 (representative of the Ti10Mo8Nb alloy). Indeed, all the peaks in the diffractograms were unambiguously indexed according to this crystallographic structure, and the corresponding diffracted planes are indicated in the plot. The micrograph depicted in figure 2 shows the microstructure of the Ti10Mo8Nb alloy.  $\beta$  equiaxial grains can be seen, in good agreement with the XRD observations.



Fig. 1. Representative X-ray diffratograms of the Ti10Mo8Nb alloy



50 um



Fig.3. Representative microhardness marks on Ti4Mo32Nb alloy

Table 1

Fig. 2. Optical micrograph of the Ti10Mo8Nb alloy showing the grain microstructure

The microhardness tests were conducted on the same flat surfaces (fig. 3). Vickers microhardness measurements results sustaine that both TiMoNb alloys formed a spontaneous similar surface layer (table 1).

# *Electrochemical test results*

Open circuit potential

The  $E_{oc}$  is a parameter which indicates the thermodynamically tendency of a material to the electrochemical oxidation in a corrosive medium. This tendency is modified when the metallic material is immersed in a corrosion medium in relation with the immersion time.

Figure 4 shows the  $E_{oc}$  curves for both stationary samples immersed in HBSS with and without aminoacids, at 37 °C. Following the immersion in both HBSS with and without aminacids, an abrupt  $E_{oc}$  displacement towards positive potentials was noticed in figure 4 during a period of 20 min. Afterwards, the  $E_{oc}$  remained slowly increased, suggesting the growth of a film onto the metallic surface. The continued increase in corrosion potential is indicating the passivation of both samples in the testing medium.

The HBSS with and without aminoacids did not exhibit potential drops associated with surface activation during 60 min exposure. This behaviour suggests that the airformed native oxides, consisting of TiO<sub>2</sub>, traces of Nb<sub>2</sub>O<sub>2</sub> and Mo<sub>s</sub>O<sub>5</sub> are thermodynamically resistant to chemical dissolution in both HBSS with and without aminoacids.

However, the variation of  $E_{\rm oc}$  increases in time on immersion in the HBSS with aminoacids than without aminoacids.

## Electrochemical Impedance Spectroscopy

The corrosion resistance can be estimate by means of the impedance method, also, know as Electrochemical Impedance Spectroscopy (EIS), this method being an powerful tool in investigating electrochemical and corrosion systems. EIS is a study state technique capable



AVERAGE VALUES OF VICKERS MICROHARDNESS OBTAINED OF 200

GRAMS						
Alloy	Ti10Mo8Nb	Ti4Mo32Nb				
Load (200 grams)	252	241				

to investigate phenomena whose relaxation times may vary over few orders of magnitudes and permits by a single averaging within a single experiment to obtain high precision results.

The Bode plots exhibited a one time constant system, indicating a compact oxide layer [5]. This fact was confirmed by the phase angle at almost -70°...-80° characteristic for compact oxide pseudo-capacitance. The obtained spectra were interpreted in terms of an equivalent circuit (EC) with the circuit elements representing electrochemical properties of the alloy and its oxide film.

Impedance spectroscopy results for both TiMoNb alloys in HBSS with aminoacids are presented as Bode plots (figs. 5A-6A). Also, Bode diagrams for both TiMoNb alloys in HBSS are presented in figures 5B-6B.

These figures showed the experimental Bode plots of tested TiMoNb materials recorded at  $E_{gc}$  and the corresponding fitting results using ZSimpWin software version 3.22 according to the equivalent circuit (EC) pointed out in figure 7.

Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data. The impedance of CPE is defined as:

$$Z_{\rm CPE} = \frac{1}{Q(j\omega)^n}$$

where Q is the combination of properties related to both the surfaces and electroactive species independent of frequency; n is related to a slope of the lgZ vs lgf Bodeplots (attributed to surface inhomogeneity); ω is the angular frequency and j is imaginary number  $(j^2 = -1)$ . Q is an adjustable parameter used in the fitting routine: when the value of *n* is equal to 1, the CPE acts as a pure capacitor. The value of the fit exponent *n* corresponds to the extent of dispersion and is attributed to surface heterogenity [23].

> Fig. 4. Open circuit potential  $(E_{0C})$  versus time in HBSS without aminoacids for Ti4Mo32Nb (A), Ti10Mo8Nb(B), and with aminoacids for Ti10Mo8Nb(C), Ti4Mo32Nb(D) alloys



The quality of fitting to the equivalent circuit was judged firstly by the chi-square ( $\chi^2$ ) value and secondly by the error distribution vs. frequency, comparing experimental with simulated data. The chi-square values (between  $10^4$  and  $10^5$ ) pointed an excellent agreement between the uses of CPE in the fitting procedure.

In table 2 are presented the main parameters of the proposed equivalent circuit obtained for the all studied samples, assuming that the corrosion of the passive metal is hindered by an oxide film that acts as a barrier-type compact layer. The equivalent circuit consists of the parallel combination terms  $(R_{_{pL}}Q_{_{pL}})$  in series with the resistance of the solution  $(R_{_{sol}})$  occurring between the sample and the reference electrode. The parameters  $\mathbf{R}_{pl}$  and  $\mathbf{Q}_{pl}$ describe the properties of the passive films formed on these metallic materials, respectively the resistance and capacitance of the compact oxide layers. Similar value of  $R_{sol}$  for HBSS with and without aminoacids (equal to 85  $\pm$  7  $\Omega$  cm<sup>2</sup>) was observed for both TiMoNb alloys. The figure 7 points out that the resistance increases with addition of aminoacids to the HBSS. Aminoacids may influence the corrosion reactions by shifting the position of equilibrium. Our data suggest that the aminoacids increased the corrosion resistance of both TiMoNb alloys, most probable through a surface adsorbing process, thus restricting the dissolution of the TiMoNb samples.



# Potentiodynamic polarization results

The Tafel slopes and the polarization resistance were evaluated from the linear polarisation curves obtained in neighbourhood of the open circuit potential, on the basis of the Evans diagram. These values and the instantaneous current density of the corrosion process are listed in table 3.

The nature of the linear polarization curves indicated that both samples were passivated immediately by immersion in HBSS with and without aminoacids (fig. 8). TiMoNb materials translated directly from the *Tafel region* into a stable passive state, without exhibiting a common active-passive transition. The polarization behaviour can be termed as stable passivity. This behaviour was noted for both samples.

For both TiMoNb alloy, the linear polarization curves shows a passive behaviour. The high value of  $\beta_{1}$  in comparison with the values of  $\beta_{2}$  for both TiMoNb alloys indicates an anodic control in the corrosion process. The control implies the existence of a passive layer on the material surface. The oxide layer on the alloys gives rise to

Samples	Immersion time	10 <sup>5</sup> Q <sub>pL</sub> (S cm <sup>-2</sup> s <sup>n</sup> )	n	10 <sup>-6</sup> R <sub>pL</sub> (Ω cm <sup>2</sup> )
Ti10Mo8Nb	1 hour	0.9	0.82	0.9
in HBSS with aminoacids	1 day	0.9	0.83	1.2
Ti10Mo8Nb	1 hour	1.2	0.80	0.5
in HBSS	1 day	0.9	0.81	0.8
Ti4Mo32Nb	1 hour	0.9	0.82	1.1
in HBSS with aminoacids	1 day	0.8	0.83	1.4
Ti4Mo32Nb	1 hour	0.9	0.81	0.8
in HBSS	1 day	0.9	0.82	1.1

Table 2VALUES OF FITTEDPARAMETERS OF THE EC ASFUNCTION OF IMMERSIONTIME FOR BOTH TINbMoALLOYS IN HBSSWITH AND WITHOUTAMINOACIDS

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Fig. 8. Representative linear potentiodynamic polarization curves of Ti10Mo8Nb alloys after 1 day immersion in HBSS without (1) and with aminoacids (2)

#### Table 3

# CORROSION PARAMETERS (AND STANDARD DEVIATION VALUES) DETERMINED FROM THE POTENTIODYNAMIC POLARIZATION CURVES MEASURED FOR BOTH TIMOND ALLOYS IN HBSS WITH AND WITHOUT AMINOACIDS

Alloys	ZCP (mVsce)	βa (mV/dec)	βc (mV/dec)	jorr (μA/cm <sup>2</sup> )
Ti10Mo8Nb in HBSS	-403 (11)	136 (8)	75 (5)	0.49 (0.04)
Ti10Mo8Nb in HBSS with aminoacids	-371 (10)	151 (9)	104 (8)	0.35 (0. 03)
Ti4Mo32Nb in HBSS	-378 (11)	152 (9)	91 (8)	0.38 (0.03)
Ti4Mo32Nb in HBSS with aminoacids	-342 (11)	179 (11)	122 (8)	0.27 (0.03)

a typical passive state with a low corrosion current density, as can be observed in table 3.

Because the corrosion current densities  $(j_{corr})$  of both samples are comparable, the corrosion rates of the samples are also comparable. The corrosion current densities are lower in HBSS with aminoacids than in HBSS.

## Conclusions

Both investigated TiNbMo alloys passivated spontaneously after immersion in simulated body fluids with and without aminoacids and the resulted passive films have a pseudo-capacitive behaviour. An improvement of the corrosion resistance of the materials in the both solutions was achieved by the addition of Nb to TiMo alloys. Potentiodynamic polarization data showed that both corrosion current densities decrease when Nb content increases. EIS analysis, the corrosion resistance of TiMoNb alloys immersed in HBSS with added aminoacids was improved with the increasing of Nb content in the ternary alloy. The EIS results indicate that the passive oxide film formed on the alloys is rather compact, characteristic of a sealing barrier layer exhibiting only one time constant in the spectra. The impedance values of the barrier layer were bigger for the Ti4Mo32Nb alloy as compared to Ti10Mo8Nb alloy with the same molybdenum equivalent.

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