SURFACE CHARACTERIZATION AND CORROSION BEHAVIOUR OF Ti BASED ALLOYS IN FETAL BOVINE SERUM

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Scopul acestei lucrări este de a evalua influența elementelor de aliere Al, V, Nb şi Ni asupra comportamentului electrochimic şi proprietăților de suprafață pentru aliajele Ti-Al-V, Ti-Al-Nb şi Ti-Ni. Aceste aliaje sunt utilizate frecvent în chirurgia ortopedică pentru înlocuirea totală a articulațiilor de sold sau genunchi. Ca tehnici electrochimice s-au folosit polarizarea potențiodinamică şi spectroscopia de impedanță electrochimică, iar pentru evaluarea proprietăților de suprafață s-a folosit tehnica microdurității Vickers. Studiile de laborator au demonstrat că folosirea Al şi Nb, ca elemente de aliere, conduce la îmbunătățirea proprietăților de suprafață şi a rezistenței la coroziune ale biomaterialelor în Ser Fetal Bovin.

The purpose of this study is to evaluate the influence of Al, V, Nb and Ni alloying elements on electrochemical behaviour and surface properties for Ti-Al-V, Ti-Al-Nb and Ti-Ni Nitinol-like alloys. These alloys are currently used in orthopaedic surgery for total hip and knee replacement. We used potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS) as electrochemical techniques and Vickers micro-hardness technique for surface properties evaluation. Laboratory studies have demonstrated that the using of Al and Nb as alloying elements led to the improving of surface properties and corrosion resistance of these metallic biomaterials in Fetal Bovine Serum (FBS).

Keywords: Ti alloys, FBS, EIS, corrosion, biomaterial

1. Introduction

Titanium alloys are used for biomedical materials, which act as a substitute for failed hard tissue [1]. Of the various titanium alloys, the Ti-6Al-4V extra-low interstitial (ELI) alloy is the most widely used for biomaterial applications.

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In spite of the fact that Ti64 was originally developed for aerospace applications, its high corrosion resistance and excellent biocompatibility led its entry into biomedical industry.

Although titanium and its alloys, mainly Ti64, have an excellent reputation for corrosion resistance and biocompatibility, long term performance of these alloys has raised some concerns due to the release of aluminium and vanadium from its Ti64 alloy. Both Al and V ions released from the Ti64 alloy are found to be associated with long-term health problems, such as Alzheimer disease, neuropathy and ostemomalacia [2]. In addition, vanadium is also toxic, both in the elemental state and oxides V_2O_5, which are present at the surface [3-5].

The Ti-6Al-4V ELI alloy, which is an a/b titanium alloy, has a good balance of strength and toughness. It also has a good balance of workability, heat treatability and weldability [6]. The Ti-6Al-4V ELI alloy is the first titanium alloy registered as a biomaterial by ASTM Standard F 136 [7]. However, the V in the Ti-6Al-4V alloy has been reported to be toxic for the human body [8]. Therefore, the V-free α/β titanium alloys Ti-6Al-7Nb and Ti-5Al-2.5Fe have been developed. The Ti-6Al-7Nb alloy has been recently standardized as a biomaterial by ASTM Standard F 1295 [9, 10].

Nitinol is a nickel–titanium nearly equiatomic alloy that has attracted considerable interest for biomedical applications, due to its shape memory and super-elastic properties and biocompatibility. The shape memory effect consists in a phase transformation induced by the temperature. When a shape memory alloy is in its cold state (below the austenite transformation start temperature – As), the material can be stretched into a variety of new shapes and will hold that same shape until it is heated above the transition temperature (the austenite transformation finish temperature – Af). Upon heating, the material recovers its original shape despite of the shape it was when cold [11]. However, the high nickel content of the alloy might result in potential negative effects on the surrounding tissue, inducing allergic response. Whatever the cause, toxicity and allergy occur in vivo if metallic materials are corroded by body fluids, releasing metallic ions for a long time, which may combine with biomolecules such as proteins and enzymes [12]. In fact, severe inflammatory reactions resulting in contact dermatitis and oral lesions have been reported [13, 14]. Also failures of implants retrieved after use in patients call for attention to the problem of Nitinol surface stability [15]. Therefore, the material should present superior corrosion resistance in contact with body fluids [16]. The good corrosion resistance and biocompatibility of Nitinol is associated to the formation on its surface of a resistant titanium oxide layer, limiting the release of Ni ions, but the toxicity hazards remain a subject of concern [11, 17–20].

2. Materials and methods

A VoltaLab 40 model electrochemical combine with dynamic EIS (Electrochemical Impedance Spectroscopy) was used for the electrochemical polarization. The polarization behavior of zirconium-based alloys was studied in a classical electrolytic cell with three electrodes. A platinum plate electrode, of 128mm^2 and a saturated calomel electrode (SCE) were used as counter and reference electrode. All three electrodes (including working electrode) were placed in a cell which has been connected to a UltraThermostat type U10 with external recirculation of heating water to maintain the temperature inside the cell close to 37 ^{0}C. The working electrode was made of titanium based alloys (Ti6Al4V, Ti6Al7Nb, TiNi). Samples with 1 cm^2 geometric surface area were used. Prior to experiments, the electrodes were polished with SiC emery paper down to #4000. After polishing, the electrodes were degreased in acetone, washed with ultra pure water (Millipore) and then introduced into the measurement cell. The working electrode potential was scanned on the potential range of -1000 mV up to +1000 mV/SCE with scan rate of 0.5 mV/sec. This scan potential range was chosen taking into account that, the potential – pH diagram for physiological conditions generally showed that, the potential value of a metallic biomaterial may vary from -1.0 to +1.0 V/SCE in the human body. The corrosion current density (i_{corr}) was determined by extrapolation of the anodic and cathodic curves in the Tafel potential range.

Impedance measurements were performed using VoltaLab 40 dynamic EIS with VoltaMaster 4 Software on the frequency range between 100 kHz and 1 mHz with an AC wave of ± 5 mV (peak-to-peak) overlaid on a DC bias potential and the impedance data were obtained at a rate of 10 points per decade change in frequency.

All tests have been performed in Fetal Bovine Serum with the chemical composition given in Table 1, at 37 ± 0.2 ^{0}C under atmospheric oxygen conditions without agitation.

Table 1.

Chemical composition of Fetal Bovine Serum

Electrolyte	Composition
Fetal Bovine Serum	Bilirubin – 2.4 mg/l; Cholesterol – 340 mg/l; Creatinine – 27.3 mg/l; Urea – 260 mg/l; Na^+ - 142 mmol/l; K^+ - 8 mmol/l; Ca^{++} - 3 mmol/l; Mg^{++} - 1.08 mmol/l; PO_4^{3-} - 2.32 mmol/l; Fe – 1.63 mg/l; Glucose – 550 mg/l; Protein – 36 g/l; Albumine – 17 g/l; α-Globulin – 17 g/l; β-Globulin – 2 g/l; γ-Globulin – 1 g/l.

Vickers hardness is a measure of the hardness of a material, calculated from the size of an impression produced under load by a pyramid-shaped diamond indenter.

For the Vickers micro-hardness evaluation of the samples surface it was used a micro-hardness tester FM 700 at 2 kgf load.

The equipment employed to make determination of ultra-trace analysis is an ICP-MS made by Perkin Elmer, model ELAN DRC-e (with reaction cell gas). Operation principles of the device are an efficient ion generation by an Argon Plasma at 6000 K, send trough a mass spectrometer which has a Quadrupole system for a better ion separation. Software methods for the determination in this paper don't use the reaction cell gas but the results were very accurate and it is in perfect concordance with the other techniques used. All samples were sent to a cross-flow nebulizer type Scott Spray chamber.

3. Results and discussion

3.1. Electrochemical measurements

In Fig. 1 are presented the polarization curves obtained for the 3 samples in Fetal Bovine Serum, under normal atmospheric conditions at 37 ^{0}C. It can be observed that in the case of polarization curves corresponding to TiAlNb and TiNi alloys, the working electrode passes directly from the active zone into a passivity one without an intermediary active – passive transition region. The passive area is followed by a sudden current increase because of the passive film penetration from the electrode surface, and at more electropositive potentials the process is diffusion controlled, the current increase being slower.

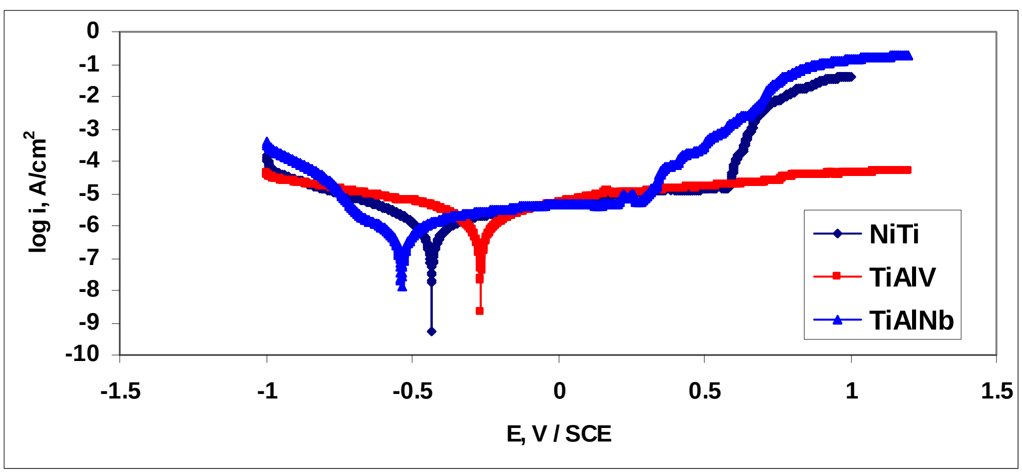


Fig 1. Potentiodynamic polarization curves of TiNi, TiAlV and TiAlNb alloys in Fetal Bovine Serum at 37 ^{0}C

Table 2 presents the kinetic corrosion parameters calculated by Tafel lines extrapolation method. As it can be observed, in the case of TiAlNb electrode are obtained the smallest values for the corrosion current and corrosion rate (0.21 μA/cm^2 and 1.571 μA/year respectively) and the highest value for the corrosion resistance of the oxide protective film from the metal / electrolyte interface (82.64 kΩcm^2). Also, the passivation domain measures 320 mV in the case of TiAlNb alloy while for TiNi it measures only 220 mV, being absent in the case of TiAlV.

Table 2.

Electrochemical kinetic parameters

Sample	E_{corr}, mV/SCE	i_{corr}, μA/cm^2	Rp, kΩcm^2	b_a, mV/dec	b_c, mV/dec	i_{pass}, μA/cm^2	ΔE_{pass}, mV	Corrosion, μm/year
TiNi	-433	0.35	58.35	145.7	-119.8	13.48	220	1.89
TiAlV	-263	0.5	45.66	154.3	-136.3	-	-	4.319
TiAlNb	-536.3	0.21	82.64	106	-97.2	4.68	320	1.571

In Figs. 2 and 3 are presented the Nyquist and Bode diagrams, respectively for the 3 samples. It can be observed on the Nyquist diagram that the semicircles diameters obtained for TiAlNb and TiNi alloys are much higher than in the case of TiAlV alloy, which means that the polarization resistances values obtained for TiAlNb and TiNi alloys are in accordance with the results obtained in the case of polarization curves. On Bode diagram it can be observed that TiAlNb and TiAlV alloys present just one time constant each, well defined at medium frequencies, with phase angles of about 80 ^{0}, fact that indicates a strong capacitive behaviour of the oxidic protective film from the metal / electrolyte interface, while on the log f – phase angle curve, corresponding to TiNi alloy 2 time constants can be observed, one at high frequencies and other at low frequencies, with phase angle values of about 40 ^{0} and 60 ^{0} , respectively, which correspond to the formation at the electrode surface of a duplex formed of 2 films, one having a diffusive behaviour with low capacitive tendencies, and the other having a capacitive behavior with diffusive tendencies.

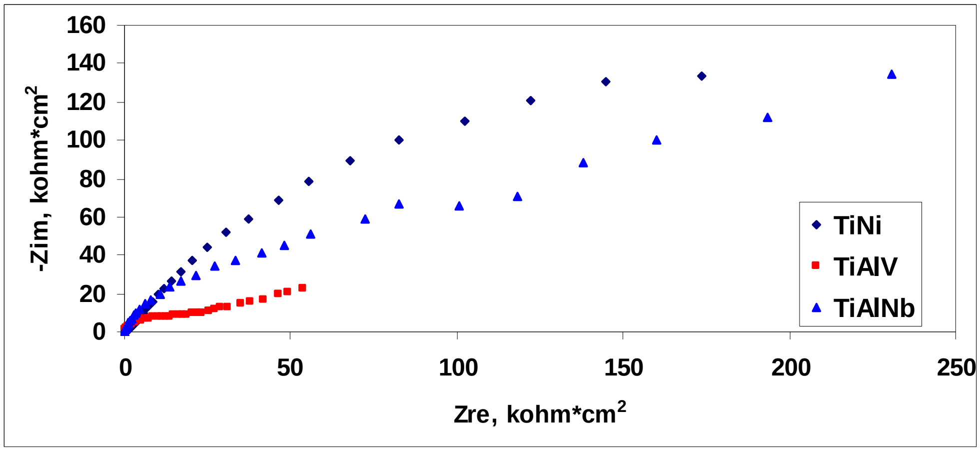


Fig. 2. Nyquist diagram of TiNi, TiAlV and TiAlNb alloys in Fetal Bovine Serum at 37 ^{0}C

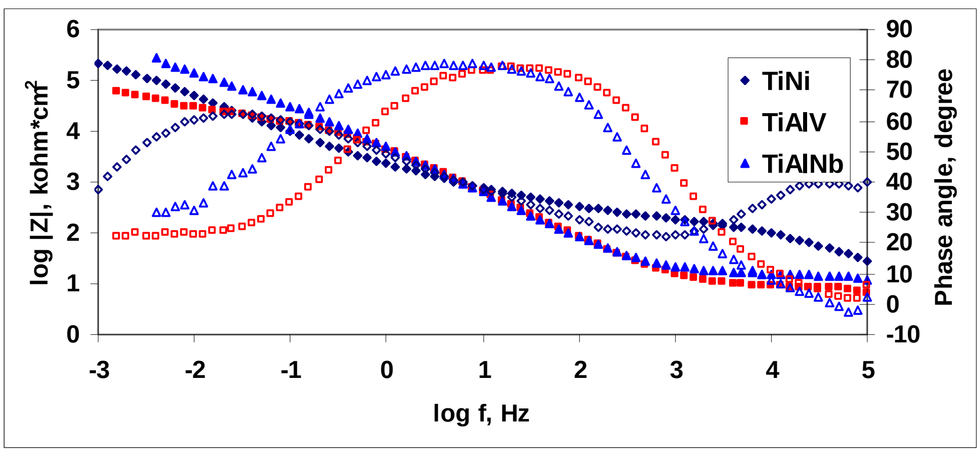


Fig. 3. Bode diagram of TiNi, TiAlV, TiAlNb alloys in Fetal Bovine Serum at 37 ^{0}C

Table 3.

Electrochemical parameters

Sample	R_{el}, kΩcm^2	R_p, kΩcm^2	C_{dl}, μF/cm^2
TiNi	0.414	413.9	384.4
TiAlV	0.02	21.46	59.31
TiAlNb	0.83	536.4	93.74

3.2. Vickers micro-hardness and Inductive Coupling Plasma-Mass Spectrometry (ICP-MS) measurements

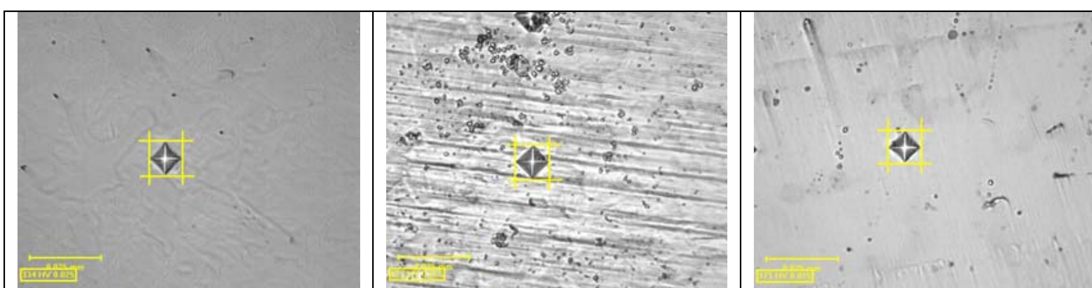
The indenter employed in the Vickers test is a square-based pyramid whose opposite sides meet at the apex at an angle of 136º. The diamond is pressed into the surface of the material at loads ranging up to approximately 2 kilograms-force, and the size of the impression (usually no more than 0.5 mm) is measured with the aid of a calibrated microscope.

The Vickers number (HV) is calculated using the following formula:

$$\mathbf{HV = 1.854(F/A)},$$

with **F** being the applied load (measured in kilograms-force) and **A** the area of the indentation (measured in square millimeters).

Figs. 4a, b and c showed the impressions of the diamond indenter on NiTi, TiAlV and TiAlNb alloys. It can be observed that the impression of the diamond indenter on TiAlNb alloy surface had the smallest area, which means that the micro-hardness value of the TiAlNb alloy (373 HV) is the largest in comparison with the micro-hardness value of TiNi alloy (334 HV) and TiAlV alloy (327 HV).



a) TiNi alloy x500 (334 HV)	**b)** TiAlV alloy x500 (327 HV)	**c)** TiAlNb alloy x500 (373 HV)

Fig. 4. Vickers micro-hardness determination

Table 4 show the ICP-MS results for fetal bovine serum electrolyte in which were performed electrochemical measurements for all type of samples. As a result of the examination of the concentration values obtained for different interest elements (Ti, Ni, Al, V, Nb as raw materials and Co, Cr as impurities from raw materials) from the composition of the „used" electrolyte, it can be observed a reduction of titanium concentration passed in solution up to 3 orders of magnitude in the case of TiAlNb sample compared with TiAlV sample, while in the case of aluminum a reduction with approximately 50% of the dissolved aluminium concentration value is observed. For cytotoxic and allergenic elements (Co, Cr, Ni, V) very low values can be observed in the case of TiAlV and TiAlNb alloys sample, while for the electrolyte in which the TiNi sample was tested, concentrations values of these elements are almost the same but the concentrations of Ni and Ti are much bigger.

Table 4.

Concentration of ions in electrolyte after polarization measurements

Element / Electrolyte	Concentration, ppm						
	Ti	Ni	Al	V	Nb	Co	Cr
After electrochemical measurements of TiNi alloy	28.3	33.62	0.14	0.02	0	0	0.12
After electrochemical measurements of TiAlNb alloy	0.04	0.02	0.1	0.02	0.1	0	0.1
After electrochemical measurements of TiAlV alloy	4.24	0.02	0.18	0.02	0	0	0.1

4. Conclusions

As a result of the performed experiments some aspects regarding corrosion resistance and Vickers micro-hardness of the studied alloys were pointed out, as well as of the concentration of metallic ions released in the electrolyte as a result of electrochemical determinations.
These are presented as follows :

1) The utilization of Al and Nb, as alloying elements, leads to the obtaining of an alloy, TiAlNb, similar to the classic one, TiAlV, but more secure from toxicity point of view, knowing that Nb is 1000 times less toxic than V.

2) The TiAlNb alloy corrosion resistance is clear superior to that of TiAlV alloy, fact pointed out both by electrochemical measurements and calculated

kinetic corrosion parameters and by the lower concentration of metallic ions released into the electrolyte during the electrochemical measurements.

3) The Ni utilization as alloying element has one purpose namely, leads to the obtaining of a special alloy having the « shape memory » feature, with the commercial name of Nitinol. From the corrosion resistance point of view it is situated between the two alloys TiAlV and TiAlNb, respectively. But, from the point of view of metallic ions concentration in the electrolyte used at electrochemical test, the obtained values are very high in comparison with the two alloys. The only advantage this alloy has is that it has the special feature of «shape memory». Its major disadvantage is that it has a very high Ni content, element known as being allergenic and even carcinogenic.

4) The surface Vickers micro-hardness determinations confirm the superiority of the TiAlNb alloy, in which case it has been obtained the highest HV number value.

From the corrosion resistance, biocompatibility and surface properties point of view, TiAlNb alloy can be considered the most secure representative of Ti based alloys class used in orthopaedic surgery.

R E F E R E N C E S

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