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# TiO<sub>2</sub> and SiO<sub>2</sub> layer deposited by sol-gel method on the Ti6Al7Nb alloy for contact with blood

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# **ABSTRACT**

**Purpose:** The study contains the analysis of TiO<sub>2</sub> and SiO<sub>2</sub> surface modification impact on physical and chemical characteristics of Ti-6Al-7Nb alloy samples in the solution simulating cardiovascular system.

**Design/methodology/approach:** Sol-gel coatings were selected on the ground of data taken from literature. The base of stock solution consisted of silicon dioxide precursor  $SiO_2$  (TEOS) and titanium oxide precursor  $TiO_2$ . Application of  $SiO_2$  and  $TiO_2$  coating on the surface of Ti alloy was preceded by mechanical working – grinding (Ra = 0.40  $\mu$ m) and mechanical polishing (Ra = 0.12  $\mu$ m). Corrosion resistance tests were performed on the ground of registered anodic polarisation curves and Stern method. Electrochemical Impedance Spectroscopy (EIS) was also used in order to evaluate phenomena taking place on the surface of the tested alloys. The tests were made in artificial blood plasma at the temperature of  $T = 37.0 \pm 1$  °C and  $pH = 7.0 \pm 0.2$ .

**Findings:** Test results obtained on the ground of voltamperometric and impedance tests showed that electrochemical characteristics of Ti-6Al-7Nb alloy differs relative to the type of surface treatment.

**Practical implications:** Potentiodynamic and EIS studies of corrosion resistance in artificial plasma enable to predict the behavior of modified Ti-6AI-7Nb implants in cardiovascular system. The topic proposed in the article is favourable for the development of entrepreneurship sector due to high demand on such technologies and relatively easy implementation of obtained laboratory test results in the industrial and clinical practice.

**Originality/value:** Suggestion of proper surface treatment variants that incorporate sol-gel method is of perspective significance and will help to develop technological conditions with specified parameters of oxide coating creation on the surface of metallic implants.

Keywords: Ti-6Al-7Nb alloys; Sol-gel method; Corrosion resistance; EIS

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# **PROPERTIES**

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### 1. Introduction

In order to increase biocompatibility of metallic biomaterials, first their corrosion resistance should be increased. Issues of implants' corrosion should be analyzed with reference to the correlation between the implantation environment, implant's mechanical and physiochemical properties [1,2].

Biomaterial introduced to the cardiovascular system cannot cause irreversible damage to protein structure, blockage of enzymes activity, change in the electrolyte composition or damage or release of a large number of morphological blood components. In addition, it cannot initiate toxic, immunologic or mutagenic reactions. The presence of a metal implant in the cardiovascular system (vascular stent, mechanical cardiac valve) initiates complex reactions between blood constituents and its surface, which can result in haemostasis [3-6].

The process of interaction between blood and the implantation materials is not fully known yet. It is generally accepted that as a result of a contact between blood and 'artificial' surface of an implant, in the first place protein adsorption (mainly fibrinogen) takes place. In the event that the adsorbed fibrinogen undergoes the processes of denaturisation, other platelet and plasma blood coagulation factors are activated in a cascade-like manner. As a result, a thrombus is formed. One of the concepts explaining the mechanism of the initiation of the coagulation processes is based on a band solid body model. Based on the Gutman study, it has been established that fibringen has an electron structure characteristic of semiconductor materials. The width of its forbidden band is 1.8 eV. The valence and the conduction band are located 0.9 eV below or over the Fermi level, respectively. Thus, the processes of transformation of the protein from an inactive form (fibringen) to an active form (fibrin) can be connected with an electrochemical reaction between the protein and the material surface that contacts with the blood. Electrons from the valence band of the fibringen, transferred to the implant material, cause protein decomposition. As a consequence, the protein is transformed to fibrin monomer and peptide monomer. Next, the process of their arrangement in a lattice takes place, leading to an irreversible thrombus formation [7-10].

Based on the analysis, it seems justifiable to modify physical properties of the surface of implant materials by means of surface processing. Creating layers of high corrosion resistance, as well as semiconductor or dielectric properties, on the surface of implants used in the cardiovascular system can effectively inhibit the transfer of electrons from the valence band of fibrinogen. As a result, it can prove an effective way of reducing the processes of blood coagulation caused by the contact with the implant surface [11-13].

One of the methods increasing biocompatibility of biomaterials is application of the sol-gel method in order to create thin oxide Ti-Si-, P-, Ca-based layers. Low deposition temperature, ensuring stability of mechanical properties of metallic substrate, is the major advantage of this method. Furthermore, this method provides homogeneity of the sol, size control of policondensate particles, large number of metaloorganic and nonorganic compounds. Moreover, the sol-gel method allows to obtain porous materials of both ordered and disordered structure [14,15].

### 2. Materials and methods

Samples made of Ti-6Al-7Nb alloy taken from wire rod with diameter  $d=14\,$  mm were selected for the tests. Chemical composition and alloy structure were both in accordance with recommendations of standards: ISO 5832-3 and ISO 5832-11 - Table 1.

The tests were made on samples with differentiated way of surface preparation. Roughness differentiation was obtained thanks to application of mechanical working - grinding (Ra = 0.40 µm) and mechanical polishing (Ra = 0.12 µm).

Table 1. Chemical compositions of investigated Ti-6Al-7Nb alloy

Element	Acc. to ISO	Ladle analysis			
•	Mass concentration, %				
Al	5.50-6.50	6.24			
Nb	6.50-7.50	6.84			
Та	max 0,50	0.37			
С	max 0.08	0.08			
Fe	max 0,25	0.22			
$H_2$	max 0,009	0.003			
$N_2$	max 0.05	0.03			
$O_2$	max 0.2	0.18			
Ti	balance	balance			

Next, sol-gel coatings, selected on the ground of data taken from literature, were applied on the surface prepared in such a way - Fig. 1.

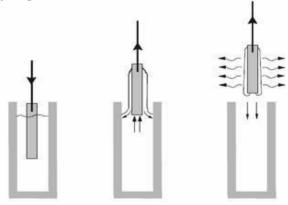


Fig. 1. Scheme of the sol-gel method [16]

The base of stock solutions were: silicon dioxide precursor  $SiO_2$  (TEOS) and titanium oxide precursor  $TiO_2$ . Sols were obtained through mixing substrates with ethanol, hydrochloric acid and surface-active compound. The last step of layers synthesis process was drying and burning. The samples were dried in the open air for the time t=1 h, and finally burned at the temperature of T=430 °C for the time of t=30 min.

Later, samples presenting consecutive steps of surface preparation were subject to pitting corrosion resistance tests. The tests were performed in accordance with recommendations of PN-ISO 17475 standard. Anodic polarisation curves were registered by means of potentiostat PGP-201 by Radiometer. Saturated Calomel Electrode (SCE) of K-113 type served as reference electrode. Platinum electrode PtP-201 was used as the auxiliary electrode. Potential changed in anodic direction at the rate of 1 mV/s. Stern method was also applied to determine parameters that characterise resistance corrosion of the tested alloys.

In order to obtain information regarding physical and chemical properties of Ti-6Al-7Nb samples, electrochemical tests were impedance spectroscopy also performed. Measurements were made with application of measurement system Auto Lab PGSTAT 302N equipped with FRA2 The applied (Frequency Response Analyser) module. measurement system enabled to perform tests in frequency range 10<sup>4</sup>-10<sup>-3</sup>Hz. The tests enabled to determine impedance spectra of the system and matching measurement data to the equivalent system. It made the ground for determination of numerical values of resistance R and capacity C of the analysed systems. Impedance spectra of the tested system were presented in the form of Nyquist diagrams for various frequency values and in the form of Bode diagrams. Obtained EIS spectra were interpreted by means of the least square method after matching to the equivalent system [17,18].

All electrochemical tests were made artificial blood plasma at the temperature of  $T = 37\pm1^{\circ}C$  and  $pH = 7.0\pm0.2$  - Tab. 2, Fig. 2.

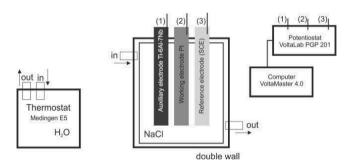


Fig. 2. Scheme of the corrosion test

Table 2. Chemical composition of artificial plasma

Ingredients	Ingredients concentration, g/dm³ distilled water		
NaCl	6.8		
KCl	0.4		
CaCl <sub>2</sub>	0.2		
$MgSO_4$	0.1		
NaHCO <sub>3</sub>	0.2		
Na <sub>2</sub> HPO <sub>4</sub>	0.126		
NaH <sub>2</sub> PO <sub>4</sub>	0.026		

# 3. Results

Potentiodynamic tests carried out in artificial plasma for Ti-6Al-7Nb alloy with modified surface proved differentiated resistance to pitting corrosion. Corrosion resistance test results (mean values of measurements) are compared in Tab. 2. Anodic polarisation curves of the selected samples are shown in Figs. 3 and 4.

On the ground of measurements it was proved that mean value of corrosion potential for grinded samples was  $E_{corr} = -309$  mV. Application of mechanical polishing caused increase of mean value of corrosion potential to  $E_{corr} = -275$  mV. Next, for samples with sol-gel coating applied on their surface, its value was: SiO<sub>2</sub>:  $E_{corr} = -172$  mV; TiO<sub>2</sub>:  $E_{corr} = +2$  mV, respectively. Values of polarisation resistance Rp and corrosion current density  $i_{kor}$ , determined additionally with application of Stern method, for the respective variants of tested samples, amounted to, respectively:

- grinded samples Rp = 216 k $\Omega$ cm<sup>2</sup>,  $i_{kor}$  = 0,120  $\mu$ A/cm<sup>2</sup>,
- grinded and mechanically polished samples Rp = 237 k $\Omega$ cm<sup>2</sup>,  $i_{corr} = 0,109 \mu A/cm^2$ ,
- samples with SiO<sub>2</sub> layer Rp = 377 k $\Omega$ cm<sup>2</sup>, i<sub>corr</sub> = 0,069  $\mu$ A/cm<sup>2</sup>.
- samples with  $TiO_2$  layer  $Rp = 3750 \text{ k}\Omega\text{cm}^2$ ,  $i_{corr} = 0,007 \text{ }\mu\text{A/cm}^2$ .

In the second stage of the study, which consisted in determination of physical and chemical characteristics of surface layers created by means of sol-gel method, EIS tests were made. Spectra determined in this way are presented in Figs. 5-8, while typical physical values are shown in Tab 4.

Table 3. Results of electrochemical corrosion resistance tests of Ti-6Al-7Nb alloy (mean measurement values)

Method of surface preparing	E <sub>corr</sub> , mV	$i_{corr.}, \mu A/cm^2$	$R_p, k\Omega cm^2$	E <sub>tr</sub> , mV
Grinded	-309	0.120	216	-
Polished	-275	0.109	237	-
Polished + SiO <sub>2</sub> layer	-172	0.069	377	+3361
Polished + TiO <sub>2</sub> layer	+2	0.007	3750	+3850

Table 4. Results of the EIS test

Method of surface preparing	$R_s$ , $\Omega$ ·cm <sup>2</sup>	$R_{ct}$ , $k\Omega \cdot cm^2$	$CPE_{dl}$		P. 1-02	$CPE_p$	
			$Y_{dl}$ , $\Omega^{-1}$ cm $^{-2}$ s $^{-n}$	n <sub>dl</sub>	$R_p$ , $k\Omega \cdot cm^2$ –	$Y_p, \Omega^{-1} cm^{-2} s^{-n}$	n <sub>p</sub>
Grinded	56	-	-	-	2123	0.393E-4	0.75
Polished	58	-	-	-	59283	2.483E-7	0.91
Polished + SiO <sub>2</sub> laver	58	13	6.258E-7	0.89	18320	5.481E-7	0.83
Polished + TiO <sub>2</sub> laver	57	25	2.478E-7	0.88	57543	6.723E-7	0.92

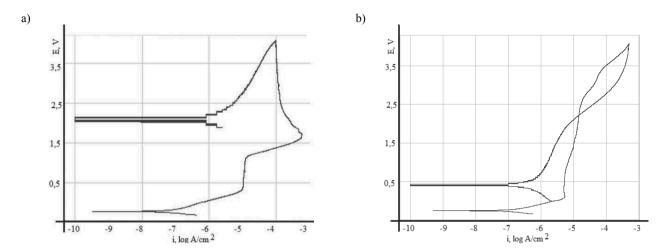


Fig. 3. Anodic polarization curves for Ti-6Al-7Nb alloy: a) after grinding, b) after grinding and mechanical polishing

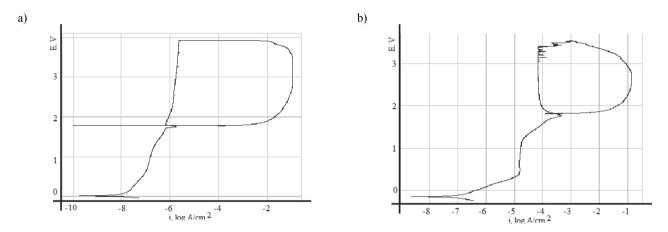


Fig. 4. Anodic polarization curves for Ti-6Al-7Nb alloy: a) after grinding, mechanical polishing and SiO<sub>2</sub> layer deposition, b) after grinding, mechanical polishing and SiO<sub>2</sub> layer deposition after grinding, mechanical polishing and TiO<sub>2</sub> layer deposition

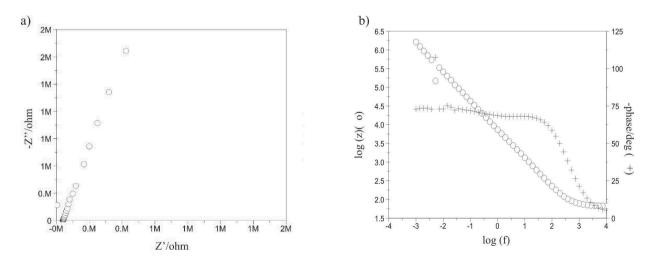
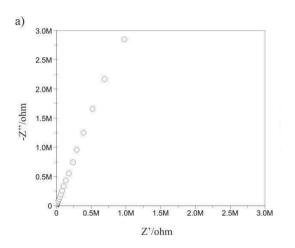


Fig. 5. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding: a) Nyquist diagram, b) Bode diagram

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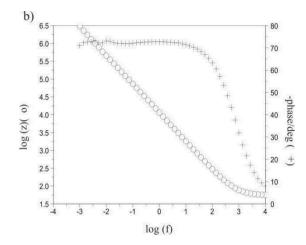
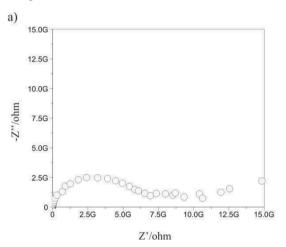


Fig. 6. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding and mechanical polishing: a) Nyquist diagram, b) Bode diagram



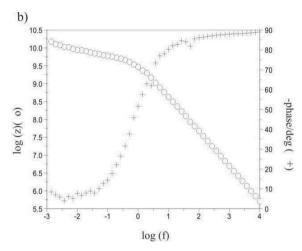
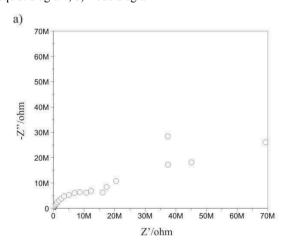


Fig. 7. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding, mechanical polishing and SiO<sub>2</sub> layer deposition: a) Nyquist diagram, b) Bode diagram



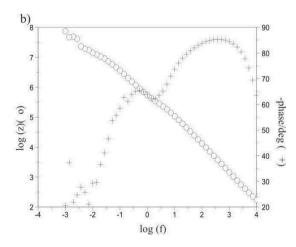


Fig. 8. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding, mechanical polishing and  $TiO_2$  layer deposition: a) Nyquist diagram, b) Bode diagram

Performed measurements aimed at determination of impedance on the phase boundary of systems: Ti-6Al-7Nb alloy passive layer - solution and Ti-6Al-7Nb alloy - surface layer (TiO $_2$  or SiO $_2$ , applied by means of sol-gel method) - solution. Phase boundary impedance characteristics was made through approximation of experimental data with application of physical electrical equivalent model. Phenomena taking place in the system of Ti-6Al-7Nb alloy - passive layer - solution were described with application of electrical equivalent model that consisted of parallel CPE system connected with resistance of ion transition through phase boundary  $R_{ct}$  and electrolyte resistance  $R_s$  - Fig. 9 [19,20].

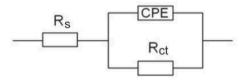


Fig. 9. Model of electrical equivalent circuit for the system: Ti-6Al-7Nb alloy - oxide layer - artificial plasma

A mathematical model of impedance for the system of: Ti-6Al-4V alloy - passive layer - solution is represented by equation [19] (1):

$$Z = R_S + \frac{1}{\frac{1}{R_p} + Y_p(j\omega)^{n_p}}$$
 (1)

Next, for the system of Ti-6Al-7Nb alloy - surface layer (TiO $_2$  or SiO $_2$ ) - solution in the equivalent model, presence of a double layer was additionally taken into consideration, by expanding the system by a parallel system of CPE $_{dl}$  and transition resistance  $R_{ct}$ -Fig. 10.

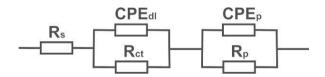


Fig. 10. Model of electrical equivalent circuit for the system: Ti-6Al-7Nb alloy - oxide layer - artificial plasma

A mathematical model of impedance for the system of: Ti-6Al-4V alloy - double layer - solution is represented by equation (2):

$$Z = R_S + \frac{1}{\frac{1}{R_{dl}} + Y_{dl} (j\omega)^{n_{dl}}} + \frac{1}{\frac{1}{R_p} + Y_p (j\omega)^{n_p}}$$
(2)

### 4. Conclusions

Corrosion resistance of biomaterials used for implants is their main biocompatibility criterion. Therefore, more and more studies related to surface modification of the existing biomaterials are made in order to obtain the best physical and chemical as well as mechanical characteristics of the material, with focus on the environment where the material will be used, and the type of work it is supposed to carry out or it will be subject to.

The structure and thickness of a surface layer play the main role in achieving the final quality of implants made of titanium alloy. There are many ways of forming it. The structure and the chemical makeup of the implants' layer, which is made of titanium and its alloys, can be modified using different methods, with the dominant methods being mechanical, chemical, electrochemical, and thermal. In addition to this, the physicochemical properties of the implants' surface can depend on the sterilization method applied in the final production process of the implants [14,21,22].

On the ground of the performed test it can be proved that the process of application of TiO<sub>2</sub> layer by means of sol-gel method performed in order to ensure proper procedures related to the quality of production of implants to be used in contact with blood, promotes positive changes by influencing improvement of corrosion resistance of this metallic biomaterial type.

# References

- [1] M.C. Advincula, D. Petersen, F. Rahemtulla, R. Advincula, J.E. Lemons, Surface analysis and biocorrosion properties of nanostructured surface sol-gel coatings on Ti6Al4V titanium alloy implants, Journal of Biomedical Materials Research Part B, Applied Biomaterials 80/1 (2006) 107-120.
- [2] S.M.A. Shibli, S. Mathai, Development and bioelectrochemical characterization of a novel TiO<sub>2</sub>-SiO<sub>2</sub> mixed oxide coating for titanium implants, Journal of Material Science 19 (2008) 2971-2981.
- [3] Z. Paszenda, J. Tyrlik-Held, Z. Nawrat, J. Żak, J. Wilczek, Usefulness of passive-carbon layer for implants applied in interventional cardiology, Journal of Materials Processing Technology 157-158C (2004) 399-404.
- [4] Z. Paszenda, Corrosion resistance of coronary stents in a coronary angioplasty, Corrosion Protection 11s/A (2004) 195-198 (in Polish).
- [5] H. Nan, Y. Ping, C. Xuan, L. Yongxang, Z. Xiaolan, C. Guangjun, Z. Zihong Z. Feng, C. Yuanru, L. Xianghuai, X. Tingfei, Blood compatibility of amorphous titanium oxide films synthesized by ion beam enhanced deposition, Biomaterials 19 (1998) 771-776.
- [6] J.Y. Chen, Y.X. Leng, X.B. Tian, L.P. Wang, N. Huang, P.K. Chu, P. Yang, Antithrombotic investigation of surface energy and optical bandgap and hemocompatibility mechanism of Ti(Ta<sup>+5</sup>)O<sub>2</sub> thin films, Biomaterials 23 (2002) 2545-2552.
- [7] N. Huang, P. Yang, Y. Leng, J. Chen, H. Sun, J. Wang et al., Hemocompatibility of titanium oxide films, Biomaterials 24 (2003) 2177-2187.

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- [8] M. Bartoszek, Z. Drzazga, A study of magnetic anisotropy of blood cells, Journal of Magnetism and Magnetic Materials 196-197 (1999) 573-575.
- [9] M. Bartoszek, M Balanda, D. Skrzypek, Z. Drzazga, Magnetic field effect on hemin, Physica B 307 (2001) 217-223.
- [10] J. Szewczenko, W. Walke, K. Nowinska, J. Marciniak, Corrosion resistance of Ti-6Al-4V alloy after diverse surface treatments. Materialwissenschaft und Werkstofftechnik 41/5 (2010) 360-371.
- [11] W. Chrzanowski, J. Szewczenko, J. Tyrlik-Held, J. Marciniak, J. Zak, Influence of the anodic oxidation on the physicochemical properties of the Ti-6Al-4V ELI alloy, Journal of Materials Processing Technology 162-163 (2005) 163-168.
- [12] A. Daymi, M. Boujelbene, J. M. Linares, E. Bayraktar, A. Ben Amara, Influence of workpiece inclination angle on the surface roughness in ball and milling of the titanium alloy Ti-6Al-4V, Journal of Achievements in Materials and Manufacturing Engineering 35 (2009) 79-86.
- [13] S. Tamilselvi, V. Raman, N. Rajendran, Evaluation of corrosion behavior of surface modified Ti-6Al-4V ELI alloy in hanks solution, Journal of Materials Science 40 (2010) 285-293.
- [14] N. Zaveri, G.D. McEwen, R. Karpagavalli, A. Zhou, Biocorrosion studies of TiO<sub>2</sub> nanoparticle-coated Ti-6Al-4V implant in simulated biofluids, Journal of Nanoparticle 12/5 (2009) 1609-1623.

- [15] J. Sieniawski, M. Motyka, Superplasticity in titanium alloys, Journal of Achievements in Materials and Manufacturing Engineering 24 (2007) 123-130.
- [16] http://large.stanford.edu/courses/2008/ph210/hellstrom1/
- [17] Z. Paszenda, W. Walke, S. Jadacka, Electrochemical investigations of Ti6Al4V and Ti6Al7Nb alloys used on implants in bone surgery, Journal of Achievements in Materials and Manufacturing Engineering 38/1 (2010) 24-32.
- [18] J. Szewczenko, M. Pochrząst, W. Walke, Evaluation of electrochemical properties of modified Ti-6Al-4V ELI alloy, Electrical Review 12 (2011) 178-181.
- [19] B. Łosiewicz, A. Budniok, Use of electrochemical impedance spectroscopy technique to investigate the passivation of intermetallic Fe24Al alloy in sulphuric acid, Corrosion of Protection 11 (2003) 49-54.
- [20] A. Baron, W. Simka, W. Chrzanowski, EIS tests of electrochemical behaviour of Ti6Al4V and Ti6Al7Nb alloys. Journal of Achievements in Materials and Manufacturing Engineering 21 (2007) 23-26.
- [21] E. Krasicka-Cydzik, A. Kierzkowska, I. Glazowska, Behavior of anodic layer in Ringer's solution on Ti6Al4V ELI alloy after bending, Archives of Materials Science and Engineering 28 (2007) 231-237.
- [22] M. Balazic, D. Recek, D. Kramar, M. Milfelner, J. Kopac, Development process and manufacturing of modern medical implants with LENS technology, Journal of Achievements in Materials and Manufacturing Engineering 32 (2009) 46-52.