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TiO_2 and SiO_2 layer deposited by sol-gel method on the Ti6Al7Nb alloy for contact with blood

W. Walke [a,*], Z. Paszenda [a], P. Karasiński [b], J. Marciniak [a]

[a] Department of Biomaterials and Medical Engineering Devices, Faculty of Biomedical Engineering, Silesian University of Technology, ul. Akademicka 16, 44-100 Gliwice, Poland

[b] Department of Optoelectronics, Faculty of Electrical Engineering, Silesian University of Technology, ul. Akademicka 8, 44-100 Gliwice, Poland

* Corresponding e-mail address: witold.walke@polsl.pl

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ABSTRACT

Purpose: The study contains the analysis of TiO_2 and SiO_2 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 μm) and mechanical polishing (Ra = 0.12 μm). 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±1°C and pH = 7.0±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-6Al-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

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 fibrinogen 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 (fibrinogen) 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 fibrinogen, 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
Ta	max 0,50	0.37
C	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.

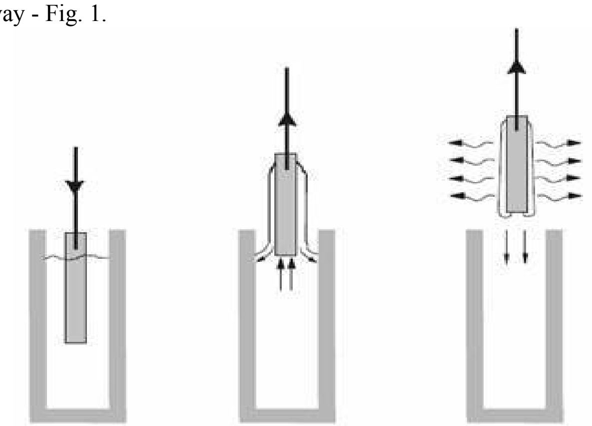

Fig. 1. Scheme of the sol-gel method [16]

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 impedance spectroscopy tests were also performed. Measurements were made with application of measurement system Auto Lab PGSTAT 302N equipped with FRA2 (Frequency Response Analyser) module. The applied measurement system enabled to perform tests in frequency range 10^4-10^{-3}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±1°C and pH = 7.0 ±0,2 - Tab. 2, Fig. 2.

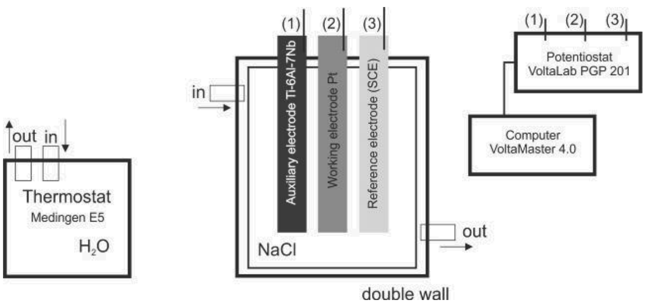

Fig. 2. Scheme of the corrosion test

Table 2.
Chemical composition of artificial plasma

Ingredients	Ingredients concentration, g/dm^3 distilled water
NaCl	6.8
KCl	0.4
$CaCl_2$	0.2
$MgSO_4$	0.1
$NaHCO_3$	0.2
Na_2HPO_4	0.126
NaH_2PO_4	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_2: E_{corr} = -172 mV; TiO_2: 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 kΩcm^2, i_{kor} = 0,120 μA/cm^2,
- grinded and mechanically polished samples - Rp = 237 kΩcm^2, i_{corr} = 0,109 μA/cm^2,
- samples with SiO_2 layer - Rp = 377 kΩcm^2, i_{corr} = 0,069 μA/cm^2.
- samples with TiO_2 layer - Rp = 3750 kΩcm^2, i_{corr} = 0,007 μA/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_{corr}, mV	$i_{corr.}$, μA/cm^2	R_p, kΩcm^2	E_{tr}, mV
Grinded	-309	0.120	216	-
Polished	-275	0.109	237	-
Polished + SiO_2 layer	-172	0.069	377	+3361
Polished + TiO_2 layer	+2	0.007	3750	+3850

Table 4.
Results of the EIS test

Method of surface preparing	R_s, Ω·cm^2	R_{ct}, kΩ·cm^2	CPE_{dl}		R_p, kΩ·cm^2	CPE_p	
			Y_{dl}, $\Omega^{-1}cm^{-2}s^{-n}$	n_{dl}		Y_p, $\Omega^{-1}cm^{-2}s^{-n}$	n_p
Grinded	56	-	-	-	2123	0.393E-4	0.75
Polished	58	-	-	-	59283	2.483E-7	0.91
Polished + SiO_2 layer	58	13	6.258E-7	0.89	18320	5.481E-7	0.83
Polished + TiO_2 layer	57	25	2.478E-7	0.88	57543	6.723E-7	0.92

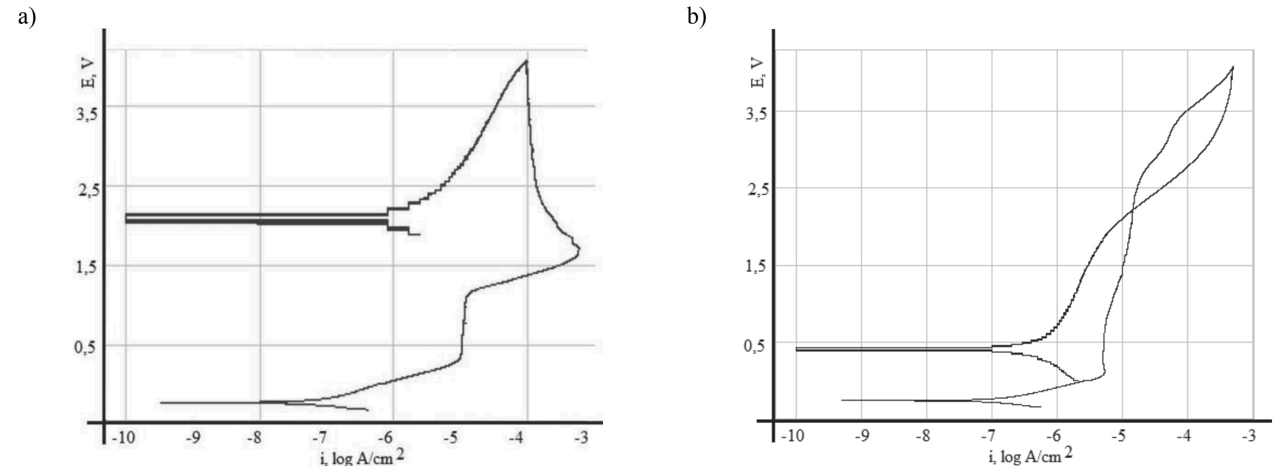

Fig. 3. Anodic polarization curves for Ti-6Al-7Nb alloy: a) after grinding, b) after grinding and mechanical polishing

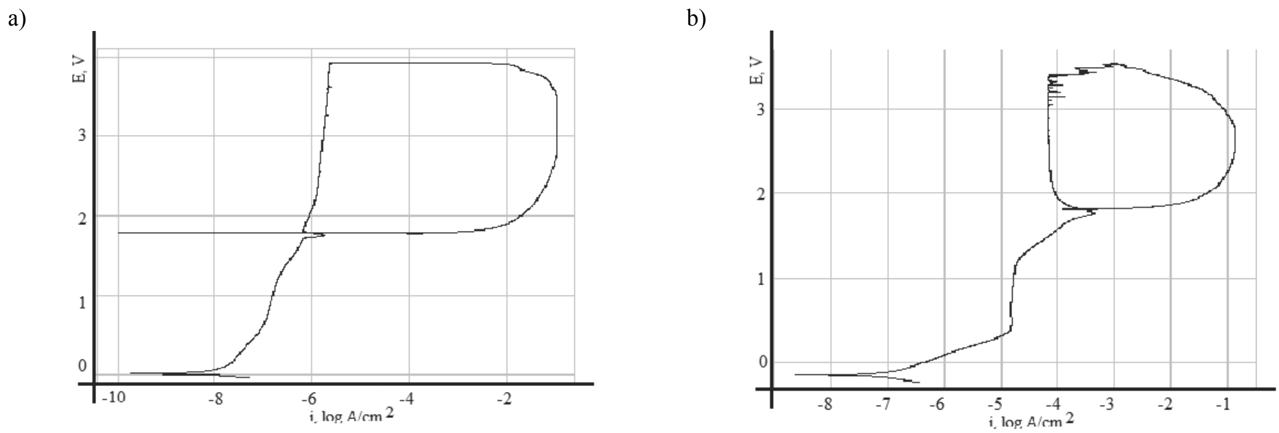

Fig. 4. Anodic polarization curves for Ti-6Al-7Nb alloy: a) after grinding, mechanical polishing and SiO_2 layer deposition, b) after grinding, mechanical polishing and SiO_2 layer deposition after grinding, mechanical polishing and TiO_2 layer deposition

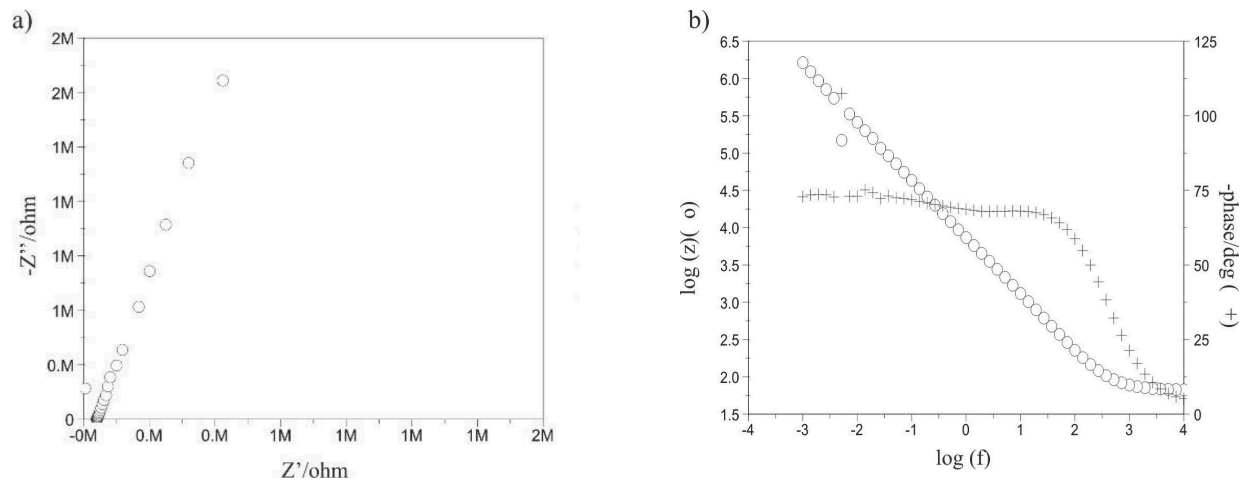

Fig. 5. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding: a) Nyquist diagram, b) Bode diagram

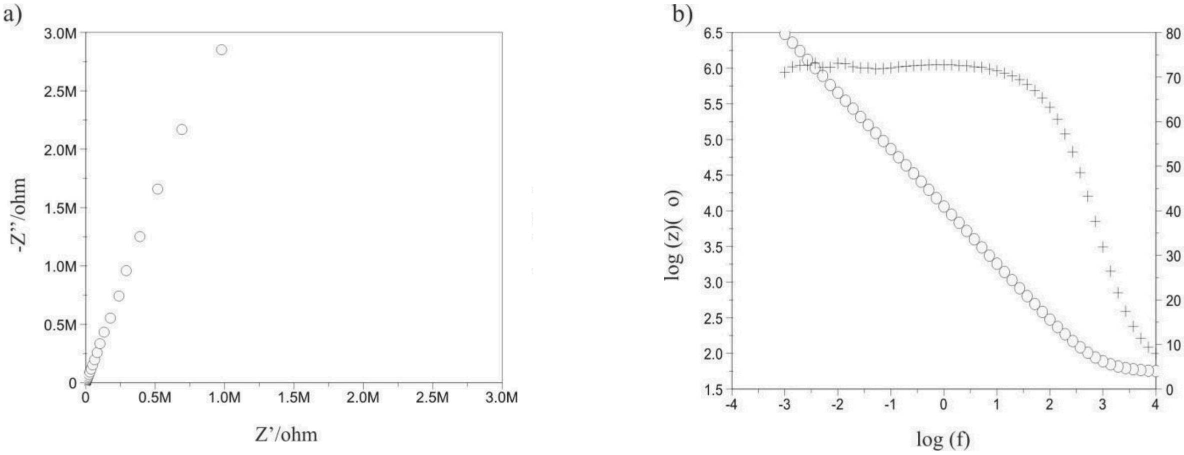

Fig. 6. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding and mechanical polishing: a) Nyquist diagram, b) Bode diagram

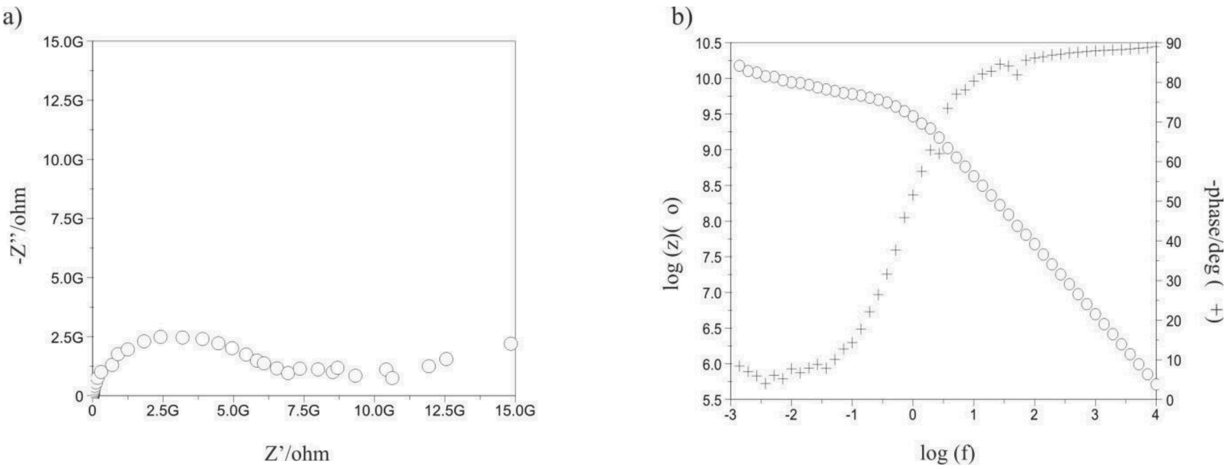

Fig. 7. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding, mechanical polishing and SiO_2 layer deposition: a) Nyquist diagram, b) Bode diagram

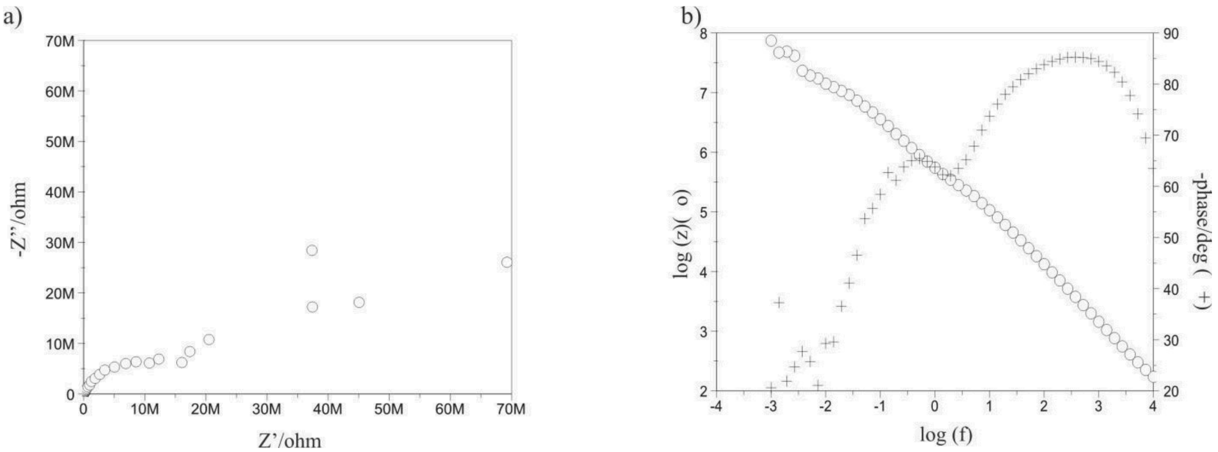

Fig. 8. Impedance spectra for samples made of Ti-6Al-7Nb alloy after grinding, mechanical polishing and TiO_2 layer deposition: a) Nyquist diagram, b) Bode diagram

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].

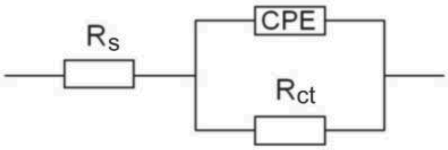

Fig. 9. Model of electrical equivalent circuit for the system: Ti-6Al-7Nb alloy - oxide layer - artificial plasma

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

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

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.

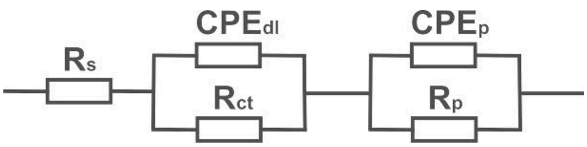

Fig. 10. Model of electrical equivalent circuit for the system: Ti-6Al-7Nb alloy - oxide layer - artificial plasma

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

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

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_2 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.

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