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The silica-titania layer deposited by sol-gel method on the AISI 316L for contact with blood

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Materials

ABSTRACT

Purpose: The study analyses influence of surface modification of Si:Ti on physical and chemical properties of samples made from AISI 316L steel in solution simulating blood-vascular system.
Design/methodology/approach: Sol-gel layer was selected on the ground of data from literature. TEOS and TET made the ground for initial solution. Application of the layer on the surface of samples made of AISI 316L steel 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. In order to evaluate phenomena that take place on the surface of the tested alloys EIS was also applied. The tests were performed in artificial blood plasma at the temperature of T = 37.0±1°C and pH = 7.0±0.2.
Findings: Obtained results on the ground of voltammetric and impedance tests showed differentiated electrochemical properties of AISI 316L steel depending on the type of surface treatment.
Practical implications: Suggested subject matter of the article supports development of entrepreneurship sector due to high social demand for this type of technologies and relatively easy way of putting obtained laboratory tests data into inductrial and clinical practice.
Originality/value: Suggestion of proper variants of surface treatment with application of sol-gel method is meaningful in future perspective and it shall promote determination of technological conditions with precise parameters of creation of oxide layers on metallic implants made of AISI 316L steel that come into contact with blood.
Keywords: AISI 316L; Sol-gel method; Corrosion resistance; EIS

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1. Introduction

Typical methods of surface modification that have been used so far, such as electrochemical polishing and chemical passivation seem to be insufficient for protection of implant from tissue environment impact. Such methods of surface modification are responsible for the appearance of atomic elements in the oxide layer that come from metallic substrate (Fe, Ni, Cr), whose presence is unfavourable. In order to improve biocompatibility of metallic biomaterials we must pay attention most of all to the increase of their corrosion resistance. Metallic material implanted to an organism remains in contact with body fluids serving as electrolytes. The issue of implant corrosion should be solved in relation to corelation between the environment the implant was placed in and the set of its mechanical properties and physical and chemical characteristics of its surface. Characteristics of initial state of the surface may be changed as early as during technological procedure through local damage of implant surface layer or undetermined modelling of corrosion environment conditions. One of the ways how to increase biocompatibility of biomaterial surface is application of sol-gel method for creation of thin oxide layers on the substrate of such elements as: Ti, Si, P, Ca. An advantage of this method is low temperature in which such layers are created, which guarantees stability of mechanical properties of metallic substrate [1-5]. The sol-gel technique is a chemical method to obtain amorphous materials from solutions [6]. Respective organic or non-organic compounds are precursors of these materials. For silica, the most commonly applied organic precursors are tetraethoxysilane $Si(OC_2H_5)_4$ referred to as TEOS and tetramethoxysilane $Si(OCH_3)_4$ referred to as TMOS. For titania the most commonly applied organic precursors are titanium(IV)ethoxide $Ti(OC_2H_5)_4$ referred to as TET or titanium(IV)methoxide $Ti(OCH_3)_4$. The author used TEOS and TET (ALDRICH) as precursors of waveguide films. The remaining output components included ethyl alcohol (EtOH) and water. Hydrochloric acid (HCL) was aplied as catalyst. The following stages can be distinguished in the generation process of respective films with the application of sol-gel technique [6,7]:

- generation of colloidal system (sol), in which the applied precursor is the disperse phase, and the dispersion phase is made up by respective alcohol and water.
- hydrolysis, which is taking place in full or partially, depending on the quantity of solvent and the presence of catalyst:

$$M(OR)_4 + H_2O \rightarrow HO-M(OR)_3 + ROH \tag{1}$$

or

$$M(OR)_4 + 4H_2O \rightarrow M(OH)_4 + 4ROH \tag{2}$$

where: M - metal atom
R - alkyl group
ROH - alcohol

- generation of manomer. The particles, which earlier were subjected to hydrolysis can now join each other forming the monomer. The reactions usually follow the scheme as presented below:

$$(OR)_3M-OH+OH-M(OR)_3 \rightarrow (OR)_3M-O-M(OR)_3+H_2O \tag{3}$$

or

$$(OR)_3M-OH+OH-M(OR)_3 \rightarrow (OH)_3M-O-M(OR)_3+ROH \tag{4}$$

- gel is formed in effect of the polymerization of manomer, and of the increase of particles, and particles join each other into chains and later into network,
- deposition of gel film on the substrate,
- drying and annealing of deposited films.

The reactions of condensation start before the reactions of hydrolysis are finished. The proportions of the applied output components, kind and amount of the applied catalyst as well as parameters characterizing particular stages of the technological process have the influence on the properties of the obtained films [8].

Data from literature shows a number of non-defined phenomena that accompany creation of oxide layers involving silicon on the surface of metallic biomaterials. What still remains an unsolved problem is the selection of proper parameters of layers creation as well as complex tests presenting full characteristics of their behaviour under conditions of implantation and long-term exposure in tissue environment during implant utilisation [1-7].

2. Materials and methods

Samples of AISI 316L alloy cut from wire rod with diameter of d= 14 mm were used in the tests. Both, chemical composition and structure of the alloys were in accordance with recommendations of ISO 5832-1 - Table 1.

The tests included samples with differentiated way of surface preparation. Differentiated surface roughness was obtained through mechanical working - grinding (Ra = 0.40 µm) and mechanical polishing (Ra = 0.12 µm).

Table 1.
Chemical compositions of AISI 316L

Element	Acc. to ISO	Ladle analysis
	Mass concentration, %	
C	<0.03	0.01
Cr	17.0-19.0	17.49
Fe	rest	rest
Mn	<2.0	1.68
N	0.1-0.2	0.087
Ni	14.0-16.0	14.49
P	<0.025	0.017
S	<0.01	0.003
Si	<1.0	0.21
Mo	2.35-4.2	2.76
Cu	<0.5	0.05

Next, sol-gel layers were applied on sample surfaces prepared in such a way. The silica-titania waveguide films were produced using the precursors tetraethyl ortosilane $Si(OC_2H_5)_4$ (TEOS) for silica and tetraethoxytitanate $Ti(OC_2H_5)_4$ (TET) for titania. The gels formation procedures were carried out in two stages. In the first stage the hydrolyses of the TEOS and the TET were carried out separately. Then partially hydrolyzed TET solution was added to partially hydrolyzed TEOS solution and the sol formation process was carried out. The two solutions were mixed in proportions ensuring that the molar ratio Si:Ti=1:0.31 and Si:Ti=1:1.25 were obtained. respectively. Ethyl alcohol was used as a homogenizing agent and hydrochloric acid was applied as a catalyst. Films were deposited on substrates using the dip coating method. We applied two different substrate withdrawal speed from sols; 2 cm/min and 2.5 cm/min. After the deposition of sols on substrates. the structures were annealed for 60 min. at temperature 400°C and 500°C. respectively [9,10].

Then, samples presenting consecutive stages of surface preparation were subject to pitting corrosion resistance tests. Tests were performed in accordance with recommendations of PN-ISO 17475. Anodic polarisation curves were registered with application of potentiostat PGP-201 by Radiometer. Saturated calomel electrode (SCE) of KP-113 type served as the reference electrode. Platinum electrode PtP-201 served as auxiliary electrode. Change of potential in anodic direction was made at the rate of 1 mV/s. Stern method was also used for determination of parameters characterising corrosion resistance of tested alloys.

In order to obtain information about physical and chemical properties of the surface of AISI 316L samples. the tests employing electrochemical impedance spectroscopy were also performed. Measurements were made with measurement system Auto Lab PGSTAT 302N equipped with FRA2 (Frequency Response Analyser) module. The employed measurement system enabled to perform tests within frequency range of 10^4-10^{-3}Hz. Impedance spectra of the system were determined in the tests and obtained measurement data was matched to the equivalent system. On that ground numerical values of resistance R and capacity C of the analysed systems were determined. Impedance spectra of the tested system are presented as Nyquist diagrams for various frequencies and as Bode diagrams. Obtained EIS spectra have been interpreted after matching by means of least square method to the equivalent electric circuit.

All electrochemical tests were performed in artificial plasma at the temperature of T = 37±1°C and pH = 7.0±0.2 - Table 2.

Fig. 1 presents a scheme of test station used for potentiodynamic and impedance tests.

3. Results

The results of performed potentiodynamic tests are presented in Table. 3 and in Figs. 2-4. Differentiated corrosion resistance depending on the way of surface preparation of AISI 316L steel was proved. Analysis of changes of parameters characterising the resistance to pitting corrosion shows favorable impact of chemical passivation process. Increase of corrosion potential. breakdown potential and polarisation resistance were noticed as well as decrease of corrosion current density - Table 3.

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

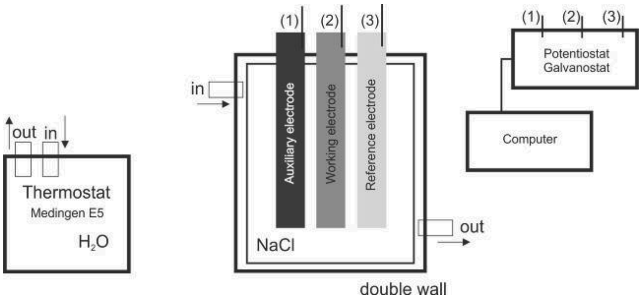

Fig. 1. Scheme of the corrosion test

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. 5-10. while typical physical values are shown in Table 4. Performed measurements aimed at determination of impedance on the phase boundary of systems: AISI 316L steel - surface layer - solution [11-13] - Fig. 11. Phase boundary impedance characteristics was made through approximation of experimental data with application of physical electrical equivalent model.

Table 3.
Results of electrochemical corrosion resistance tests of AISI 316L (mean measurement values)

Surface	E_{cor}. mV	$i_{cor.}$. μA/cm^2	R_p. kΩcm^2	E_b. mV
Polished	-188	0.046	560	+731
Polished + Si:Ti=1:0.31	-408	0.361	72	+335
Polished + Si:Ti=1:1.25	-354	0.839	31	+274
Passivated	-132	0.013	2040	+1411
Passivated + Si:Ti=1:0.31	-182	0.124	209	+629
Passivated + Si:Ti=1:1.25	-135	0.230	113	+832

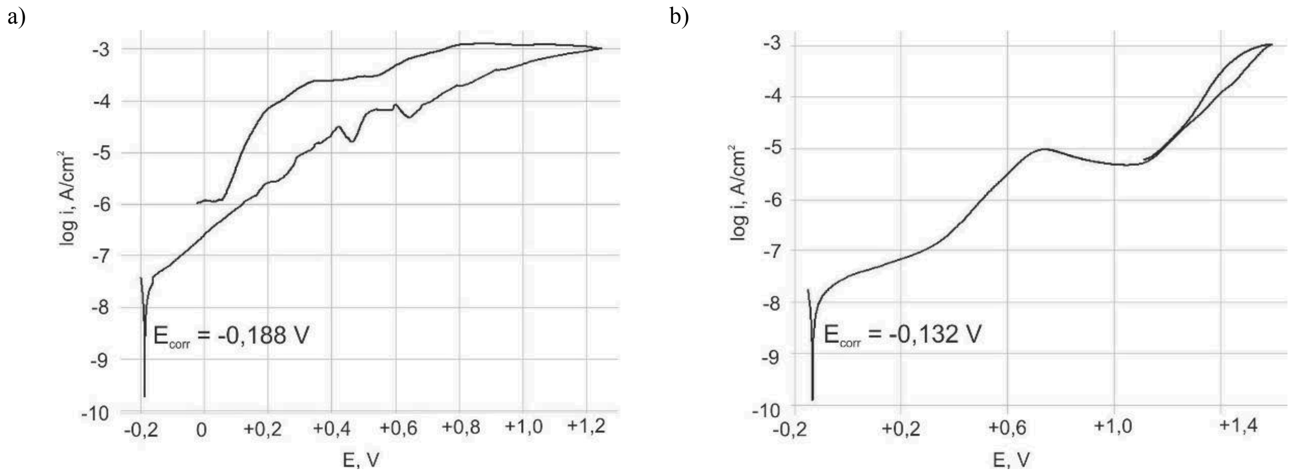

Fig. 2. Anodic polarization curves for AISI 316L: a) after polishing, b) after polishing and chemical passivating

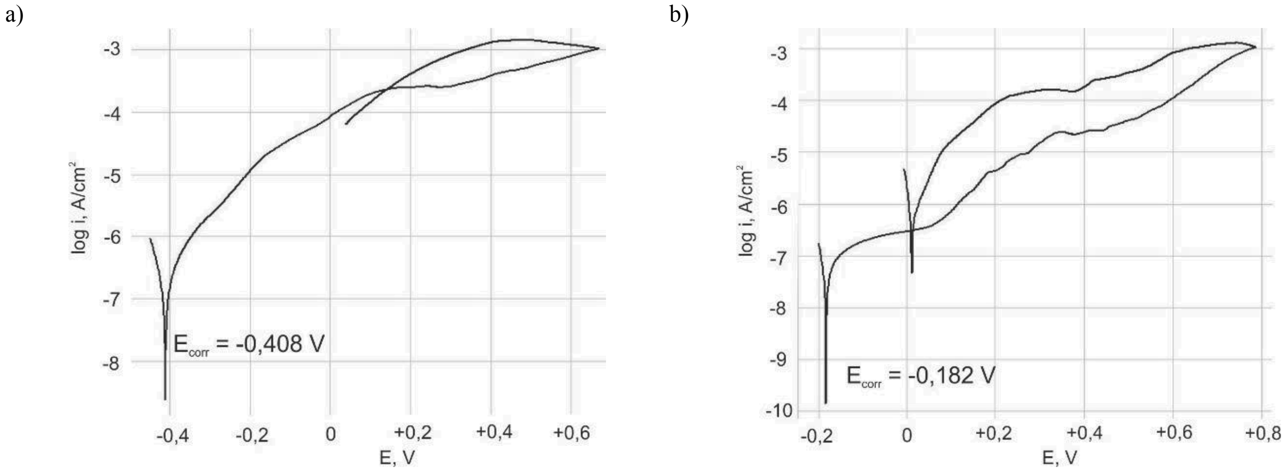

Fig. 3. Anodic polarization curves for AISI 316L: a) after polishing + Si:Ti=1:0.3, b) after passivating + Si:Ti=1:0.31

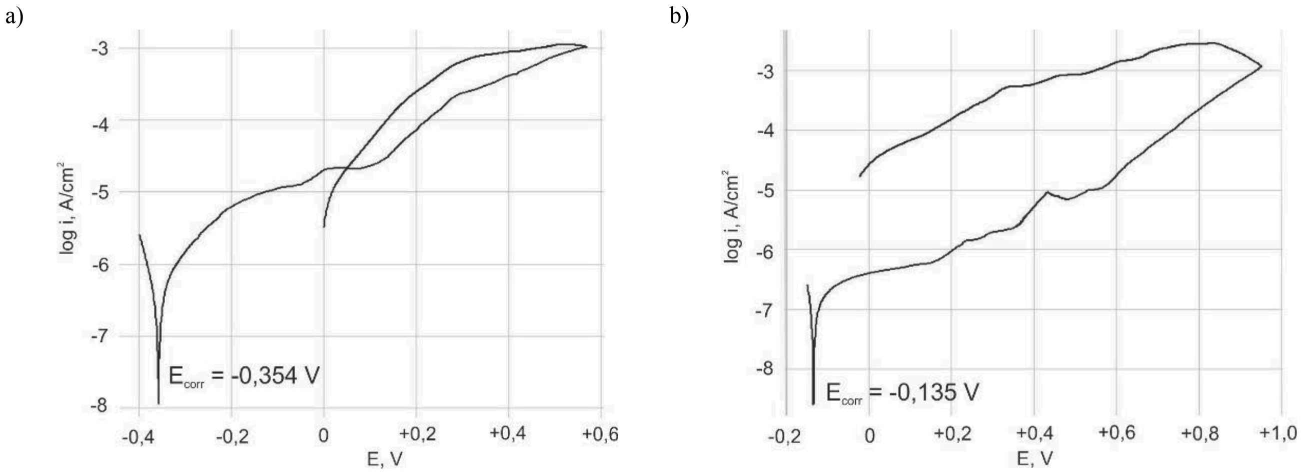

Fig. 4. Anodic polarization curves for AISI 316L: a) after polishing + Si:Ti=1:1.25, b) after passivating + Si:Ti=1:1.25

Table 4.
Results of the EIS test

Surface	R_s, $\Omega\cdot cm^2$	R_{ct}, $k\Omega\cdot cm^2$	CPE_{dl}		R_p, $k\Omega\cdot cm^2$	CPE_p		W,
			Y_{dl}, $\Omega^{-1}cm^{-2}s^{-n}$	n_{dl}		Y_p, $\Omega^{-1}cm^{-2}s^{-n}$	n_p	$m\Omega$
Polished	24	829	0.2668e-4	0.92	-	-	-	-
Polished + Si:Ti=1:0.31	23	61	0.8006e-4	0.57	4	0.3014e-4	0.94	-
Polished + Si:Ti=1:1.25	25	34	0.2563e-4	0.63	-	-	-	0.236
Passivated	22	1550	0.2951e-4	0.90	-	-	-	-
Passivated + Si:Ti=1:0.31	23	1793	0.6179e-4	0.84	53	0.2327e-6	0.99	0.207
Passivated + Si:Ti=1:1.25	24	908	0.1710e-3	0.84	45	0.6140e-5	0.76	1.759

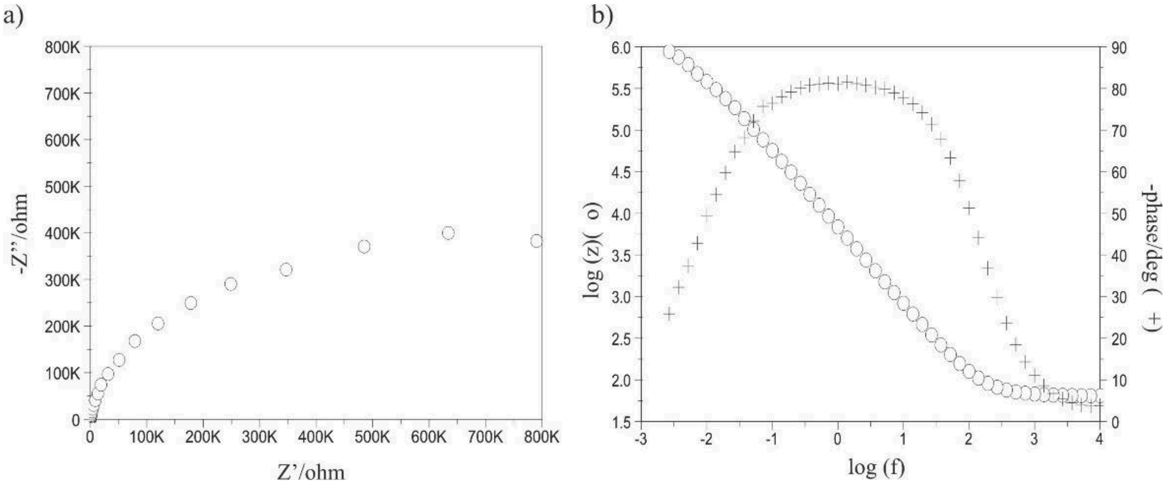

Fig. 5. Impedance spectra for samples made of AISI 316L after polishing: a) Nyquist diagram, b) Bode diagram

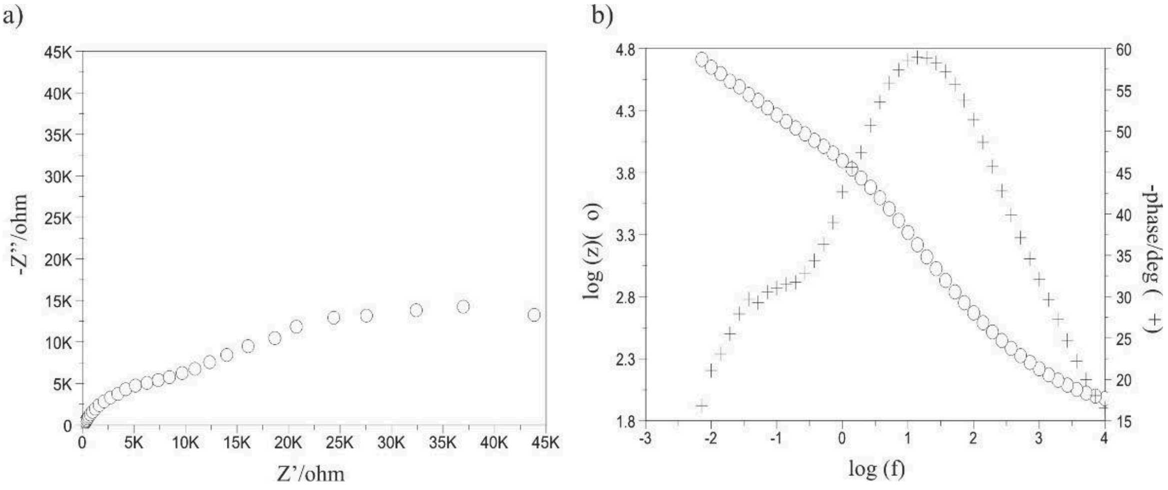

Fig. 6. Impedance spectra for samples made of AISI 316L after polishing + Si:Ti=1:1.25 : a) Nyquist diagram, b) Bode diagram

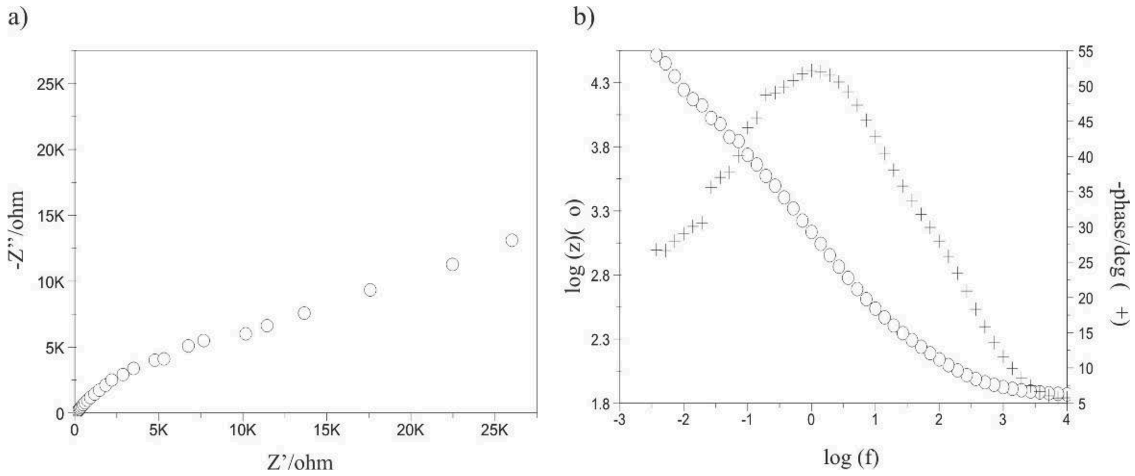

Fig. 7. Impedance spectra for samples made of AISI 316L after polishing + Si:Ti=1:0.31 : a) Nyquist diagram, b) Bode diagram

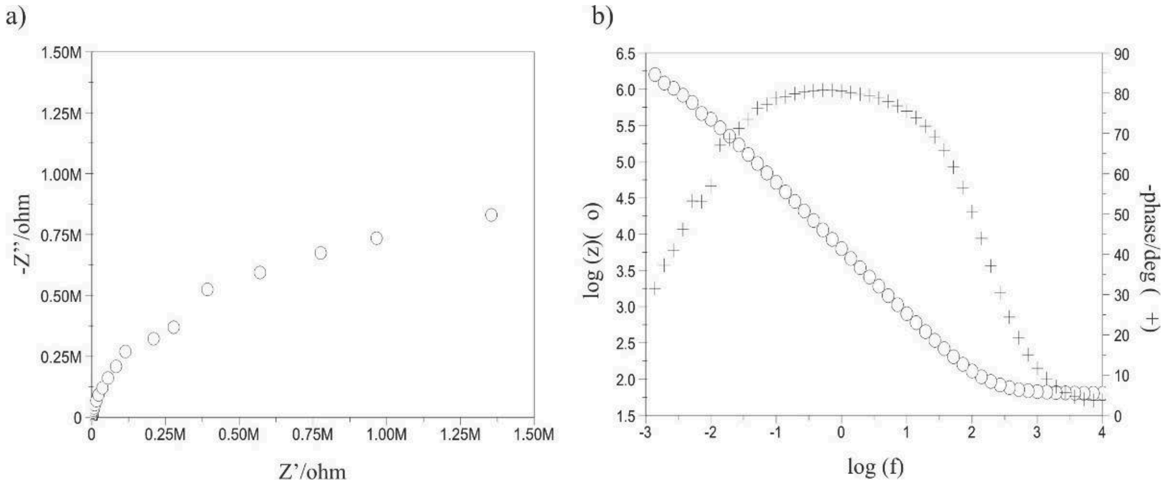

Fig. 8. Impedance spectra for samples made of AISI 316L after passivating: a) Nyquist diagram, b) Bode diagram

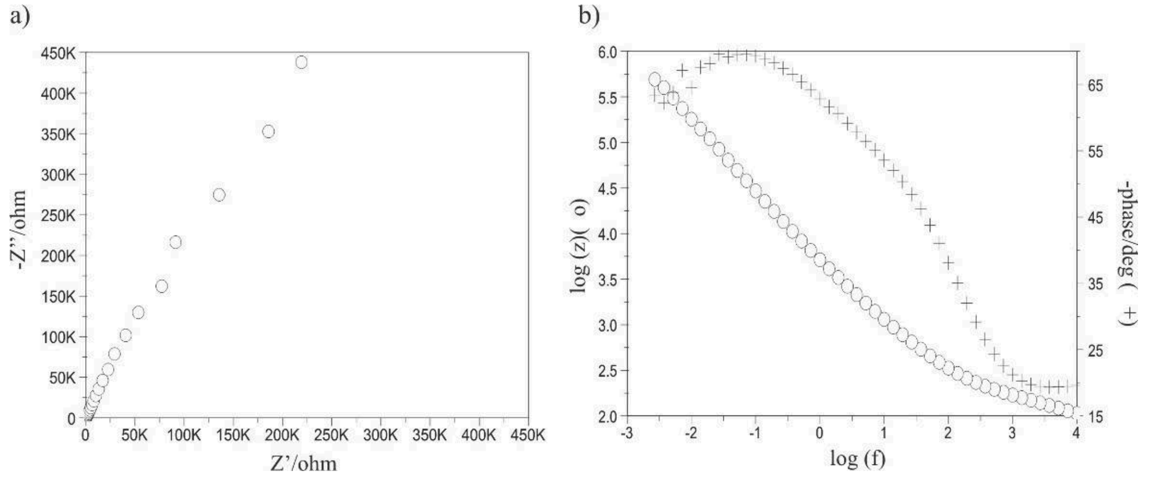

Fig. 9. Impedance spectra for samples made of AISI 316L after passivating + Si:Ti=1:1.25 : a) Nyquist diagram, b) Bode diagram

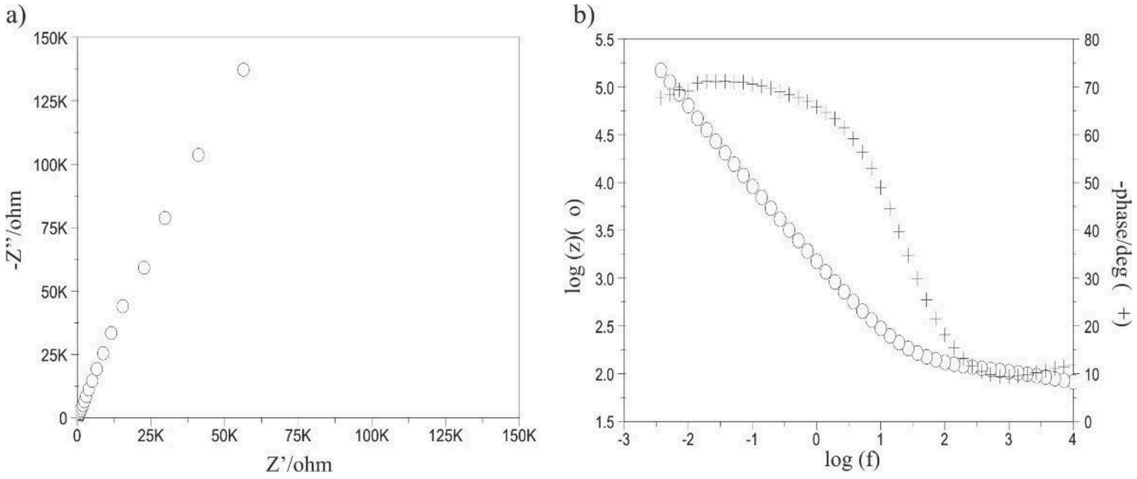

Fig. 10. Impedance spectra for samples made of AISI 316L after passivating + Si:Ti=1:0.31 : a) Nyquist diagram, b) Bode diagram

Phenomena taking place in the system of AISI 316L steel - surface layer - solution were described with application of electrical equivalent models presented in Fig. 11. Symbols presented in Fig. 11 indicate, respectively: R_s - electrolyte resistance, CPE_{dl} - capacity of double layer, R_{ct} - resistance of charge transfer on phase boundaries, CPE_P - capacity of porous layer, R_P - resistance of solution in pores, W -Warburg element.

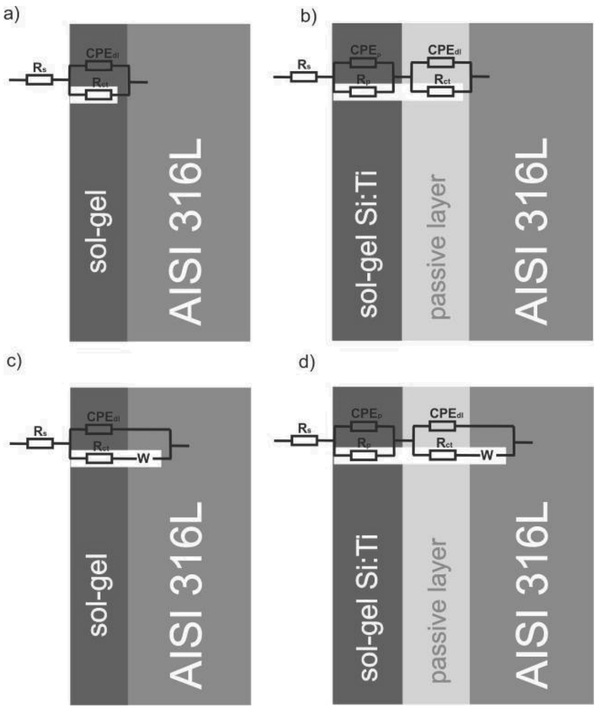

Fig. 11. Model of electrical equivalent circuit for the AISI 316L: a) polished and passivated, b) polished + Si:Ti=1:0.31, c) polished + Si:Ti=1:0.31, d) passivated + Si:Ti=1:0.31 and passivated + Si:Ti=1:1.25

4. Conclusions

Corrosion resistance of biomaterials used for implants for invasive cardiology is the basic criterion for hemocompatibility. Therefore, there are more and more studies related to modification of surface of the existing biomaterials in order to obtain the best physical and chemical properties of the material, taking into consideration the environment in which it will be placed and the type of task it is supposed to perform or it will be subject to. Despite benefits arising from application of metallic goods, some unfavourable processes that limit treatment efficiency can be observed. Among them, one can find blood creation of restenosis. The main way to limit those unfavourable processed is creation of physical and chemical characteristics of surface layer of cardiologic implants [14-18].

In order to ensure the required morphologic structure and physical and chemical characteristics of the surface of AISI 316L steel, conditions of surface treatment with participation of Si and Ti as well as interstitial elements (there: oxygen, nitrogen and carbon) were elaborated. Surface treatment process was performed with application of sol-gel method. Application of this type of surface treatment seems to be purposeful in order to ensure stable structural features and mechanical properties of steel subjected to surface treatment

Performed electrochemical tests showed that chemical passivation has a significant impact on improvement of corrosion resistance of AISI 316L steel. It also has favourable influence on characteristics of the layer Si:Ti by improving its tightness, which was proved in impedance tests. Application of Si:Ti layer on the surface of AISI 316L steel preceded by chemical passivation process seems to be justified and shall be used to improve hemocompatibility of that steel in contact with blood.

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