Haemocompatibility of Surface Modified AISI 316L Austenitic Stainless Steel Tested in Artificial Plasma

W. Walke, J. Przondziono, K. Nowińska

Abstract—The study comprises evaluation of suitability of passive layer created on the surface of AISI 316L stainless steel for products that are intended to have contact with blood. For that purpose, prior to and after chemical passivation, samples were subject to 7 day exposure in artificial plasma at the temperature of T=37°C. Next, tests of metallic ions infiltration from the surface to the solution were performed. The tests were performed with application of spectrometer JY 2000, by Yobin – Yvon, employing Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). In order to characterize physical and chemical features of electrochemical processes taking place during exposure of samples to artificial plasma, tests with application of electrochemical impedance spectroscopy were suggested. The tests were performed with application of measuring unit equipped with potentiostat PGSTAT 302n with an attachment for impedance tests FRA2. Measurements were made in the environment simulating human blood at the temperature of T=37°C. Performed tests proved that application of chemical passivation process for AISI 316L stainless steel used for production of goods intended to have contact with blood is well-grounded and useful in order to improve safety of their usage.

Keywords—AISI 316L stainless steel, chemical passivation, artificial plasma, ions infiltration, EIS.

I. INTRODUCTION

ONE of the negative phenomena taking place in blood environment is haemostasis brought about by the presence of metallic material [1], [2]. The process of interaction of blood with implant materials or materials used for production of surgical tools still is not fully understood. Generally, it is assumed that due to the contact of blood with artificial surface, first of all protein adsorption (mainly fibrinogen) takes place there. In the situation when adsorbed fibrinogen undergoes denaturation process in the cascade way, successive blood clotting agents, platelet- and plasma-related, are activated. It results in creation of a clot. Subject matter literature has featured relations explaining the essence of clotting process initiation based on band model of solid body [3], [4]. On the ground of the research made by Gutmann and his collaborators it was proved that fibrinogen has an electron structure typical of semi-conductors. The width of its forbidden band is 1.8 eV. Valence and conduction bands are placed respectively, 0.9 eV below or above Fermi level [5]. Therefore, the process of transformation of protein from inactive into active form may be connected with electrochemical reaction between protein and the surface of the material that has contact with blood. Electrons from valence band of fibrinogen cause protein decomposition. Consequently, protein is transformed into monomer and fibrin peptide. Next process is their cross-linking to the form of thrombus, which is irreversible. The performed analysis proves that it seems to be purposeful to modify physical properties of the surface of metallic materials by means of their surface treatment. Creation of a layer featuring high corrosion resistance and semi-conductive or dielectric properties on the surface of products used in blood system may efficiently impede the transfer of electrons from valence band of fibrinogen. Consequently, it may create an efficient way to limit blood coagulation process.

One of the ways how to increase corrosion resistance of AISI 316L stainless steel, and at the same time reduce blood coagulation process is obtaining a passive layer on its surface. Process of passive layer application proceeds in two stages. It comprises the stage of electrochemical polishing that aims at obtaining surface roughness of $R_a < 0.16$ µm, and chemical passivation. Selection of proper process parameters prevents the removal of passive layer during sterilisation with pressurised water steam. In order to verify correctness of process parameters selection, the authors of the study performed measurement of the amount of ions released from the surface before and after chemical passivation. Next, tests with application of electrochemical impedance spectroscopy were suggested for characterising physical and chemical properties of electrochemical processes taking place during sample exposure to artificial plasma.

II. MATERIALS AND METHODS

A. Material for Samples

Samples made of AISI 316L stainless steel in the form of rods with diameter of d=5mm and length of l=60mm were selected for the tests. The samples were subject to electrochemical polishing in phosphate-sulfate acid with corrosion inhibitors until surface roughness of R_a=0.16µm was obtained. Later, samples were subject to chemical passivation in 40% nitric acid [6].

B. EIS Studies

Impedance measurements were made with application of measurement system AutoLab PGSTAT 302N equipped with FRA2 (Frequency Response Analyser) module in artificial

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blood plasma at the temperature of T=37±1°C and pH=7.0± 0.2. The applied measurement system enabled to perform the tests within frequency range $10^4 \div 10^{-3}$ Hz. Sinusoidal voltage amplitude of perturbation signal was 10mV. The tests enabled to determine system impedance spectra and match obtained measurement data to equivalent circuit [7], [8]. Impedance spectra of the tested system were presented as Nyquist diagrams for various frequencies and as Bode diagrams. Selection of that method enabled to characterise impedance of phase boundary: AISI 316L – surface layer – artificial plasma through approximation of impedance data by means of electric equivalent circuit.

C. Ions Infiltration

In order to assess coating density of the surface layer and also the amount of ions infiltrating from steel substrate to artificial plasma solution, metallic ions permeability tests were performed. The amount of ions Fe, Cr, Ni and Mo that infiltrated to the solution was designated. Each sample was placed for 7 days in 100ml of artificial plasma at the temperature of 37±1°C. Metallic ions concentrations were measured with spectrometer JY 2000, by Yobin – Yvon, applying ICP-AES method. The source of induction was plasma torch coupled with generator of frequency 40.68 MHz. When making analytical curve, diluted analytical materials by Merck were applied [9]-[11].

III. RESULTS

Figs. 1 and 2 present impedance spectra of AISI 316L stainless steel, and Figs. 3 and 4 impedance spectra of the same steel covered with oxide layer created during 7 day exposure in artificial plasma. Electric equivalent circuits presented in Fig. 5 were used for analysis of the experimentally determined impedance spectra of corrosion systems of AISI 316L stainless steel. Results of measurements of samples before and after exposure were matched to the simplest model the oxide layer, i.e. such that consists of a parallel CPE (Constant Phase Element) connected with the resistance of oxide layer (passive) R_p and resistance at high frequencies, that may be attributed to the resistance of electrolyte R_s – Fig. 5 a. Next, the best matching of model spectra to impedance spectra determined experimentally in artificial plasma for samples after exposure is ensured by a simple equivalent circuit with one time constant, consisting of four electric elements – Fig. 5 b. In that circuit, element R_s models resistance of electrolyte i.e. artificial plasma, R_{ct} – characterises resistance of electric charge transfer on phase boundary: AISI 316L – oxide layer – electrolyte, CPE_{dl} – electrical properties of double layer on the boundary of those phases, whereas Warburg element – W represents the impact of diffusion on the course of corrosion processes [12]-[14].
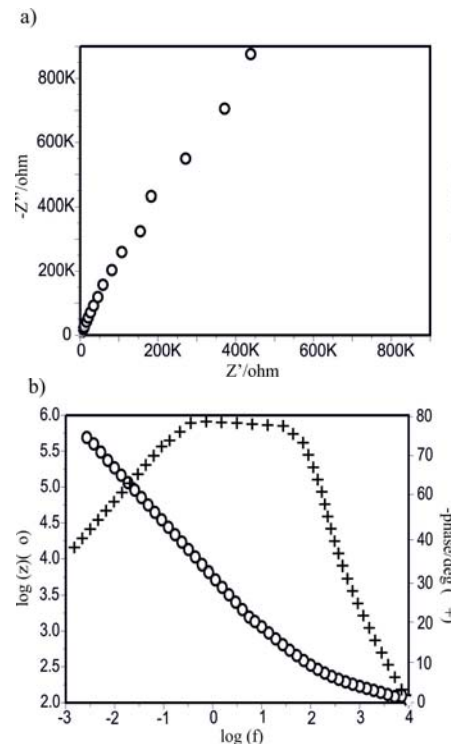

Fig. 1 Impedance spectra for AISI 316L (polished):
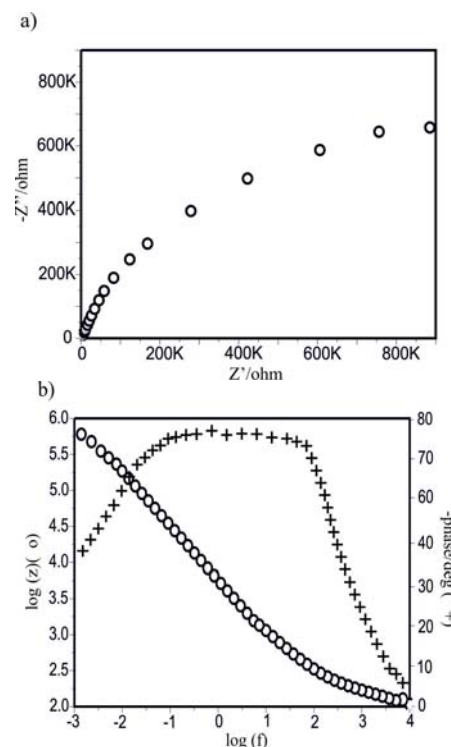a) Nyquist diagram, b) Bode diagram

Fig. 2 Impedance spectra for AISI 316L (passivated):
a) Nyquist diagram, b) Bode diagram

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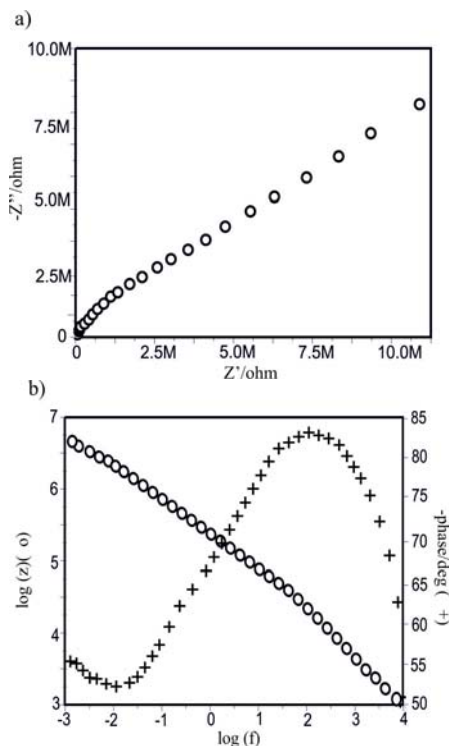International Journal of Biomedical and Biological Engineering
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Fig. 3 Impedance spectra for AISI 316L (polished) after 7 days in artificial plasma: a) Nyquist diagram, b) Bode diagram
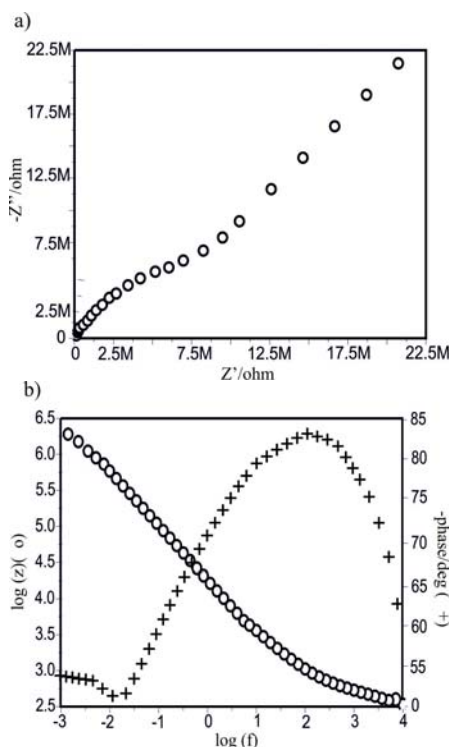

Fig. 4 Impedance spectra for AISI 316L (passivated) after 7 days in artificial plasma: a) Nyquist diagram, b) Bode diagram
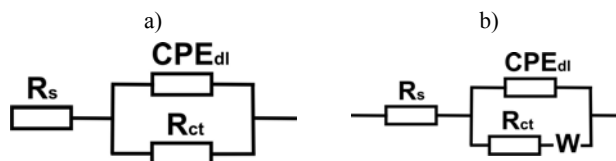

Fig. 5 Electrical model of equivalent circuit for AISI 316L – passive layer – artificial plasma

Mathematical impedance model of the AISI 316L – passive layer – artificial plasma system is presented in (1) and mathematical impedance model of the AISI 316L – passive layer – artificial plasma system after 7 day exposure is presented in (2):

$$Z = R_s + \cfrac{1}{\cfrac{1}{R_{ct}} + Y_0(j\varpi)^n} \tag{1}$$

$$Z = R_s + \cfrac{1}{\cfrac{1}{R_{ct} + W} + Y_0(j\varpi)^n} \tag{2}$$

In all Nyquist plots near the beginning of coordinate system there are visible fragments of semi-circles, marked and deformed to a various extent, that next, in some cases, become a linear dependence of constituent imaginary impedance (Z'') on real impedance (Z'). Warburg impedance that is present there shows that corrosion process in that case is controlled by the rate of mass transport i.e. diffusion of positive ions of corroding metal and anions causing corrosion in artificial plasma. The results of performed tests show that the module of systems impedance, irrespective of the way of AISI 316L stainless steel surface modification, decreases with the increase of frequency. Chemical passivation process of steel surface resulted in high electrochemical stability, which is proved by relatively high resistance of ion transition R_{ct}. Obtained forms of characteristics for samples after exposure suggest presence of porous oxide layer, resulting from the influence of the solution, where parallel ducts with ion conduction are created. Change of angle of inclination of straight section was observed for those samples within low-frequency part of spectrum, which passed from the angle typical of Warburg impedance to the angle typical of layers of membrane type. It can be explained by penetration of the solution into the surface layer, destruction of oxide (passive) layer created previously and recreation of this type of layer in deeper areas of the passive layer up to creation of the oxide layer bordering AISI 316L steel. It is probably the result of partial degradation of the oxide layer in the surface passive layer with simultaneous creation of layers of membrane type in the internal layer.

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TABLE I
RESULTS OF EIS

Surface	E_{OCP} (mV)	R_s (Ωcm^2)	R_{ct} ($k\Omega cm^2$)	CPE Y_0 ($\Omega^{-1}cm^{-2}s^{-n}$)	n	W ($\mu\Omega$)
Before exposure						
polished	-92	22	1506	0.5873e-4	0.80	-
passivated	-45	21	2429	0.3743e-4	0.85	-
After exposure						
polished	-24	22	270	0.5847e-4	0.62	54.28
passivated	+25	21	896	0.7782e-4	0.65	29.38

The results of the tests of metallic ion penetration to artificial plasma after 7 day exposure of samples made of AISI 316L stainless steel before and after chemical passivation process are presented in Table II. Test of chemical composition of artificial plasma in which the samples were immersed after various surface modification treatment, enabled to determine presence of Fe, Cr, Ni and Mo ions, irrespective of the way of surface modification.

TABLE II
RESULTS OF THE TESTS OF METALLIC ION PENETRATION

Surface	Concentration of metallic ions, ppm (mean value)							
	Fe	SD	Cr	SD	Ni	SD	Mo	SD
polished	1.4	0.05	0.35	0.009	0.09	0.001	0.02	0.003
passivated	1.3	0.04	0.33	0.010	0.08	0.002	0.01	0.002

Assuming the amount of degeneration products permeating to artificial plasma as the main criterion indicating the level of haemocompatibility of the tested material, the benefits of chemical passivation of AISI 316L stainless steel in nitric acid seem to be inconclusive. Obtained results show the need for further tests aimed at improving haemocompatibility of that steel through surface modification.

IV. CONCLUSION

Test results presented in this study constitute an attempt to determine hemocompatibility of AISI 316L stainless steel chemically passivated in nitric acid. Chemical passivation process was preceded by electro-chemical polishing in order to obtain adequate surface roughness. Created passive layer featured relatively high resistance of ion transition in relations to the polished surface. Despite its partial degradation, that tendency was also observed for samples subject to exposure in artificial plasma – Table I. Therefore, on the ground of performed tests, it was proved that application of chemical passivation process for AISI 316L stainless steel used for production of goods intended to have contact with blood is well-grounded and useful for improvement of their application safety.

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