Witold WALKE[1], Joanna PRZONDZIONO[2]

Silesian University of Technology, Department of Biomaterials and Medical Engineering Devices (1)
Silesian University of Technology, Department of Technology Materials (2)

Passivation and corrosion behaviours of AISI 316L stainless steel as implant materials in simulated blood environment

Streszczenie. *Celem pracy była ocena odporności korozyjnej stali 316L stosowanej w zabiegach kardiologicznych głównie na stenty naczyniowe. Analizowano wpływ elektrochemicznej i chemicznej obróbki powierzchniowej stali z uwzględnieniem procesu sterylizacji parą wodną pod ciśnieniem na jej właściwości korozyjne. Badania realizowano w sztucznym osoczu symulującym środowisko krwi. W celu zasymulowania warunków występujących w środowisku krwi próbki poddawano ekspozycji w sztucznym osoczu o temperaturze T = 37±1°C przez okres 30. dni. Dla oceny zjawisk zachodzących na powierzchni badanej stali zastosowano metodę elektrochemicznej spektroskopii impedancyjnej (EIS – Electrochemical Impedance Spectroscopy). Zaproponowanie odpowiednich wariantów obróbki powierzchniowej ma perspektywiczne znaczenie i przyczyni się do opracowania warunków technologicznych o sprecyzowanych parametrach wytwarzania powłok tlenkowych na stentach naczyniowych. (**Ocena odporności korozyjnej stali 316L stosowanej w zabiegach kardiologicznych**)*

Abstract*. The purpose of the study was evaluation of corrosion resistance of steel 316L used in cardiologic treatment mainly for vascular stents. The study analysed influence of electrochemical and chemical treatment of the steel surface, including sterilisation with pressurised water steam, on its corrosion characteristics. The tests were performed in artificial blood plasma simulating human blood environment. In order to simulate the conditions present in blood, the samples were subject to exposure in artificial blood plasma at the temperature T = 37±1°C for 30 days. To evaluate the phenomena that take place on the surface of the tested steel, electrochemical impedance spectroscopy was applied. Suggestion of proper variants of surface treatment is of a long-range importance and it will contribute to elaboration of technological conditions with specified parameters of formation of oxide layers on vascular stents.*

Słowa kluczowe: stali AISI 316L, sztuczne osocze, pasywacja chemiczna, EIS,
Keywords: AISI 316L, artificial plasma, chemical passivation, EIS,

Introduction

High requirements regarding functional characteristics of AISI 316L steel as a metallic biomaterial used for cardiologic implants (e.g. vascular stents) extort application of proper methods of forming electrochemical characteristics of the surface. Applicabiliy as well as correctness of the adopted surface modification methods should be verified under laboratory conditions. Restrictions arising from introduction of metallic biomaterial implant into vascular system prompted many scientists to seek ways of their effective reduction. It turn out when analysing data from subject matter literature that one of the main factors influencing the course of the aforementioned processes is roughness of stent surface. Sheth et al. [1-3] determined the effects of polishing implants made of Ni-Ti alloy and Palmaz-Schatz stents made of Cr-Ni-Mo steel in the tests in vivo. On the ground of performed tests they found substantial decrease of coagulation tendency on polished surface of implants in comparison with unpolished. Similar tests were performed on rats and pigs by de Scheerder, who by implanting polished stents made of Cr-Ni-Mo steel obtained substantial decrease of occurrences of most of all early thrombosis [2]. Next method how to minimise the risk of treatment failure is creation of additional passive layer on polished surface in order to reduce metallic ion transport to blood environment, and consequently to improve resistance to electrochemical corrosion of AISI 316L steel [4,5]. Therefore, this study presents evaluation of applicability of passive layer creation on AISI 316L steel surface, taking into consideration steam sterilisation process and 30 days' exposure in artificial blood plasma on the ground of electrochemical characteristics.

Material and method

Samples made of saturated austenitic steel AISI 316L in the form of wire with diameter of d = 0.2 mm were used for the tests. Chemical composition as well as steel structure was in accordance with recommendations of ISO. Proper surface roughness was obtained through electrochemical polishing (R_a = 0.12 μm) and chemical passivation (R_a = 0.12 μm) in 40 % HNO_3. In the last stage samples were subject to steam sterilisation in autoclave Basic Plus by Mocom at the temperature of T = 134 °C, pressure p = 2.1 bar and time t = 12 min. Next, in order to simulate conditions present in blood vessels, samples were subject to exposure in artificial blood plasma at the temperature of T = 37±1°C for 30 days.

In order to obtain information about electrochemical properties of the surface of AISI 316L steel samples, tests that made use of electrochemical impedance spectroscopy were performed. Measurements were made with application of measurement system Auto Lab PGSTAT 302N equipped with FRA2 module (Frequency Response Analyser). The applied measurement system enabled performance of tests within frequency range of $10^4 \div 10^{-3}$Hz. Amplitude of activating signal sinusoidal voltage was 10 mV. Impedance spectra of the system were determined in the tests and obtained data was matched to the equivalent circuit. It made the ground for determination of numerical values of resistance and capacity of the analysed systems. Impedance spectra of the tested system are presented as Nyquist diagrams for various frequencies and as Bode diagrams [11-14]. The tests were performed in artificial blood plasma at the temperature of T = 37 ±1 °C, pH = 7.0 ±02.

Results

The results of electrochemical analysis of impedance spectroscopy made for AISI 316L steel with modified surface before and after exposure in artificial blood plasma for 30 days are presented in table 1.

Characteristics of impedance of phase boundary steel AISI 316L – oxide layer – artificial blood plasma, was made through approximation of experimental data by means of an electrical equivalent circuit model. [6,7,11-13]. Measurement results were matched to the simplest model of oxide layer, i.e. a model that consists of a parallel Constans Phase Element connected with the resistance of ion transition through phase boundary electrode – solution R_{ct} and resistance at high frequencies R_s, that may be attributed to electrolyte resistance [6,7,11-13] – fig. 5.

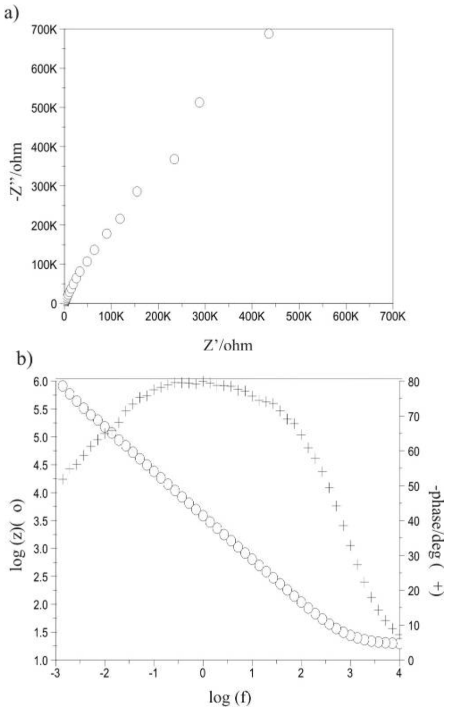


Fig. 1. Impedance spectrums for AISI 316L alloy test pieces after polished: a) Nyquist diagram, b) Bode diagram

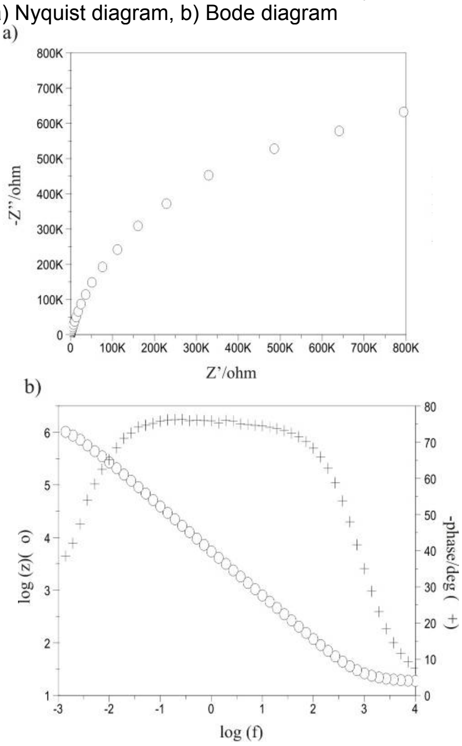
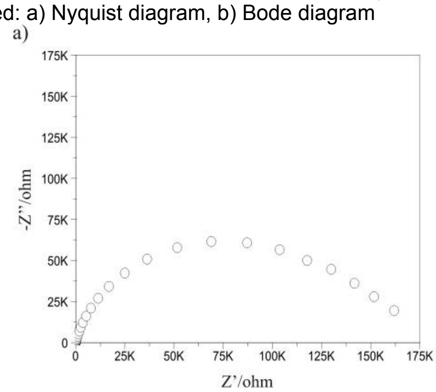


Fig. 1. Impedance spectrums for AISI 316L alloy test pieces after passivated: a) Nyquist diagram, b) Bode diagram



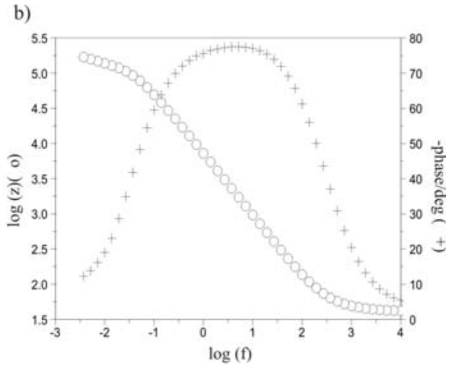


Fig. 3. Impedance spectrums for AISI 316L alloy test pieces after polished and exposure in the artificial solution: a) Nyquist diagram, b) Bode diagram

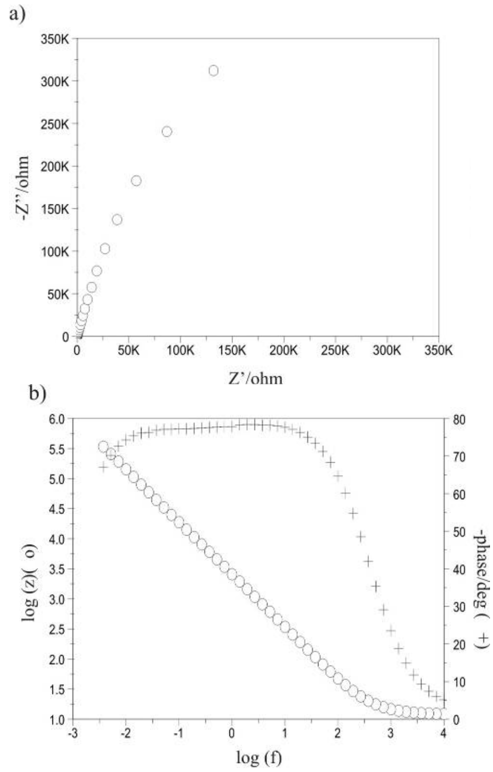


Fig. 4. Impedance spectrums for AISI 316L alloy test pieces after passivated and exposure in the artificial solution: a) Nyquist diagram, b) Bode diagram

Table 1. Results of electrochemical impedance spectroscopy

Surface	E_{OCP}, mV	R_s, Ωcm^2	R_{ct}, $k\Omega cm^2$	CPE_{dl}	
				Y_0, $\Omega^{-1}cm^{-2}s^{-n}$	n
before exposure in artificial plasma					
Polished	-92	22	1506	0.5873e-4	0.80
Passivated	-45	21	2429	0.3743e-4	0.85
after 30. days exposure in artificial plasma					
Polished	-225	23	158	0.2732e-4	0.88
Passivated	-49	22	2324	0.7872e-4	0.88

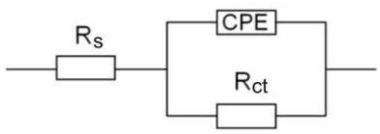


Fig. 5. Electrical model of equivalent circuit for stal AISI 316L – [11-13]

In the electrical equivalent system, resistor R_{ct} and CPE represent, respectively, resistance of ion transition and capacitance of the passive oxide layer created on the surface of the alloy, whereas resistor R_s represents resistance of artificial blood plasma in which the tests were performed.

Mathematical model of impedance of the system AISI 316L steel – passive layer – solution is presented by the equation [6-8] (1):

$$Z = R_s + \frac{1}{1/R_{ct} + Y_0(j\omega)^n} \quad (1)$$

Summary

Podstawową A basic quality of material, which decides about its applicability for medical purposes, is its corrosion resistance. Types of corrosion revealed on the ground of macro– and microscopic observations after various periods of immersion of the implant in blood environment have not been systematised yet. Stochastics of changes of the conditions responsible for initiation and development of vascular implants corrosion has its specificity and the image of effects is often different from the one obtained under simulated laboratory conditions. Corrosion resistance of non-metallic materials is determined in comparative tests that are performed by means of generally accepted research methods under laboratory conditions, simulating real biological environment. It is determined among other things on the ground of impedance spectroscopy. Analysis of obtained results enables to make full corrosion characteristics of the implant in the respective environment. Corrosion dynamics is finally determined by chemical and phase composition, material structure homogeneity, local work hardening condition or stress condition, which explains frequent differences in the course of corrosion at the respective areas of the same implant. [9-15].

Currently, the material most frequently used for vascular stents is austenitic steel Cr-Ni-Mo (ca. 80 ÷ 90 %). Allowedly, formation of a passive payer on its surface effectively protects it from corrosion. That layer is made during the last stage of polishing or separately through passivation. Local damage of that layer leads to creation of active – passive cells, and as a consequence, to creation and development of pitting corrosion.

EIS tests enabled characteristics of impedance of phase boundary: material – passive layer (created during passivation or after exposure in artificial plasma) – solution, on the ground of approximation of impedance data by means of electrical equivalent system model. Performed analysis enabled to determine impedance spectra of the tested system and to match data to the equivalent circuit consisting of parallel constant phase element CPE connected with resistance of ion transition R_{ct} and residuary resistance R_s at high frequencies attributed to ohm resistance of artificial blood plasma [6-8].

To sum up, on the ground of performed EIS test it was proved that chemical passivation process has favourable impact on corrosion resistance of AISI 316L steel. Exposure in artificial blood plasma did not have negative influence on electrochemical properties of the passive layer.

Acknowledgments

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***Authors**: dr inż. Witold Walke, Silesian University of Technology, Department of Biomaterials and Medical Engineering Devices, ul. Gen. Ch. de Gaulle'a 72, 41-800 Zabrze, E-mail: witold.walke@polsl.pl; dr inż. Joanna Przondziono, Silesian University of Technology, Department of Technology Materials, ul. Krasińskiego 8, 40-019 Katowice, e-mail: joanna.przondziono@polsl.pl*