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ELECTROCHEMICAL BEHAVIOR OF GUIDEWIRES MADE OF X10CrNi 18-8 STEEL

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Preliminary Note – Prethodno priopćenje

The purpose of this study was to evaluate corrosion resistance of wires with differentiated of surface preparation and with differentiated work hardening, used in low-invasive cardiology in sterile environment. The study is devoted to voltamperometric and impedance tests, which were used to determine typical features describing corrosion resistance. Measurement system PGSTAT 302n together with a set of measurement electrodes were used for the tests. The tests were carried out in artificial blood plasma at the temperature of T = 37 °C. Obtained results were used as the ground for selecting the way of preparation of the surface of X10CrNi 18-8 steel in order to improve its biotolerance in blood environment.

Key words: X10CrNi 18-8 steel, corrosion guidewires, artificial plasma, potentiodynamic tests

INTRODUCTION

Invasive cardiology is a branch of cardiology dealing with invasive diagnostics and treatment with application of vascular catheter. Main types of treatment performed in invasive cardiology include: electrotherapy and coronary aorta angiography. Various types of steel guide wires featuring complicated construction are of great importance for such treatment. Guide wires should feature high resistance to electrochemical corrosion in the environment of body tissue and fluids and proper mechanical characteristics. Those features are influenced by, among other things, chemical composition of material, its metallurgical purity and production process parameters. But what influences final quality of steel guide wires most is their surface layer structure and thickness. There are many ways how it can be formed [1–3].

Structure and chemical composition of the layer can be modified with application of various methods, among which mechanical, chemical and electrochemical methods are the most widely used. Physical and chemical properties of guide wires surface may in addition depend on sterilisation method applied in the final stage of production process [4–6].

Mechanical working is used for modification of surface topography. Oxide layers properties after application of this method are hard to control. Chemical methods include mainly etching and passivation, which leads to creation of a thin (< 10 nm) film of oxides composed mainly of Cr_2O_3 as well as impurities coming from chemical reagents [7, 8].

Applicability of certain ways of product surface modification requires performance of a number of tests, both laboratory and clinical. Initial stage of tests includes corrosion tests under in vitro conditions simulating specific environment of human tissue of the system into which the product is to be inserted [9]. That is why this study present analysis of the impact of cardiologic guide wires surface topography and steam sterilisation on corrosion characteristics of samples made of X10CrNi 18-8 steel in artificial blood plasma simulating human blood and vascular system.

MATERIAL AND METHODS

X10CrNi 18-8 steel with differentiated strain hardening was used in tests. Supersaturated wire rod with diameter of d = 5,65 mm served as stock material. Wire rod was drawn to diameter of d = 1,5 mm. Logarithmic strain in drawing process ε was 2,65. Chemical composition of X10CrNi 18-8 steel is presented in Table 1.

Table 1 **Chemical composition of X10CrNi18-8 steel / % of mass**

C	Mn	Si	P	S	Cr	Ni
0,08	0,91	0,61	0,028	0,001	17,96	8,42

Samples surface modification was made with application of: electrochemical polishing and chemical passivation – Figure 1.

Steam sterilisation was made in sterilisation device Basic Plus by Mocom, in temperature of T = 134 °C, pressure p = 2,1 bar for the time of t = 12 minutes.

Pitting corrosion resistance tests were performed with application of potentiodynamic method in accordance with ASTM F746 standard. Potentiostat PGP201 by Radiometer was used for tests. Saturated calomel electrode

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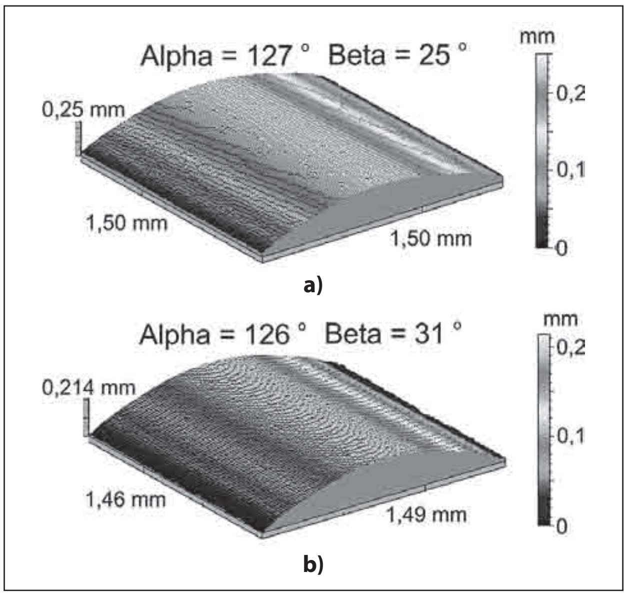

Figure 1 Surface of wire subject to: a) electrochemical polishing and steam sterilisation, b) chemical passivation and steam sterilisation

(SCE) of KP-113 type served as reference electrode, while Platinum electrode of PtP−201 type served as auxiliary electrode. Pitting corrosion resistance tests started with determination of open circuit potential E_{OCP}. Next, anodic polarisation curves were registered, the measurement started with potential equal $E_{start} = E_{OCP} - 100$ mV. Potential changed in anodic direction at the rate 3 mV/s. When anodic current reached density of i = 1 mA/cm^2, polarisation direction was changed and return curve was registered. On the ground of registered anodic polarisation curves, typical values describing resistance to electrochemical corrosion were determined, i.e.: corrosion potential, breakdown potential. Stern method was applied to determine polarisation resistance.

Tests were performed in artificial blood plasma solution in accordance with PN-EN ISO 10993-15 [10].

In order to obtain information regarding physical and chemical characteristics of the surface of X10CrNi 18-8 steel samples, additional tests with application of electrochemical impedance spectroscopy (EIS) were performed. Measurements were made with application of measurement system AutoLab PGSTAT 302N equipped with FRA2 (Frequency Response Analyser) module. This measurement system enabled to perform tests in the range of frequencies $10^4 \div 10^{-3}$ Hz. Sinusoidal voltage amplitude of perturbation signal was 10 mV. The tests enabled to determine system impedance spectra and match obtained measurement data to equivalent system. Characteristics of surface layers was made through approximation of impedance data by means of electric equivalent circuit model [11].

RESULTS

The first stage of test included pitting corrosion resistance tests of wire rod (d = 5,65 mm) with surface after electrolytic polishing and surface after electrolytic polishing and chemical passivation, but not subject to steam sterilisation. The average value of corrosion potential of samples with polished surface was, respectively, E_{corr} = -68 mV. Chemical passivation increased corrosion potential to E_{corr} = +105 mV. Next, wire rod was subject to sterilisation with pressurised water steam, which caused the change of corrosion potential in case of polished surface to E_{corr} = -29 mV and for passivated surface to E_{corr} = +14 mV. Determined values of polarisation resistance R_p and perforation potential E_b for the respective variants of tested samples were, respectively:

– polished samples – R_p = 567 kΩcm^2, E_b = +612 mV,
– polished samples after steam sterilisation – R_p = 219 kΩcm^2, E_b = +275 mV,
– passivated samples – R_p = 2 220 kΩcm^2, E_b = +858 mV,
– passivated samples after steam sterilisation – R_p = 330 kΩcm^2, E_b = +1 133 mV.

Next stage of tests included pitting corrosion resistance tests of samples deformed in drawing process (d = 1,5 mm). Registered corrosion potential for this group of samples was E_{corr} = -132 mV for polished samples and E_{corr} = +94 mV for chemically passivated samples. Sterilisation with pressurised water steam also changed its value, and therefore: E_{corr} = -29 mV – for polished samples and E_{corr} = -8 mV for chemically passivated samples. Values of polarisation resistance R_p and perforation potential E_b determined for individual variants of tested samples were, respectively:

– polished samples – R_p = 229 kΩcm^2, E_b = +380 mV,
– polished samples after steam sterilisation – R_p = 195 kΩcm^2, E_b = +384 mV,
– passivated samples – R_p = 1 070 kΩcm^2, E_b = +695 mV,
– passivated samples after steam sterilisation – R_p = 300 kΩcm^2, E_b = +1 054 mV.

Exemplary anodic polarisation curve determined for wire rod after electrochemical polishing and steam sterilisation is presented in Figure 2.

Nyquist diagrams registered for X10CrNi 18-8 steel samples irrespective of the way of surface preparation show fragments of large incomplete semicircles that are a typical impedance response for thin oxide layers. Next, maximum values of phase angles, presented in Bode diagrams in a wide range of frequencies, are, irrespective of surface modification, similar and their value is θ ≈ 75 °. Exemplary spectrum obtained for wire rod after electrolytic polishing and steam sterilisation is presented in Figure 3. Slopes log|Z| within the whole range of frequency changes are close to -1, which proves capacitive character of the passive layer – Figure 3b. Next, high values of impedance for wire rod $|Z| > 10^6$ Ωcm^2 in the range of the smallest frequencies prove good dielectric and protective characteristics of passive layers created on the surface of samples made of

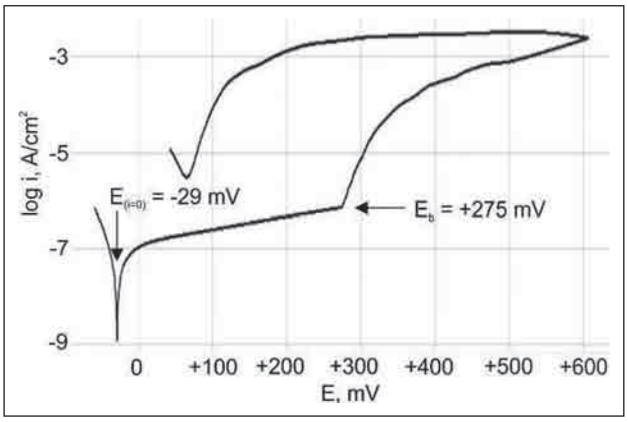

Figure 2 Anodic polarisation curve determined for wire rod after electrochemical polishing and steam sterilisation

X10CrNi 18-8 steel after sterilisation with pressurised water steam.

Characteristics of impedance of phase boundary: electrode – passive layer – solution in the process of sterilisation with pressurised water steam was made through approximation of experiment data by means of electric equivalent circuit model – Figure 3.

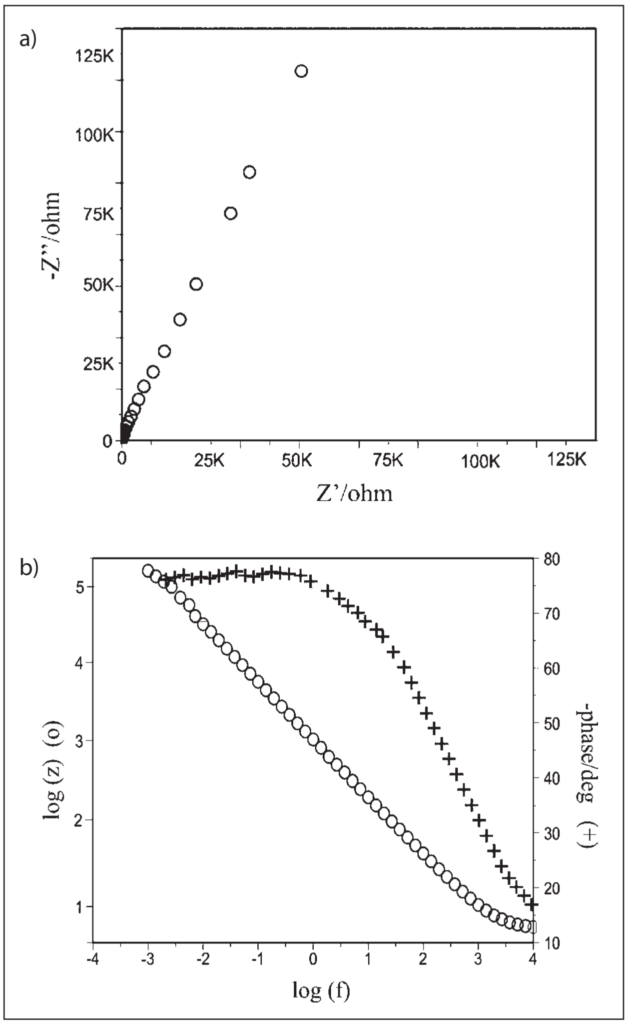

Figure 3 Impedance spectrums for X10CrNi 18-8 steel test pieces after exposure in the Ringer's solution: a) Nyquist diagram, b) Bode diagram

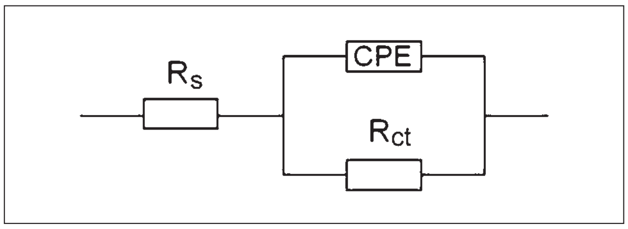

Figure 4 Electrical model of equivalent circuit for X10CrNi 18-8 steel – passive film – artificial plasma

Values of typical parameters describing electrical characteristics of the analysed system were similar to the values of determined for the samples that were not subject to long-term exposure to the solution – Table 2.

Measurement results for samples before and after sterilisation were matched to the simplest model of oxide layer, i.e. such that consists of a parallel CPE (Constant Phase Element) connected with resistance of ion transition through phase boundary: electrode – R_{ct} solution and resistance at high frequencies R_s that can be attributed to electrolyte resistance [12] – Figure 4.

Table 2 **The results of EIS**

d /mm	Method of surface preparing	R_s /Ωcm²	R_{ct} /MΩcm²	CPE	
				Y_0 /$\Omega^{1}cm^{-2}s^{-n}$	n
5,65	Polished	59	1,23	0,5684E-4	0,81
	Polished + sterylized	58	0,45	0,2897E-3	0,83
1,5	Polished	58	0,92	0,4586E-4	0,88
	Polished + sterylized	57	0,06	0,6071E-4	0,76
5,65	Pasivated	59	1,25	0,6952E-4	0,81
	Pasivated + sterylized	57	3,42	0,2135E-3	0,86
1,5	Pasivated	59	1,05	0,3524e-3	0,81
	Pasivated + sterylized	58	2,54	0,4728E-4	0,82

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

Mathematical model of impedance of the system: X10CrNi 18-8 steel – passive layer – solution is presented by the equation (1):

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

CONCLUSIONS

Analysis of test results describing changes of all corrosion resistance parameters shows differentiated impact of steam sterilisation, depending on the way of surface preparation. It was proved that chemical passivation has a favourable effect on improvement of corrosion resistance under sterilisation conditions. Chemical passivation is responsible for creation of compact and continuous layer of oxides with mostly amorphous structure, which in turn serves as a barrier for reaction products diffusing into the solution or which serves as chemically adsorbed coating. This layer is more resistant to water steam during sterilisation process when compared to the layer created by mechanical or electrochemical polishing.

Acknowledgements

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Note: The responsible translator for English language is A. Budziak, Siemianowice, Poland