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ELECTROCHEMICAL CHARACTERISATION OF X10CrNi 18-8 STEEL IN ARTIFICIAL PLASMA

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Quality of applied guide wires conditions the course of treatment and its success to a great extent. In order to simulate conditions that can be found in blood vascular system samples were exposed to artificial blood plasma (T = 37 ± 1 °C) for the time of 8 h. In order to obtain information regarding physical and chemical properties of modified surface of wire made of X10CrNi 18-8 steel, electrochemical impedance spectroscopy (EIS) test and tests of chemical composition of the surface layer X-ray photoelectron spectroscopy (XPS) were made. On the ground of performed EIS and XPS tests, favourable impact of steam sterilisation process on corrosion resistance of X10CrNi 18-8 steel was observed only for the case when chemical passivation was applied prior to sterilisation.

Key words: wires for invasive cardiology, X10CrNi 18-8 steel, steam sterilization, EIS, XPS

INTRODUCTION

The last decade witnessed dynamic development of invasive cardiology. Continuance increase of coronary treatment, both diagnostic (mostly coronarography) as well as therapeutic (mostly percutaneous transluminal coronary angioplasty – currently connected mainly with stent implementation) has been seen. Success of invasive cardiology depends on a number of factors, one of which is proper selection of instruments and auxiliary materials. Various types of guidewires are of crucial importance as far as proper realisation of angioplasty and stent implementation are concerned. Angioplasty guidewire is used for insertion of instruments used for widening arteries whose clearance decreased due to atherosclerosis [1, 2].

A substantial problem in the process of shaping functional properties of guidewires used in invasive cardiology is selection of proper mechanical characteristics of metallic material and its physical and chemical characteristics of the surface. Physical and chemical properties of guidewire surface should be adapted to the features of human tissue environment. Corrosion resistance of metallic materials is one of the basic criteria of their evaluation. A crucial issue connected with metallic materials used for vascular treatment is the possibility of coagulation processes initiated on their surface. A basic way how to limit that unfavourable phenomenon is application of antithrombotic coatings but proper fluoroscopic visibility [3-6]. Surface quality when coming into contact with blood is also determined by topography and presence of certain chemical groups, which in turn determine electric properties and hydrophilicity. In a situation when those properties are far from optimal, it may result in coagulation of blood when guidewire surface comes into contact with blood, and in vessel blockage.

Therefore, the authors of the study suggested proper surface treatment that enables to obtain the required surface roughness and to create an oxide layer improving haemocompatibility of steel X10CrNi 18-8. In order to verify applicability of the implied surface modification treatment, impedance tests were suggested as well as chemical composition analysis. These tests constitute an initial stage of evaluation of suggested layers. Due to the fact that guidewire may be present in the vessel for a prolonged period of time, the tests were also performed on samples that were subject to 8 hour exposure to artificial blood plasma.

MATERIAL AND METHODS

Wires made of X10CrNi 18-8 steel with diameter of $d = 1{,}5$ mm were used for the tests. Samples surface was differentiated by means of mechanical working – grinding ($R_a = 0{,}40$ μm) and polishing ($R_a = 0{,}12$ μm). Steam sterilisation process was carried out at the temperature of $T = 121$ °C, pressure $p = 1{,}1$ bar for $t = 30$ min. In order to simulate conditions that can be found in blood vascular system samples were exposed to artificial blood plasma ($T = 37 \pm 1$ °C) for the time of 8 h – Table 1.

In order to obtain information regarding physical and chemical properties of modified surface of wire made of X10CrNi 18-8 steel, EIS test and tests of chemical composition of the surface layer XPS were made.

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Table 1 **Chemical composition of artificial plasma**

Components	Components concentration / g/dm^3 distilled water
$NaCl$	6,800
KCl	0,400
$CaCl_2$	0,200
$MgSO_4$	0,100
$NaHCO_3$	0,200
Na_2HPO_4	0,126
NaH_2PO_4	0,026

In order to obtain information regarding electrochemical properties of sample surface, the tests with application of electrochemical impedance spectroscopy (EIS) were also performed [7]. Measurement were made with application of measuring system Auto Lab PGSTAT 302N equipped with FRA2 (Frequency Response Analyser) module. Testing station included a PC with suitable software, electrochemical cell with electrode set – tested electrode – X10CrNi 18-8 steel subject to various surface modification treatment, reference electrode – saturated calomel electrode (SCE), auxiliary electrode – platinum electrode (Pt) and thermostat ensuring constant temperature during measurement. The applied measurement system enabled to make measurements within frequency range of $10^4 \div 10^{-3}$ Hz. Sinusoidal voltage amplitude of activation signal was 10 mV [7]. The tests enabled to determine impedance spectra of the system and obtained measurement data was matched to the equivalent circuit. It made the ground for determination of numerical values of resistance R and capacitance C of the testes systems. Impedance spectra of the tested system were presented in the form of Nyquist diagrams for various frequencies and as Bode diagrams. Obtained EIS spectra were interpreted after matching using least squares method to the equivalent electrical circuit. All electrochemical tests were performed in artificial blood plasma at the temperature of $T = 37 \pm 1$ °C and $pH = 7,0 \pm 0,2$ – Table 1.

Analysis of chemical composition of the surface layer was made with application of multifunctional electron spectrometer by Physical Electronics PHI 5700/660. Photoelectrons were activated with X-ray tube with aluminium anode and quartz monochromator providing radiation $Al_{K\alpha}$ with energy 1486,6 eV. Spectra were tested in a wide range of electron binding energy, as well as detailed spectra – of high resolution, made in the in-depth profile mode. Ion etching was performed with Ar^+ ions with energy of 4 keV. Chemical composition was determined by integration of respective photoemission lines with application of programme MULTIPAK by Physical Electronics. Analysis of spectral lines of the respective elements enabled to obtain information regarding chemical composition, changes of that state with the depth of the analysed layer of the material [8]. The time of one etching cycle was determined at 30 s.

RESULTS

The first stage of electrochemical tests consisted in measurements with application of electrochemical impedance spectroscopy. Equivalent circuits, presented in Figure 1, have been used for the analysis of experimental impedance spectra of corrosion system of steel X10CrNi 18-8.

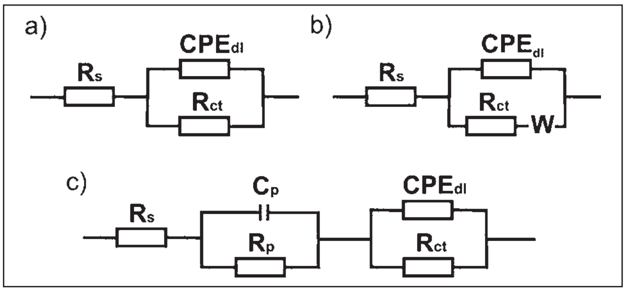

Figure 1 Electrical models of equivalent circuit for X10CrNi 18-8 steel oxide film – artificial plasma: a) polished, pasivated, passivated and sterilised and passivated, sterilised (exposure 8 h – blood), b) polished and sterilised, c) polished, sterilised (exposure 8 h – blood)

Characteristics of impedance of phase boundary steel X10CrNi 18-8 – oxide layer – artificial blood plasma for samples after chemical passivation prior to and after 8-hour exposure was made through approximation of experimental data by means of a model of electrical equivalent circuit – Figure 1a.

In the electrical equivalent circuit, resistor R_{ct} and CPE_{dl} (Constant Phase Element) represent, respectively, resistance of ion transition and capacitance of passive oxide layer created on the surface of the alloy. Then, resistor R_s represents resistance of artificial blood plasma in which the tests were performed. Next, the best matching of model spectra to impedance spectra determined experimentally for samples after polishing and sterilisation in water steam is provided by a simple equivalent circuit with one time-constant, consisting of four electrical elements – Figure 1b.

In that circuit, element R_s models resistance of the electrolyte, i.e. artificial blood plasma, R_{ct} – features resistance of electric charge transfer on phase boundary: steel X10CrNi 18-8 – oxide layer – artificial blood plasma, CPE_{dl} – electrical properties of a double layer on their phase boundary, whereas Warburg element W represents the impact of oxygen diffusion to the surface on the course of corrosion process. Then, impedance spectra obtained from samples that were polished and exposed to artificial blood plasma were interpreted through comparison with electric equivalent circuit that indicates presence of oxide layer consisting of two sub-layers: internal double layer and external porous layer, mainly made of oxide Cr_2O_3 – Figure 1c. Additionally, the element c_p models capacitance of the surface area of the material with large development of surface, when R_p reflects electrolyte resistance in that area of the material [8-11].

Table 2 **Results of the EIS test**

Surface	E_{OCP}/ mV	R_s/ Ωcm^2	R_{ct}/ MΩcm^2	CPE_{dl}		R_p/ kΩcm^2	c_p	W/ Ω
				Y_{dl}/ Ω^{-1}cm^{-2}s^{-n}	n_{dl}			
before 8 h exposed								
Polished	+77	17	0,059	0,6071E-4	0,56	-	-	0,1984E-4
Passivated	+75	18	35,21	0,4698E-4	0,82	-	-	-
after 8 h exposed								
Polished	-61	18	6,40	0,3398E-4	0,71	148	41,2	-
Passivated	+91	17	41,2	0,1262E-4	0,85	-	-	-

To sum up, obtained impedance measurement results confirm a significant impact of the respective stages of surface treatment on corrosion resistance of steel X10CrNi 18-8. It was proved that in all cases impedance modulus of tested corrosion systems decreases with the increase of frequency and phase angle also changes with the change of frequency.

Determined impedance spectra for samples after chemical passivation prove high electrochemical stability of the oxide layer created on steel surface prepared that way. In both cases (prior to and after exposure), resistance of ion transition R_{ct} takes high values, which proves proper characteristics of the material creating the layer (chemical passivation process), its relatively high thickness and proper chemical composition that enables proper creation of the oxide layer (mainly Cr_2O_3).

Additional presence of surface layer created as the result of the influence of artificial blood plasma on the surface of the oxide layer with high surface development results in additional protective barrier for polished samples. The tests proved, though, that polishing process as such did not protect completely steel surface from the impact of corrosion environment, namely blood, which resulted in the appearance of Warburg element in the oxide layer equivalent circuit. It proves the existence of corrosion phenomena in that area, which is expressed by ions diffusion from the surface of the alloy and adsorption of the elements from corrosion environment.

Then, created surface layer is the result of the reaction between oxide layer and corrosion environment. Observed values of R_{ct} were definitely lower, which proves faster process. Obtained values of R_{ct} prove a relatively easy electrical charge transfer on phase boundary, which may cause little electrochemical stability of steel surface prepared in such a way – Table 2.

Performed XPS tests proved the presence of Cr in the passive layer, in oxidised form, mainly Cr_2O_3. There is also a weak line at about 574,3 eV, typical for metallic chromium [12]. Chromium was discovered in the second spectral line. It was present on the surface mostly as an oxide, whose participation decreased with the layer depth, whereas participation of metallic Cr increased.

As far as analysis of Fe spectrum is concerned, two chemical states are visible: metallic Fe (707 eV) [12] and in the form of oxide Fe_2O_3 (711 eV), which may be determined through comparison with spectra of the respective iron oxides and analysis of satellites, e.g. 719 eV – typical position of Fe_2O_3 [13]. Similarly as for chromium, concentration of Fe_2O_3 decreased with the layer deepening, whereas metallic Fe concentration increased.

Table 3 **Chemical composition of the surface layer determined with XPS method**

Element	Atomic concentration /% mas.	Ingredients
C	31,54	Surface pollution's
Fe	28,40	Fe_2O_3
Cr	39,55	Cr_2O_3, of Cr_3C_2
Ni	0,51	NiO_2

For Ni, the only observed chemical state was metallic (852,6 eV). Nickel is present in the surface layer closer to the substrate in very small quantities. Oxygen was present at least in two chemical states – derived from oxides and surface adsorbates.

Carbon from adsorbates (ca. 285,3 eV) indicates single bonds C-C and C-H, whereas the line at 288,5 eV double bond, e.g. C=O [14]. Carbon is present in large quantities only on the surface, which results from contamination.

Calcium was detected only on the surface in oxidised state CaO – Table 3. Analysis of obtained spectra proved that only for samples subject to exposure was the presence of such elements as Na, P, Cl detected in the surface layer, which may prove adhesion of these elements to the surface.

CONCLUSIONS

Performed EIS analysis enabled to determine impedance spectra of the tested system and to match the data to the equivalent circuit made of a parallel CPE connected with resistance of ion transition R_{ct} and residual resistance R_s at high frequencies attributed to ohm resistance of artificial blood plasma. Determined values of admittance (Z^{-1}) and n coefficient for samples after chemical passivation showed that the oxide layer created in that process is a stable layer. To sum up, performed electrochemical tests helped to prove favourable impact of chemical passivation process and steam sterilisation on corrosion resistance of stainless steel X10CrNi 18-8.

Passive layer, created on the steel surface, protects the alloy more effectively from the impact of corrosion environment and is resistant to reaction with artificial blood plasma. Next, concentration of the respective main elements (Fe, Cr, Ni) in the surface layer after chemical passivation and steam sterilisation in relation to chemical substrate was substantially decreased, which must be seen as extremely favourable for haemocompatibility. All elements were in oxidised state – Table 2.

Exposure to the solution simulating blood and vascular system (artificial blood plasma) did not influence physical and chemical properties of created passive layer in a negative way. Employment of chemical passivation process of X10CrNi 18-8 steel used for cardiological instruments is reasonable and entirely useful in order to improve safety of its application.

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REFERENCES

[1] S. Sheth, F. Litvak, M. Fishbein, J. Forrester, N. Eigler, Journal of the American College of Cardiology, 27 (1997) Suppl A, 197A.

[2] R. Hoffmann, G. Mintz, European Heart Journal, 21 (2000) 21, 1739-1749.

[3] N.D. Nam, S.H. Lee, J.G. Kim et al., Diamond & Related Mat., 18 (2009) 9, 1145–1151.

[4] W. Walke, J. Przondziono, Przegląd Elektrotechniczny, 88 (2012) 12B, 144-147.

[5] W. Walke, J. Przondziono, Metalurgija, 51 (2012) 2, 237-240.

[6] W. Walke, J. Przondziono, Acta of Bioengineering and Biomechanics, 14 (2012) 3, 93-99.

[7] G. Blanco, A. Bautista, H. Takenouti, Cement & Concrete Composites, 28 (2006) 3, 212–219.

[8] I. Milosev, T. Kosec, H. Strehblow, Electrochimica Acta, 53 (2008) 9, 3547–3558.

[9] J. Przondziono, W. Walke, R. Młynarski, W. Szatka, IOP Conference Series: Materials Science and Engineering, 35 (2012) art. no. 012016, 1-8.

[10] T. Hryniewicz, R. Rokicki, K. Rokosz, Surface & Coatings Technology, 202 (2008) 9, 1668 –1673.

[11] C. Valero Vidal, A. Igual Muńoz, Corrosion Science, 50 (2008) 7, 1954–1961.

[12] J. Grimal, P. Marcus, Corrosion Science, 33 (1992) 5, 805-814.

[13] S. Ciampi, V. Di Castro, Surface Science, 331/333 (1995) 1, 294-299.

[14] C.R. Clayton, Y.C. Lu, Journal Electrochemical Society, 133 (1986) 12, 2465-2473.

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