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The influence of ethylene oxide sterylization on the corrosion behavior of 18-8 steel for contact with blood

Streszczenie. *Celem pracy była ocena odporności korozyjnej drutów wykonanych ze stali nierdzewnej X10CrNi18-8 stosowanych w zabiegach kardiologicznych. Analizowano wpływ modyfikacji powierzchni drutów z uwzględnieniem procesu sterylizacji w tlenku etylenu na ich właściwości korozyjne. Badania realizowano w sztucznym osoczu symulującym środowisko krwi. Dla oceny zjawisk zachodzących na powierzchni badanej stali zastosowano metodę elektrochemicznej spektroskopii impedancyjnej (EIS – Electrochemical Impedance Spectroscopy). Zaproponowanie odpowiednich wariantów obróbki powierzchniowej z wykorzystaniem metod elektrochemicznych i chemicznych ma perspektywiczne znaczenie i przyczynia się do opracowania warunków technologicznych o sprecyzowanych parametrach wytwarzania powłok tlenkowych odpornych na działanie czynnika sterylizującego na wyrobach medycznych wykonanych ze stali 18-8 do kontaktu z krwią (**Wpływ sterylizacji w tlenku etylenu na procesy korozyjne w stali 18-8 przeznaczonej do kontaktu z krwią**).*

Abstract. *This study is aimed at evaluation of corrosion resistance of wires made of stainless steel X10CrNi18-8 used in cardiologic treatment. Influence of modification of wire surface, involving sterilisation process with ethylene oxide (EO) on their corrosion properties, was analyzed. The tests were performed in artificial blood plasma simulating human blood environment. Electrochemical Impedance Spectroscopy (EIS) was used in order to evaluate phenomena taking place on the surface of the tested steel. Offering specific variants of surface modification with application of electrochemical and chemical methods is of a long-range importance and it contributes to elaboration of technological conditions featuring definite parameters of creation of oxider layers resistant to sterilising agent effect, on medical products made of steel 18-8 intended to come into contact with blood .*

Słowa kluczowe: stal X10CrNi18-8, sztuczne osocze, tlenek etylenu, EIS,
Keywords: X10CrNi18-8 steel, artificial plasma, ethylene oxide, EIS,

Introduction

Gas sterilization with ethylene oxide (EO) is mainly used on an industrial scale for sterilization of medical products and equipment. Pure EO or its mixture with carbon dioxide or hydroxyfreon is used in the process. Sterilization is performed in gas-tight chamber in the temperature of 30 – 65 °C and relative humidity of 40-60 %. Gas concentration should not exceed 1200 mg/l. Ethylene oxide is an extremely chemically-reactive substance, both in its liquid and gas phase. Its reactivity results in high biocidal properties [1]. Some medical devices due to their sensitivity to high temperatures and humidity cannot be sterilised in traditional cycles in water steam. Continuous progress in medical technology is responsible for the fact that in hospitals one can find technologically advanced materials and devices, for which the only safe sterilisation method is sterilisation at low temperatures. Application of high-temperature sterilisation, e.g. for thermally-unstable materials, may result in destruction and even direct threat to patient's and personnel's health and life, which is connected with application of products defected during sterilisation process [2]. Medical products that are sterilized with ethylene oxide are among other things cardiologic guide wires or needles for biopsy. The main metallic material used for this type of instruments is stainless steel, chrome-nickel of 18-8 type. Hemocompatibility is the basic criterion for material applicability for production of goods that come into direct contact with blood. Introduction of catheter to blood system initiates complex reaction between blood components and its surface. Therefore, a crucial factor in shaping physical and chemical characteristics of guide wire is the quality of its surface. When you analyse data given by literature, it turns out that one of the main factors that influence safety of guide wire application is proper surface roughness (R_a ≤ 0.16 μm). Moreover, structure and thickness of surface layer is also important. There are many ways how it can be shaped. Structure and chemical composition of the surface layer may be modified with various methods among which the dominant ones are mechanical, chemical and electrochemical. Physical and chemical characteristics of the surface of medical products may in addition be dependent on sterilization method applied in the end of the production process. Therefore, the authors of this study tried to evaluate the impact of chemical sterilization with ethylene oxide on corrosion characteristics of steel of 18-8 type with created passive layer [3,4].

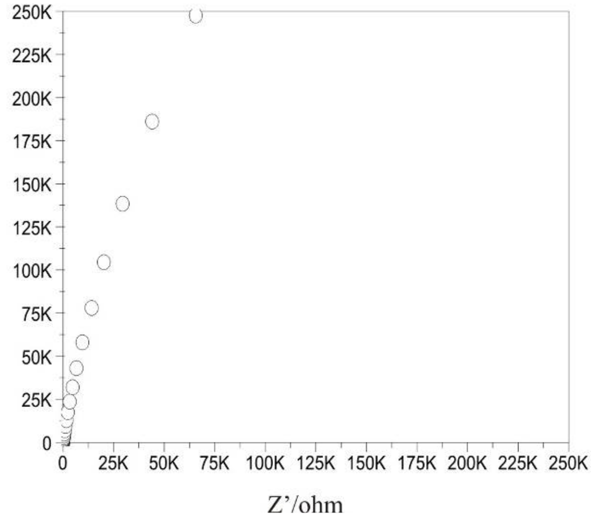
Material and method

Samples made of steel X10CrNi18-8 in the form of wire with diameter of d = 1.5 mm were used for tests. Both chemical composition and steel structure were in accordance with recommendations of ISO. Proper roughness of the surface 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 sterilization in ethylene oxide at the temperature of T = 55 °C in Steri-Vac 5XL sterilization machine. Next, samples presenting consecutive stages of surface preparation in the initial state and after sterilization in ethylene oxide were subject to impedance tests. Measurements were made with application of measurement system Auto Lab PGSTAT 302N equipped with FRA2 module (Frequency Response Analyser). The applied measurement system enabled to perform tests in frequency range of 10^4 ÷ 10^{-3} Hz. Voltage amplitude of sinusoidal activating signal was 10 mV. The tests enabled determination of impedance spectra of the system and obtained measurement data was matched to the equivalent system. On that ground numerical values of resistance and capacity of the analysed systems were determined. Impedance spectra of the tested system were presented as Nyquist diagrams for various values of frequency and as Bode diagrams. The tests were made in artificial blood plasma at the temperature of T = 37±1 °C, a pH = 7.0±0.2.

Results

The results of electrochemical analysis of impedance spectroscopy performed for surface-modified steel X10CrNi18-8 before and after sterilisation in ethylene oxide are presented in Table 1.

a)



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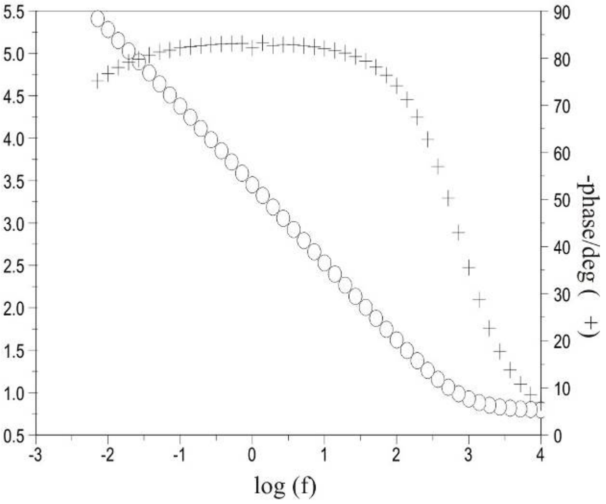
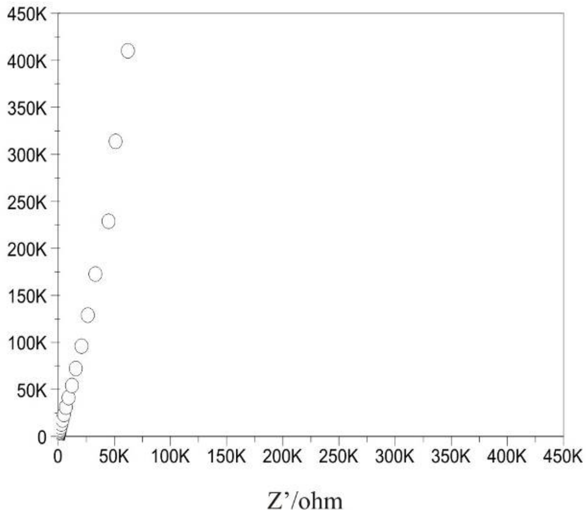


Fig. 1. Impedance spectra registered for samples with polished surface: a) Nyquist diagram, b) Bode diagram

a)



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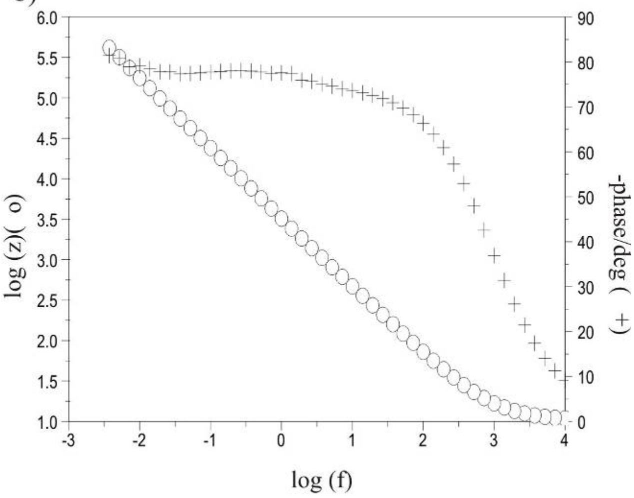
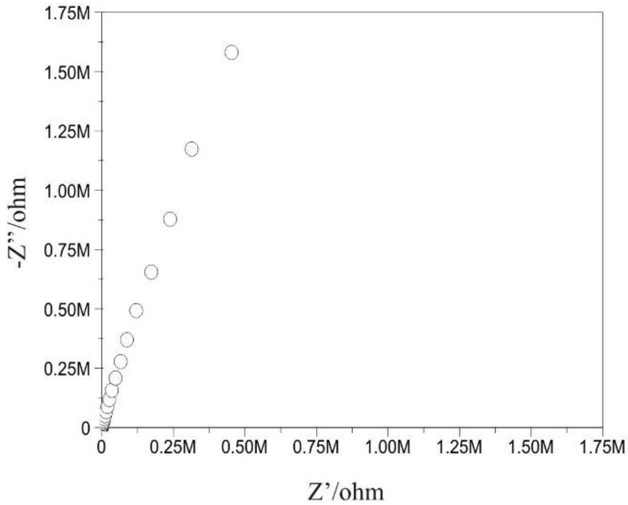


Fig. 2. Impedance spectra registered for samples with passivated surface: a) Nyquist diagram, b) Bode diagram

a)



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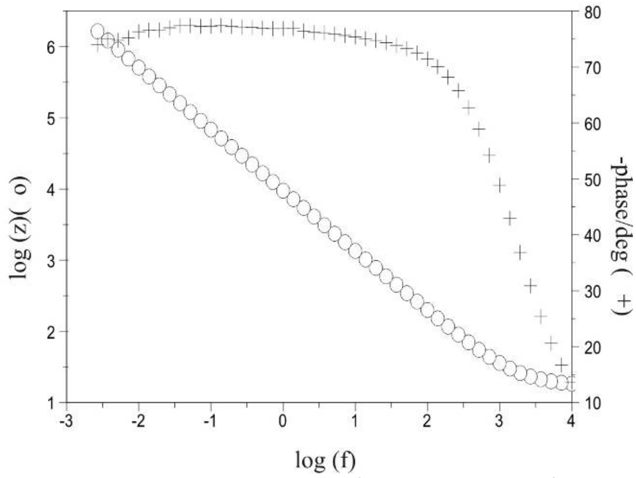
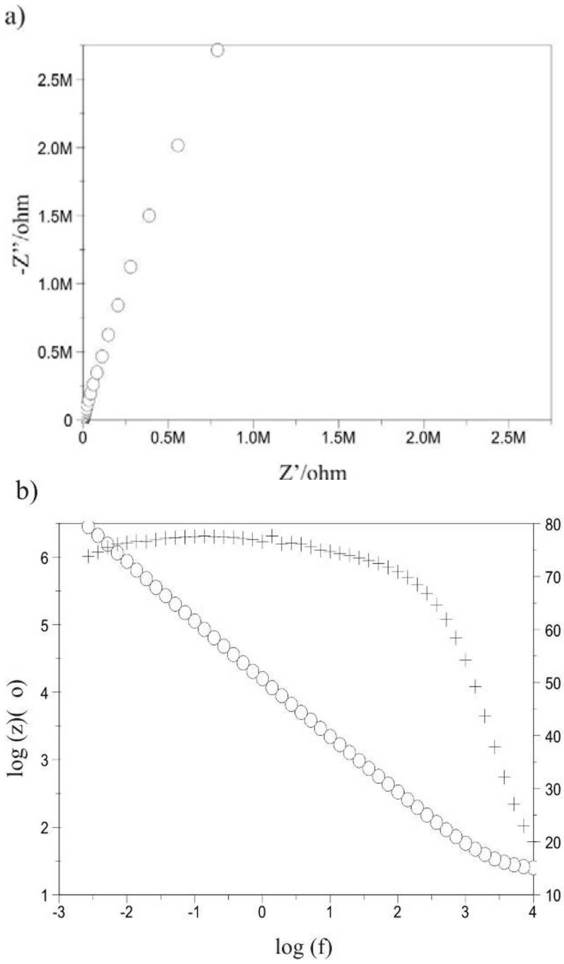


Fig. 3. Impedance spectra registered for samples with surface that was polished and sterilised in ethylene oxide: a) diagram Nyquista, b) diagram Bode



Rys. 4. Impedance spectra registered for samples with surface that was passivated and sterilised in ethylene oxide: a) diagram Nyquista, b) diagram Bode

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

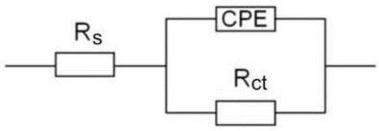


Fig.5. Model of electrical equivalent circuit for the system: steel X10CrNi18-8 – oxide layer – artificial blood plasma [5-7]

In the electrical equivalent circuit, resistor R_{ct} and CPE represent, respectively, resistance of ion transition and capacitance of 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 made.

Mathematical model of impedance of the system: steel AISI 316L – passive layer – solution is presented in the equation [7] (1):

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

Summary

Technology of low-temperature sterilisation based on 100 % ethylene oxide is the only low-temperature sterilisation method of such a universal character. It remains the basis for sterilisation of medical materials and products sensitive to high temperature and humidity, used both in hospitals and in the industry.

Table 1. EIS analysis results for steel X10CrNi18-8 before and after sterilisation in ethylene oxide

Surface	E_{ocp}, mV	R_s, Ωcm^2	R_{ct}, $M\Omega cm^2$	CPE_{dl}	
				Y_0, $\Omega^{-1}cm^{-2}s^{-n}$	n
before ethylene oxide sterylization					
Polished	-44	23	1.7	0.6505e-4	0.92
Passivated	-29	23	21.3	0.6271e-4	0.85
after ethylene oxide sterylization					
Polished	-72	21	62.6	0.8527e-4	0.85
Passivated	-41	22	56.8	0.1289e-4	0.85

EIS tests enabled to characterise impedance of phase boundaries: material – passive layer (created during passivation or after sterilisation) – solution, through impedance data approximation by means of electrical model of equivalent circuit. Performed analysis enabled to determine impedance spectra of the tested system and matching data to equivalent circuit made of parallel CPE element connected with resistance of ion transition R_{ct} and residual resistance R_s at high frequencies, attributed to ohm resistance of artificial blood plasma [5] – Fig. 5.

To sum up, on the ground of performed EIS test it was proved that chemical passivation process has beneficial influence on corrosion resistance of X10CrNi18-8 steel. Chemical sterilization with ethylene oxide in addition had beneficial influence on electrochemical characteristics of passive layer.

Acknowledgments

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