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IMPACT OF STERILISATION AND STRAIN HARDENING IN DRAWING PROCESS ON RESISTANCE TO ELECTROCHEMICAL CORROSION OF WIRES INTENDED IN CARDIOLOGY

The study presents results of tests of impact of work hardening in cold drawing process, surface treatment and sterilisation on resistance to electrochemical corrosion of wires made of stainless steel X2CrNiMo 17-12-2 intended for cardiology. Potentiodynamic tests were performed on the ground of registered anodic polarisation curves in artificial plasma solution. Static uniaxial tension test made the ground for determination of strength characteristics of wires and the flow curve. Functions presenting the change of polarisation resistance according to strain applied in drawing process were selected.

Test results show deterioration of corrosion properties of wires with work hardening. Surface modification of passivated surface caused increase of resistance of stainless steel wires to electrochemical corrosion, whereas sterilisation with pressurised water steam deteriorated that resistance.

Keywords: wires made of stainless steel X2CrNiMo 17-12-2, flow stress and flow curve, electrochemical corrosion in artificial plasma solution, sterilisation

1. Introduction

In invasive cardiologic treatment, guide wires and cardiologic implants are generally made of wires and wire products made of stainless steel [1-8]. They should feature proper biotolerance, and what follows – high resistance to electrochemical corrosion in contact with blood. Corrosion properties of materials for medicine depend to a great extent on production technology (among other things strain in plastic forming, the way of surface preparation) [9-12].

Selection of optimal parameters of wire drawing process depends on proper characteristics of technological plasticity of materials. Both, obtaining structures prone to drawing as well as obtaining a product featuring required functional characteristics depend on them. Curves of yield stress changes in strain function (so called flow curves) enable to predict material behaviour during plastic forming processes [13]. Strain applied in drawing process also has a significant influence on corrosion properties of the wire [14, 15]. Production engineers make use of flow curves for such selection of drawing parameters that would enable to obtain wires with mechanical properties required for a specific purpose. In the study, a similar attitude was suggested in order to forecast corrosion properties depending on strain applied in drawing process. Thanks to application of suggested methodology it will be possible to state what corrosion properties will be featured by wire with required strength drawn with applied strain.

The purpose of the study was to evaluate the impact of strain applied in drawing process on electrochemical corrosion resistance of wires intended for cardiology, made of stainless steel X2CrNiMo 17-12-2. What was also analysed was the impact of wire surface modification by means of grinding, electrochemical polishing and chemical passivation on their corrosion properties. Technological treatment used in surface engineering for the improvement of physical and chemical characteristics of medicine-intended products must take sterilisation process into consideration [16-19]. The most frequently used sterilisation method of medical products is bactericidal action of water steam. Therefore, an analysis of the impact of pressurised water steam sterilisation on corrosion characteristics of wires was made.

2. Material and methods

Wire rod made of X2CrNiMo 17-12-2 steel with diameter of d = 5.58 mm, annealed, drawn to diameter of 1.25 mm served as stock material. Total logarithmic strain in drawing process was $\varepsilon = 2.99$. Wire work hardening took place during the process of cold plastic forming. Strength characteristics of wires (R_m, $R_{p0.2}$) were determined on the ground of static uniaxial tension test. Tests were made on Instron 1116 testing machine. Next, the course of flow curve was determined.

Then, wires were subject to surface modification that included in turn: grinding, electrolytic polishing and chemical passivation. Passivation was performed in 40% nitric acid at the temperature of 65°C and time of 20-60 min. After surface treatment, wires were sterilised with pressurised eater steam. The process was performed in autoclave Basic Plus by Mocom at the temperature of T = 134°C and pressure p = 1.1 bar and time t = 12 min. After surface treatment and sterilisation, wires were subject to corrosion tests.

Resistance to electrochemical corrosion was evaluated on the ground of registered anodic polarisation curves with

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potentiodynamic method with application of a system for electrochemical tests VoltaLab PGP 201 by Radiometer. Potentiodynamic tests of wires were performed in artificial plasma solution. TABLE 1 presents composition of artificial plasma. Stern method was used for determination of polarisation resistance. The tests were performed at the temperature of T = 37 ± 1°C, and pH = 7.0 ± 0.2. Saturated calomel electrode (NEK) of KP-113 type served as the reference electrode, whereas platinum electrode of PtP-201 type was used as the auxiliary electrode.

TABLE 1

Chemical composition of artificial blood plasma solution

Component	Amount of distilled water, g/l
NaCl	6.8
$CaCl_2$	0.2
KCl	0.4
$MgSO_4$	0.1
$NaHCO_3$	2.2
Na_2HPO_4	0.126
NaH_2PO_4	0.026

TABLE 2

Strength properties of wire

Wire diameter d, mm	Logarithmic strain in the drawing process, ε	Tensile strength R_m, MPa	Yield point $R_{p0,2}$, MPa
5.58	0	540.7	224.8
3.02	1.23	1372.4	1213.7
2.12	1.94	1532.4	1339.4
1.25	2.99	1800.2	1454.7

3. Results and discussion

TABLE 2 presents a compilation of strength characteristics of wires with selected dimeters determined in tensile test. Values of proof stress were used for determination of flow curve of tested wires and determination of mathematical form of flow stress function. The curve was approximated with a function of $\sigma_p=\sigma_{p0}+C\varepsilon^n$ type, that takes into consideration the value of stress for initial state (i.e. for annealed wire, intended for drawing). Mathematical form of flow stress function is a follows (1):

$$\sigma_p = 224.8 + 878\varepsilon^{0.4}. \quad (1)$$

Fig. 1 presents flow curve of wires made of X2CrNiMo 17-12-2 steel (ε means strain in drawing process).

Potentiodynamic tests in artificial plasma enabled to determine the changes of resistance of wires to electrochemical corrosion both in relation to strain applied in drawing process and to the way of wire surface preparation and sterilisation in water steam. OCP potential for all tested samples was determined after 60 min. Selected results of corrosion tests are presented in TABLES 3 and 4.

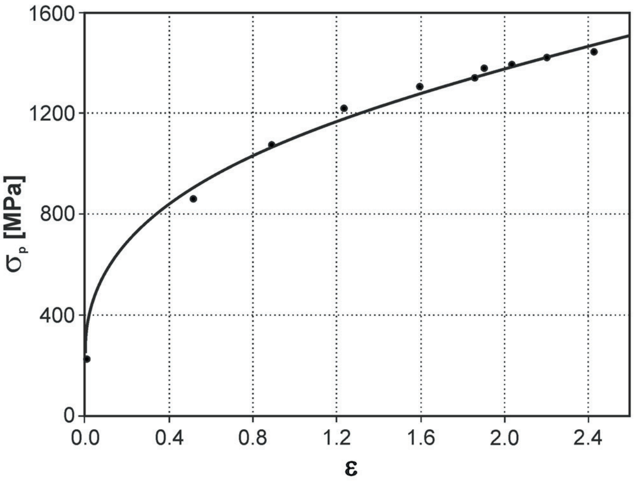


Fig.1. Flow curve of wire made of X2CrNiMo 17-12-2 steel

The tests showed varied resistance of wires drawn with strain within the range of ε = 0-2.99 to electrochemical corrosion. It was proved that annealed wire rod features the highest corrosion resistance. For the majority of wire diameters, the increase of strain brings about deterioration of corrosion characteristics of wires. One can observe decrease of corrosion potential, perforation potential and polarisation resistance as well as corrosion current density.

Performed tests showed that modification of wire surface significantly improved their corrosion characteristics. For example, corrosion potential of wire rod increases from E_{corr} = –28 mV (polished wire rod) to E_{corr} = –19 mV (polished and chemically passivated wire rod). Polarisation resistance of wire rod that was subject to surface treatment increases from R_p = 341 kΩcm^2 (polished wire rod) to R_p = 1030 kΩcm^2 (polished and chemically passivated wire rod). Breakdown potential increases from E_b = +371 mV (polished wire rod) to E_b = +1159 mV (polished and chemically passivated wire rod). Moreover, it was proved that sterilisation in water steam in most tested cases affected deterioration of wire corrosion properties.

Potentiodynamic tests results were then subject to static analysis. It was determined whether there is a significant dependence between corrosion characteristics and strain in drawing process. Performed tests enabled to select functions showing the change of polarisation resistance, depending on strain applied in drawing process. They have the following form (2-5):

$$R_p = -174.9\varepsilon + 968.6 \text{ (polished wire)}, \quad (2)$$

$$R_p = -88.6\varepsilon + 1019.1 \text{ (polished and passivated wire)}, \quad (3)$$

$$R_p = -162.6\varepsilon + 814.9 \text{ (polished and sterilised wire)}, \quad (4)$$

$$R_p = -91.9\varepsilon + 738.3 \text{ (polished, passivated and sterilised wire.} \quad (5)$$

TABLE 3

Test results of electrochemical corrosion resistance of wires

Wire surface	d, mm	ε	E_{corr}, mV	E_b, mV	R_p, kΩcm²	I_{corr}, µA/cm²
Polished	5.58	0	-28	+371	341	0.076
	3.02	1.23	-81	+363	800	0.033
	2.12	1.94	-82	+344	230	0.113
	1.25	2.99	-122	+126	145	0.179
Polished and passivated	5.58	0	-19	+1159	1030	0.025
	3.02	1.23	-36	+1094	917	0.028
	2.12	1.94	-61	+940	805	0.032
	1.25	2.99	-40	+639	779	0.033

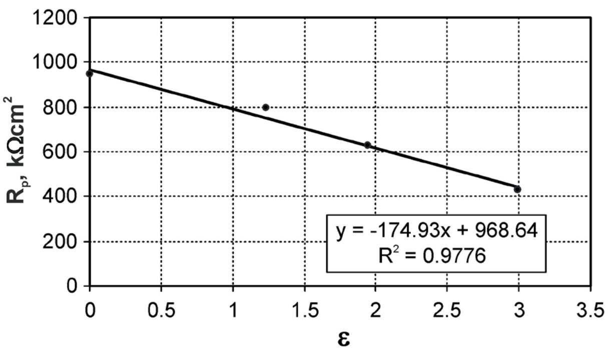
TABLE 4

Test results of electrochemical corrosion resistance of wires after sterilisation

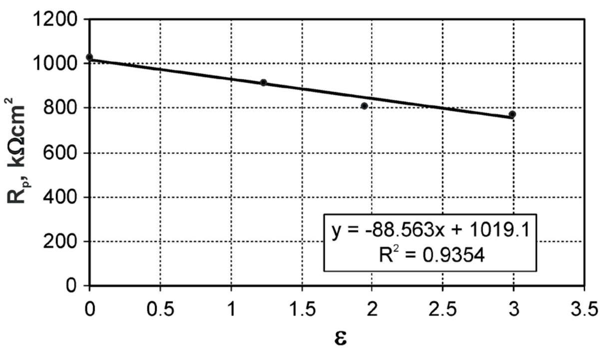
Wire surface	d, mm	ε	E_{corr}, mV	E_b, mV	R_p, kΩcm²	I_{corr}, µA/cm²
Polished	5.58	0	-41	+230	801	0.032
	3.02	1.23	-59	+259	624	0.042
	2.12	1.94	-87	+395	524	0.050
	1.25	2.99	-185	+240	309	0.084
Polished and passivated	5.58	0	-20	+722	715	0.036
	3.02	1.23	-41	+644	694	0.037
	2.12	1.94	-65	+632	511	0.051
	1.25	2.99	-47	+615	467	0.056

In tested samples the level of significance was $p<0,05$.

Figs. 2 and 3 present curves obtained on the ground of selected results of corrosion tests, namely change of polarisation resistance as the function of strain applied in drawing process.

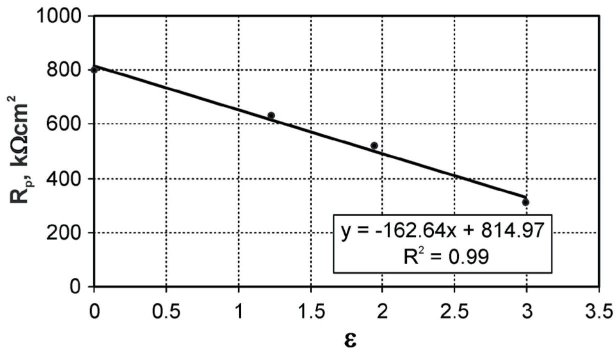


a)

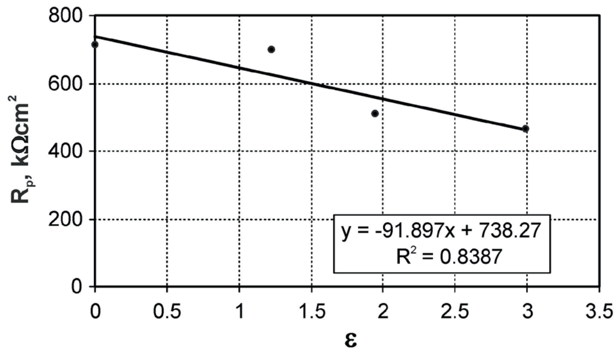


b)

Fig.2. Dependence of polarisation resistance on strain in the drawing process: a) of electrochemically polished wire b) of electrochemically polished and passivated wire



a)



b)

Fig.3. Dependence of polarisation resistance on strain in the drawing process:
a) of electrochemically polished wire after sterilisation
b) of electrochemically polished and passivated wire after sterilisation

Values of polarisation resistance Rp determined thanks to elaborated dependences (2-5) approximate to those determined experimentally. The biggest differences of polarisation resistance values may be seen for wires with initial diameter (wire rod).

4. Summary

Corrosion tests performed in artificial plasma solution enabled to find out how resistance to electrochemical corrosion of wires made of stainless steel X2CrNiMo 17-12-2 changes under the influence of strain in drawing process. Potentiodynamic tests results explicitly show deterioration of corrosion resistance with work hardening taking place in drawing process.

Wire corrosion resistance also depends on the way of surface preparation. Grinding is performed as pre-treatment that aims at smoothening the surface and removing the remains of grease and sub-grease layers. Polishing gives the surface proper smoothness, and the purpose of passivation is to create a compact oxide layer protecting the surface of metal from oxidation. Obtained results prove that further wire surface modification treatment caused the increase of their corrosion characteristics. The highest corrosion to electrochemical corrosion can be attributed to wires for which the final treatment was chemical passivation. Chemical passivation is responsible for creation of compact and continuous oxides layers on the surface, with mostly amorphous structure, that in turn act as a barrier for reaction products that diffuse inside the solution or that create a chemically adsorbed coating.

Statistical analysis showed that there is a significant dependence between corrosion properties (polarisation resistance) and strain in drawing process. On the ground of curves and functional relations, it can be concluded how polarisation resistance of wires subject to surface treatment changed depending on strain applied. The value of polarisation resistance proves how reasonable chemical passivation is in case of wires intended for cardiology. It must be noted that functions presented in the article were prepared for one melt. In order to make them universal dependences for stainless steel X2CrNiMo 17-12-2, it is necessary to repeat the tests for a larger number of melts.

Presented topic is crucial for engineers designing technologies of plastic forming of materials intended for medicine. Having specific curves or functional dependences at disposal, it will be possible to anticipate polarisation resistance that will be featured by products with required strength properties subject to cold plastic forming with applied strain.

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