www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S

Volume 60 2015 Issue 3

DOI: 10.1515/amm-2015-0318

J. PRZONDZIONO*, E. HADASIK*,#, W. WALKE**, J. SZALA*

IMPACT OF STRAIN IN DRAWING PROCESS AND SURFACE MODIFICATION ON RESISTANCE TO ELECTROCHEMICAL CORROSION OF WIRES USED IN DENTISTRY

WPŁYW ODKSZTAŁCENIA W PROCESIE CIĄGNIENIA I MODYFIKACJI POWIERZCHNI NA ODPORNOŚĆ NA KOROZJĘ ELEKTROCHEMICZNĄ DRUTÓW PRZEZNACZONYCH DLA STOMATOLOGII

The study presents the results of research into the impact of strain in cold drawing and surface modification treatment on corrosion properties of wires made of X10CrNi 18-8 steel used in maxillofacial surgery. Scanning microscopy enabled to make images of the surface of wires after drawing process as well as after surface modification treatment. Resistance to electrochemical corrosion was evaluated on the ground of registered anodic polarisation curves in artificial saliva. In order to evaluate physical and chemical properties of the surface, electrochemical impedance spectroscopy was performed.

Test results show deterioration of corrosion properties of wires along with strain taking place in drawing process. It was proved that electrochemical polishing and chemical passivation caused sudden increase of resistance of wires made of stainless steel to pitting corrosion in artificial saliva.

Keywords: wires made of stainless steel X10CrNi 18-8, electrochemical corrosion in artificial saliva solution, anodic polarisation curves, EIS, SEM

W pracy przedstawiono wyniki badań nad wpływem odkształcenia w procesie ciągnienia na zimno oraz zabiegów modyfikacji powierzchni na właściwości korozyjne drutów wykonanych ze stali X10CrNi 18-8 przeznaczonych do zabiegów chirurgii twarzowo - szczękowej. Przy pomocy mikroskopii skaningowej zobrazowano powierzchnię drutów zarówno po procesie ciągnienia, jak i po zabiegach obróbki powierzchniowej. Odporność na korozję elektrochemiczną oceniano na podstawie rejestracji krzywych polaryzacji anodowej w roztworze sztucznej śliny. W celu oceny właściwości fizykochemicznych powierzchni przeprowadzono elektrochemiczną spektroskopię impedancyjną.

Wyniki badań wskazują na pogorszenie właściwości korozyjnych drutów wraz z zachodzącym w procesie ciągnienia umocnieniem odkształceniowym. Stwierdzono, że zabiegi elektrochemicznego polerowania i chemicznej pasywacji spowodowały wzrost odporności drutów wykonanych ze stali nierdzewnej na korozję wżerową w roztworze sztucznej śliny.

1. Introduction

Metallic biomaterials used in maxillofacial surgery include stainless steels with austenitic steel, alloys with shape memory, alloys on cobalt matrix and titanium alloys. The basic material used for production of wires is stainless steels of Cr-Ni type and Cr-Ni-Mo. Treatment of facial cranium fractures consists in stable osteosynthesis which means surgical setting of bone fractions and their integration. Modern maxillofacial surgery has at its disposal a wide range of wires and wire products, such as clips and splints that are used for osteosynthesis of bone splinters of maxillofacial skeleton [1-3].

Setting or immobilisation of bones is often performed with application of wire linkage and wire splints. The material used for linkage is thin wires made of stainless steel. Wire diameters are selected individually for each case, with consideration to the width of the space between teeth and linkage load. Thinner wires with diameter of 0.3-0.4 mm are used for small space between teeth and small load to the linkage. For large load and wide spaces between teeth, wire with diameter of 0.5 mm is used. In case of fractures with bone splinters relocation various kinds of sutures (single, double, crossed) made of wires are applied [4-8].

The study presents the analysis of the impact of strain hardening taking place in cold drawing process and the impact of surface modification on corrosion resistance of wires made of X10CrNi 18-8 steel used in maxillofacial surgery. Scanning microscopy was employed to make images of the surface of wires after consecutive plastic forming and surface treatment. Resistance to electrochemical corrosion was evaluated on the ground of registered anodic polarisation curves with potentiodynamic method. The tests were performed in a solution simulating human saliva. Physical and chemical

* SILESIAN UNIVERSITY OF TECHNOLOGY FACULTY OF MATERIALS SCIENCE AND METALLURGY, 8 KRASINSKIEGO STR., 40-038 KATOWICE, POLAND

** SILESIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF BIOMEDICAL ENGINEERING, ZABRZE, POLAND

Corresponding author: Eugeniusz.Hadasik@polsl.pl

surface properties were evaluated with EIS method.

2. Material and methods

Wire rod with diameter of 5.5 mm made of X10CrNi 18-8 steel subject to drawing was used as stock material for tests. Corrosion tests were performed on wires with diameters of 3.0 mm, 2.2 mm, 1.6 mm, 1.45 mm. Wires were subject to surface treatment, namely grinding, electrochemical polishing and chemical passivation. Passivation was performed in 40 % HNO3 at the temperature of 21°C and time 40 min.

Observation of wire surface after drawing and surface treatment was performed with scanning microscope with field emission FE SEM S-4200 Hitachi.

Resistance to electrochemical corrosion was evaluated on the ground of registered anodic polarisation curves with testing system VoltaLab PGP201 by Radiometer. Tests were performed in artificial saliva whose chemical composition is presented in TABLE 1. The temperature of the solution during the test was 37 ± 1°C, and pH = 7.2. 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. Prior to the tests, all samples were cleaned in 96 % ethanol in ultrasonic washer. The tests started with determination of corrosion potential, which was followed by registration of anodic polarisation curves. Corrosion potential for all samples stabilised after 30 min. Registered curves enabled to determine typical factors describing resistance to pitting corrosion, i.e. corrosion potential, perforation potential or transpassivation potential, repassivation potential and corrosion current density. Stern method was used to determine polarisation resistance [9-12].

TABLE 1

Chemical composition of artificial saliva

Component	Amount of distilled water, g/l
Na_2HPO_4	1.3
NaCl	3.5
KSCN	1.65
KH_2PO_4	1.0
$NaHCO_3$	7.5
KCl	6.0

In order to find out physical and chemical characteristics of wire surface, EIS tests were performed. Measurements were performed with application of measurement system AutoLab PGSTAT 302N equipped with FRA2 (Frequency Response Analyser) module. Nyguist and Bode diagrams were registered. Performed tests enabled direct comparison of real object behaviour with its equivalent system, which is a model referring to physically realised impedance.

3. Results and discussion

Resistance of wires to electrochemical impedance, and therefore possibility of their application in medicine, depends to a great extent on the way of preparation of their surface that should feature the lowest roughness possible. The results of observation of the surface of wires with selected diameters after plastic working and surface modification, made with application of electron scanning microscope, are presented in Figs. 1-4. The tests proved that the surface of wire rod and drawn wires features defects after plastic forming process. Presence of scratches and grooves, arranged in accordance with strain direction, can be observed, and also the remains of sub-grease layers and drawing grease. Grinding contributed to a great extent to removal or reduction of those defects. Electrochemical polishing and chemical passivation resulted in substantially better wire surface quality.

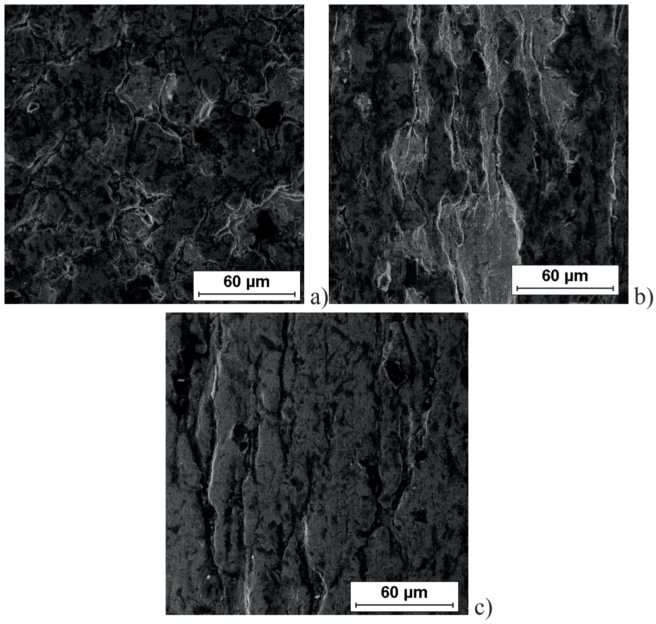

Fig. 1. Surface of wire rod (a) and drawn wires with diameter of 3 mm (b) and 1.45 mm (c)

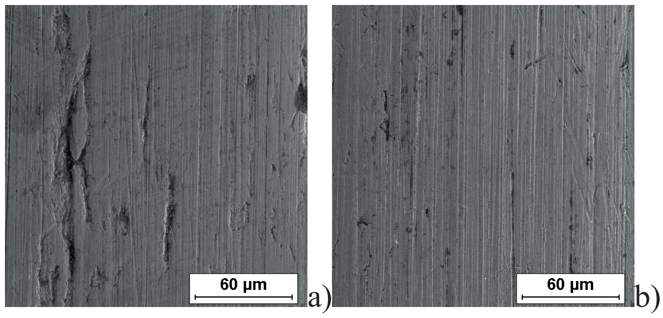

Fig. 2. Surface of wires with diameter of 3 mm (a) and 1.45 mm (b) after grinding

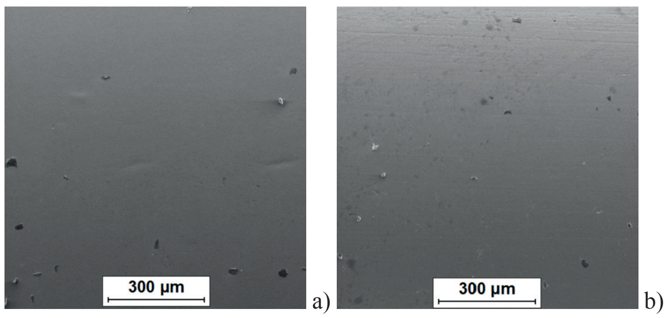

Fig. 3. Surface of wires with diameter of 3 (a) and 1.45 mm (b) after polishing

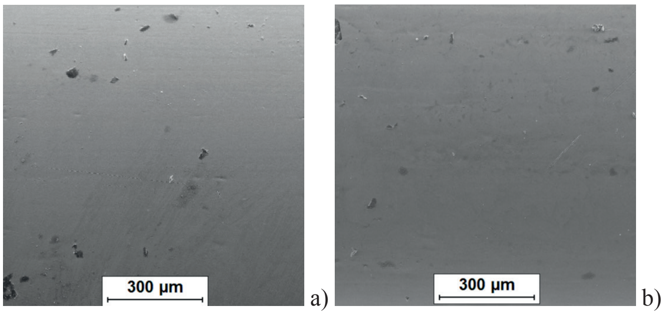

Fig. 4. Surface of wires with diameter of 3 mm (a) and 1.45 mm (b) after passivation

Analysing anodic polarisation curves it was proved that strain applied in the process of wire drawing has a substantial impact on the course of those curves. The highest corrosion resistance could be attributed to wire with diameter of 3.0 mm. With the increase of strain during drawing, corrosion potential and polarisation resistance decrease and corrosion current density increases. For example, polarisation resistance for polished wire with diameter of 3.0 mm decreased from the value of R_p = 237 kΩcm^2 to R_p = 63 kΩcm^2, and for chemically passivated wire from R_p = 2140 kΩcm^2 to R_p = 313 kΩcm^2. Surface modification of wires made of X10CrNi 18-8 steel results in their improved corrosion characteristics. Chemical passivation process substantially increased the value of polarisation resistance. For passivated wires hysteresis loop and therefore perforation potential was not detected, which proves that wires are resistant to pitting corrosion. Potentiodynamic tests results are presented in TABLE 2. Fig. 5 shows anodic polarisation curves for polished as well as polished and then passivated wire.

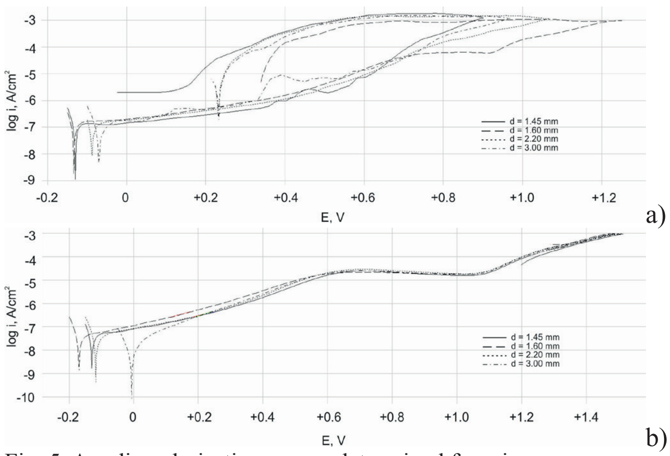

Fig. 5. Anodic polarisation curves determined for wire: polished (a), polished and passivated (b)

Favourable impact of chemical passivation was also proved in impedance tests. Registered Nyquist diagrams show fragments of incomplete large semi-circles, which is a typical impedance response for thin oxide layers. Then, maximum values of phase angles in a wide range of frequencies, presented in Bode diagrams, are similar and equal Θ = 75^o-85^o. Log inclination |Z| in the whole area of frequency changes is close to -1, which proves capacitive character of the passive layer – Figs. 6 and 7. It was proved that the best matching of experimental impedance spectrum to the generated by the programme model curve for the real and imaginary component of circuit impedance depending on changes of measurement signal is obtained by application of equivalent circuit. It consists of a parallel system of CPE (Constant Phase Element) connected with resistance of ion transitions through phase boundary: electrode – R_{ct} solution and resistance at high frequencies R_s, that might be attributed to the resistance of electrolyte (artificial saliva) – Fig. 8. Mathematical impedance model for the system: X10CrNi 18-8 steel – passive layer – artificial saliva is presented by the equation (1):

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

For samples subject to chemical passivation, positive impact of ion transition resistance Rct irrespective of wire diameter, was observed in relation to polished samples – TABLE 3. The highest value of Rct was obtained for passivated wires with diameter of 3.0 mm (Rct = 19.12 MΩcm^2).

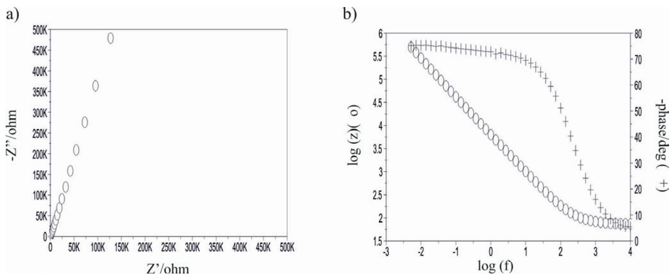

Fig. 6. Impedance spectra for wires made of steel X10CrNi 18-8 (polished): a) Nyquist diagram, b) Bode diagram

TABLE 2

Test results of electrochemical corrosion resistance of wires

Wire surface	d, mm	E_{corr}, mV	E_b, mV	E_{tr}, mV	R_p, kΩcm^2	I_{corr}, µA/cm^2
Polished	3.00	-73	+745	-	237	0.110
	2.20	-92	+784	-	68	0.382
	1.60	-139	+896	-	61	0.426
	1.45	-136	+763	-	63	0.412
Polished and passivated	3.00	-5	-	+1325	2140	0.012
	2.20	-118	-	+1316	491	0.053
	1.60	-171	-	+1298	343	0.076
	1.45	-132	-	+1266	313	0.083

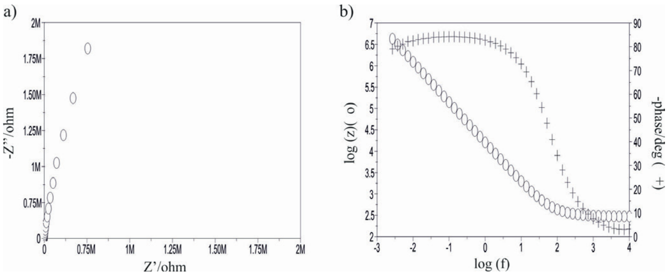

Fig. 7. Impedance spectra for wires made of steel X10CrNi 18-8 (polished and passivated): a) Nyquist diagram, b) Bode diagram

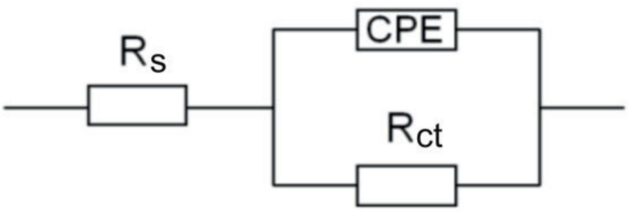

Fig. 8. Electrical model of equivalent circuit for: X10CrNi 18-8 steel – oxide layer – artificial saliva

4. Summary

Modern maxillofacial surgery has at its disposal a wide range of wires and wire products, such as clamps, splints, bindings and sutures that can be used for reconstruction of damaged parts of face and jaw. Metallic biomaterials should meet a number of quality requirements that include biocompatibility in tissues and body fluids as well as relatively high resistance to electrochemical corrosion. Therefore the research involved tests related to evaluation of corrosion properties of wires made of X10CrNi 18-8 steel in artificial saliva.

Potentiodynamic tests performed in artificial saliva enabled to find out how the strain applied in drawing process influences resistance to electrochemical corrosion of wires made of stainless steel X10CrNi 18-8. The results prove explicitly deterioration of resistance to corrosion with work hardening resulting from drawing process.

Wire resistance to electrochemical corrosion is also influenced by the way of its surface preparation. Grinding is performed as pre-treatment used for surface smoothening and removal of the remains of grease and sub-grease layers. Polishing gives the surface respectively low roughness, and passivation aims at creation of compact oxide layer protecting the surface from corrosion environment impact. Obtained results prove that wire surface modification treatment performed in sequence caused the increase of their corrosion characteristics. Wires for which the final stage was chemical passivation featured the highest resistance to electrochemical corrosion.

EIS tests proved that the character of the upper layer did not change for polished as well as polished and passivated samples. Oxide layer featuring better properties protecting the steel from the impact of corrosion environment was created on the surface of the wire subject to chemical passivation.

Proper preparation of drawn wire is decisive as far as product quality is concerned, and therefore influences proper utilisation of wires and wire products in medicine. To sum up, it must be stated that chemical passivation brought about, irrespective of work hardening, resistance of wires made of stainless steel to pitting corrosion in artificial saliva. It proves proper preparation of the surface of wire for maxillofacial surgery treatment.

REFERENCES

[1] J. Marciniak, M. Kaczmarek, A. Ziębowicz, Biomateriały w stomatologii, Wyd. Politechniki Śl., Gliwice (2008).

[2] L. Kryst, Chirurgia twarzowo-szczękowa, PZWL, Warszawa (2010).

[3] M. Zmorzyński, H. Wanyura, Z. Stopa, Czas. Stomatol. **62**, 974 (2009).

[4] V. Cipruš, J. Pirš, Stahl und Eisen **101**, 69 (1981).

[5] O. Parulska, M. Dobrzyński, Dent. Med. Probl. **48**, 595 (2011).

[6] R. Mukerji, G. Mukerji, M. McGurk, Br. J. Oral Maxillofac. Surg. **44**, 222 (2006).

TABLE 3

EIS analysis results

d, mm	E_{OCP}, mV	R_s, Ωcm^2	R_{ct}, MΩcm^2	CPE	
				Y_0, Ω^{-1}cm^{-2}s^{-n}	n
Polished wires					
3.00	-103	75	11.24	0.3453E-4	0.89
2.20	-127	75	7.28	0.2325E-4	0.87
1.60	-135	76	4.62	0.3023E-4	0.83
1.45	-138	77	1.74	0.5563E-4	0.82
Polished and passivated wires					
3.00	-39	74	19.12	0.4398E-4	0.93
2.20	-70	76	9.84	0.3462E-4	0.92
1.60	-72	76	9.14	0.2892E-4	0.88
1.45	-131	75	3.17	0.3434E-4	0.87

[7] J.E. Hausamen, J. Craniomaxillofac Surg. **29**, 2 (2001).
[8] J. Marciniak, A. Ziębowicz, Acta Bioeng. Biomech. 6, 17 (2004).
[9] A. Ziębowicz, J. Marciniak, J. Achiev. Mater. Manuf. Eng. 18, 19 (2006).
[10] W. Walke, J. Przondziono, Metallurgija 50, 201 (2011).
[11] J. Przondziono, W. Walke, E. Hadasik, J. Szymszal, IOP Conference Series: Materials Science and Engineering 35, 1757 (2012).
[12] K.K Chew, S.H.S. Zein, A.L. Ahmad, Natural Science, 4, Article ID:18077, 1 (2012).

Received: 20 December 2014.