

W. WALKE, J. PRZONDZIO

ISSN 0543-5846

METABK 50(3) 201-204 (2011)

UDC – UDK 669.77:78:669.26:669.24:669.28:620.193=111

PHYSICO-CHEMICAL PROPERTIES OF PASSIVE LAYER ON THE SURFACE OF GUIDE WIRE USED IN ENDOUROLOGY

Received – Prispjelo: 2010-06-21

Accepted – Prihvaćeno: 2010-11-05

Preliminary Note – Prethodno priopćenje

The main criterion for austenitic steel X2CrNiMo 17-12-2 suitability for guide wire in endourology is its biotolerance. It is most of all connected with physical and chemical properties of wire surface, which should be adjusted to the characteristics of the environment of human urinary system tissues. Suitability of the proposed passive layer for purification of wire surface was determined to a great extent by its chemical composition. Therefore, this study included chemical composition tests by means of X-ray Photoelectron Spectroscopy (XPS), during which atomic concentration of elements in tested passive layers was identified and determined. Resistance to pitting corrosion was evaluated on the ground registered anodic polarisation curves by means of potentiodynamic method.

Key words: X2CrNiMo 17-12-2 steel, passive layer, artificial urine, corrosion resistance, XPS

Fizikalno-kemijska svojstva pasivnog sloja na žicama vodilicama u endourologiji. Glavni kriterij za primjenu austenitnog Cr-Ni-Mo čelika za žice vodilice u endourologiji je biotolerancija. Ovaj zahtjev ovisi o fizikalnim i kemijskim svojstvima površine žice, koja moraju biti prilagođena uvjetima koji vladaju u ljudskom urinarnom sustavu. Pogodnost predloženog pasivnog sloja za žicu vodilicu, prvenstveno ovisi o njegovom kemijskom sastavu. Stoga, istraživanje u ovom radu obuhvaća određivanje kemijskog sastava pasivnog sloja žice metodom fotoelektronske rendgenske spektroskopije (XPS). Otpornost na jamičastu koroziju određena je korištenjem potenciodinamičke polarizacije, snimanjem anodnih polarizacijskih krivulja.

Ključne riječi: Cr-Ni-Mo čelik, pasivni sloj, umjetna otopina urina, otpornost na koroziju, XPS

INTRODUCTION

Development of modern urology requires improvement of surgical techniques, which in turn determines the necessity to produce modern equipment and a range of auxiliary materials for treatment. One should mention here guide wires. Thanks to their application during operation, it is possible to insert endoscopes, catheters or urological stent efficiently. Both, guide wires and stents, are made of stainless steel. They must feature suitable application properties for individual applications [1-3].

MATERIAL AND METHODS

The following material was selected for experimental tests: wire made of X2CrNiMo 17-12-2 steel in accordance with PN-ISO 5832 – 1, generally used for production of urological stents.

Samples for tests, taken both from wire were subjected to the following treatment: mechanical grinding, which was made by means of hydrous abrasive paper with granularity of $120 \div 500$ grains/mm²; electrochemical poli-shing: for steel it was performed in the solution

with chemical composition presented in Table 1 in the period of 4 minutes; chemical passivation for both biomaterials was made in 40 % solution of HNO₃ in the temperature of 65 ± 1 °C in the period of 60 minutes.

Tests of physical and chemical characteristics of steel wires with created passive layer were conducted in two stages. Stage one consisted in determination of applicability of the layer in urine-like solution [4], which in clinical conditions the tested material has contact with.

The aim of stage two was to determine characteristics of passive layer after 30-day immersion in artificial urine.

Measurement of surface roughness

Tests of surface roughness were carried out with application of linear mechanical contact measurement method by means of profilometer SURTRONIC 3+ by Taylor/Hobson. The measurement was made on the sections with $l = 0,8$ mm and precision $\pm 0,02$ μm. The value of parameter R_a was determined.

Corrosion resistance testing

The pitting corrosion tests were realized with the use of potentiodynamic method by means of recording of

W. Walke, Faculty Of Mechanical Engineering, The Silesian University of Technology, Gliwice, Poland

J. Przondziona, Faculty of Materials Science and Metallurgy, The Silesian University of Technology, Katowice, Poland

Table 1 Chemical composition of the solution polishing

Component	Amount	Conditions
H ₃ PO ₄	55 ÷ 60 % wt	T = 60 ± 1 °C, i = 40 ± 1 A/dm ²
H ₂ SO ₄	35 ÷ 45 % wt	
C ₂ H ₂ O ₄	40 ÷ 60 g/dm ³	
C ₈ H ₉ NO	40 ÷ 60 g/dm ³	
Inhibitor of corrosion	3 g/dm ³	

anodic polarization curves [4,5]. The VoltaLab® PGP 201 system (Radiometer) for electrochemical tests was applied. The saturated calomel electrode (SCE) of KP-113 type was applied as the reference electrode. The PtP-201 platinum electrode was the auxiliary electrode. Corrosion resistance of all samples was investigated. The corrosion tests were undertaken in artificial urine [6]. Temperature of the solution was equal to 37 ± 1 °C and pH = 7,0 ± 0,2.

The measurements were carried out after 60 min immersion in the artificial urine while the open circuit potential (OCP) was recorded. The potential scan was started at 100 mV more cathodic potential than the OCP, increasing toward the anodic values at a constant rate of 1 mV/s up to 1 mA/cm², and then a reverse scan was carried out toward the cathodic value.

XPS study

Chemical composition investigations of surface layers were realized with the use of the multifunctional electron spectrometer Physical Electronics PHI 5 700/660. The X-ray photo-electron spectroscopy (XPS) with monochromatic radiation AlK α of 1 486,6 eV was applied.

The tests were carried out on the samples of polished as well as polished and passivated surfaces in the form of bar. The measurement of photoelectron spectrum in the wide range of binding energy from 0 ÷ 1 400 eV and precise measurements of the spectrum lines of elements from the surface layer were conducted. For the applied excitation energy, the mean free path of photoelectrons was in the range 5 Å ÷ 20 Å.

SEM study

Scanning microscopy was applied to enable evaluation of wire surface condition after corrosion tests in artificial urine. By means of scanning electron microscope with field emission FE SEM S-4 200 HITACHI cooperating with spectrometer Voyager 3 500 NORAN INSTRUMENTS, qualitative and quantitative analysis of surface layer chemical composition was made.

RESULTS

Mean arithmetic value of profile deviation from average line for samples with ground surface equalled $R_a = 0,45 \mu\text{m}$, for samples with polished as well as polished

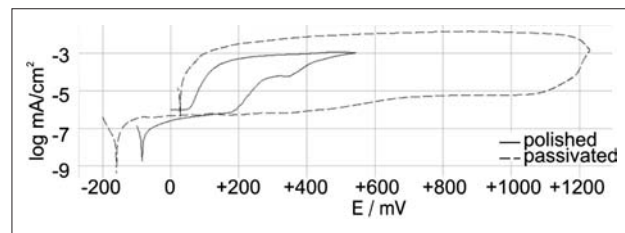


Figure 1 Anodic polarisation curves determined for wire polished and passivated

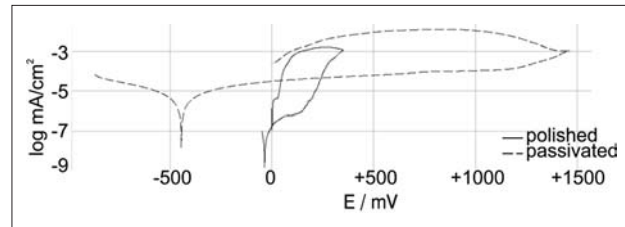


Figure 2 Anodic polarisation curves determined for wire polished and passivated (30 days)

and passivated surface $R_a = 0,12 \mu\text{m}$. Surface roughness of polished as well as polished and passivated surface expressed by R_a parameter did not exceed $0,16 \mu\text{m}$, which is the maximum value of surface roughness allowable for such goods.

In the first stage of tests anodic polarisation curves were determined for wires in initial condition – Figure 1. On the ground of carried out tests it was determined that mean value of corrosion potential for wires that were only polished equalled $E_{\text{corr}} = -83 \text{ mV}$.

Application of chemical passivation process brought about the change of mean value of corrosion potential to $E_{\text{corr}} = -157 \text{ mV}$ - Figure 1. Next, for wires that were exposed to artificial urine solution for 30 days, its value equalled respectively: for polished surface $E_{\text{corr}} = -34 \text{ mV}$; for polished and passivated surface $E_{\text{corr}} = -501 \text{ mV}$ – Figure 2.

Determined anodic polarisation curves were characterised by the presence of hysteresis loop. Rapid increase in anodic density current in analysed measurement range was observed, which proved that pitting corrosion process was initiated. A typical image of a pit resulting after corrosion tests in artificial urine on the surface of polished as well as polished and passivated wire is shown in Figure 3.

For polished wire in initial condition, the value of perforation potential remained at the average level $E_b = +350 \text{ mV}$, and after exposure it was slightly lower and equalled $E_b = +202 \text{ mV}$. Chemical passivation process caused the increase in perforation potential up to the value of $E_b = +1 203 \text{ mV}$ for wire in initial condition. Identical value was registered for passivated wire after exposure in artificial urine solution for 30 days. Determined in addition, by means of Stern method, values of polarisation resistance R_p and corrosion current density i_{corr} for particular variants of tested wire were respectively:

- polished wire – $R_p = 216,3 \text{ k}\Omega\text{cm}^2$,
 $i_{\text{corr}} = 0,120 \mu\text{A/cm}^2$,

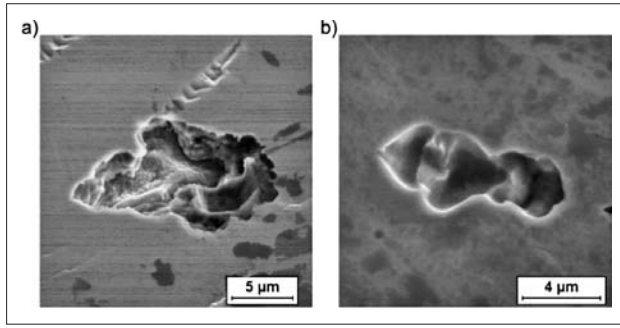


Figure 3 Typical image of a pit created after corrosion tests: a) electrochemically polished surface, b) surface that was electrochemically polished and chemically passivated

- polished wire after exposure in artificial urine solution – $R_p = 203,9 \text{ k}\Omega\text{cm}^2$, $i_{\text{corr}} = 0,128 \mu\text{A}/\text{cm}^2$,
- polished and passivated wire $R_p = 232,1 \text{ k}\Omega\text{cm}^2$, $i_{\text{corr}} = 0,112 \mu\text{A}/\text{cm}^2$,
- polished and passivated wire after exposure in artificial urine solution $R_p = 8,1 \text{ k}\Omega\text{cm}^2$, $i_{\text{corr}} = 3,174 \mu\text{A}/\text{cm}^2$.

Applicability of proposed passive layer for the refinement of steel wire surface is determined to a great extent by its chemical composition. Therefore, at the next stage of work tests of chemical composition of passive layer, created as the result of electrochemical polishing, were carried out – Figure 4, Table 2, as well as electrochemical polishing and chemical passivation – Figure 5, Table 2.

For the electropolished and passivated wire of the X2CrNiMo 17-12-2 steel the presence of the following elements was revealed: C, N, O, Na, Ca, Cr, Fe, Ni.

Analysis of the obtained results shows that the C1s carbon line (with the maximum reached for the energy $E_b = 285,3 \text{ eV}$) corresponds with carbon compounds of C-C double bond – air origin impurities. Wide oxygen line with the peak of $E_b = 530,5 \text{ eV}$ corresponds to metal oxides (Fe, Mo, Zn). The Mo3d5/2 line (the maximum for the energy $E_b = 228,1 \text{ eV}$) confirms the presence of metallic Mo. The asymmetry of line in the direction of

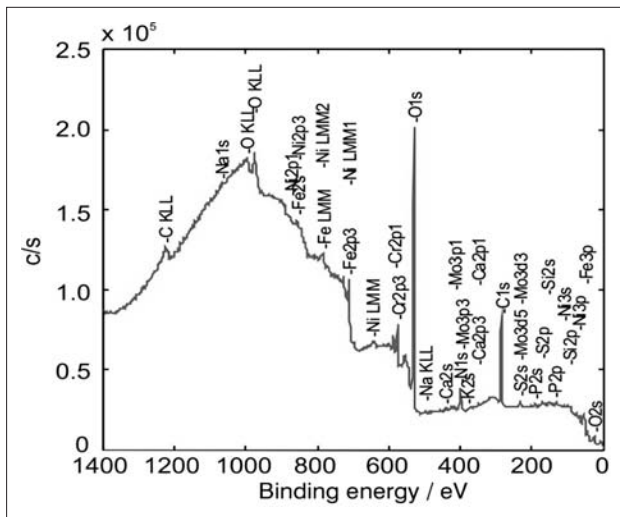


Figure 4 XPS spectrums of X2CrNiMo 17-12-2 steel samples of electro-polished surface

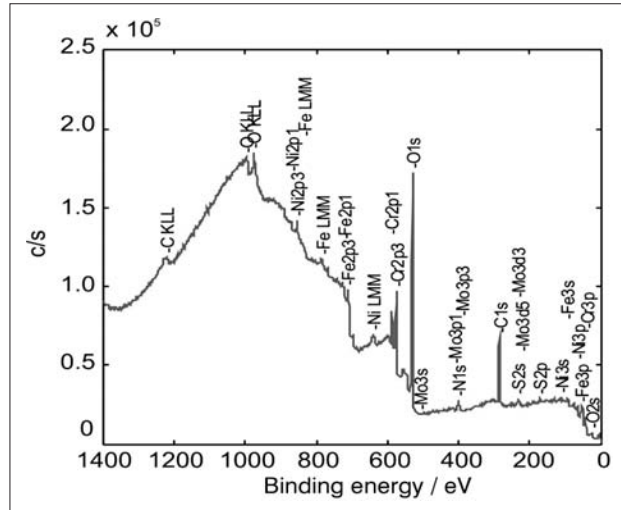


Figure 5 XPS spectrums of X2CrNiMo 17-12-2 steel samples of electro-polished and chemically passivated surface

higher energy shows the influence of molybdenum oxide. The Cr2p3/2 line refers to three chemical states of chromium – metallic, CrO_2 and Cr_2O_3 . The 852,8 eV binding energy (Ni2p3/2 line) relates to metallic Ni. The recorded Fe2p3/2 line (with the maximum reached for the energy $E_b = 706,9 \text{ eV}$) shows dominant, metallic state of iron. Deformation of the line observed for higher energy indicates that iron is also present in the form of the Fe_2O_3 oxide.

Measurement of inspection spectra for wire after exposure in artificial urine revealed the presence of the following elements in the upper layer: C, N, O, Na, Mg, Si, P, Cl, K, S, Ca, Ni, Cr, Fe and Mo – Figure 6. and 7. Spectra presented in Figures 4 – 7 show lines coming from electronic states of respective elements, as well as lines of Auger electrons designated as KLL or LMM. Obtained spectra of respective elements showed that the impact of artificial urine on the sample surface, irrespective of the type of surface modification, contributed to the increase in oxygen concentration connected mainly

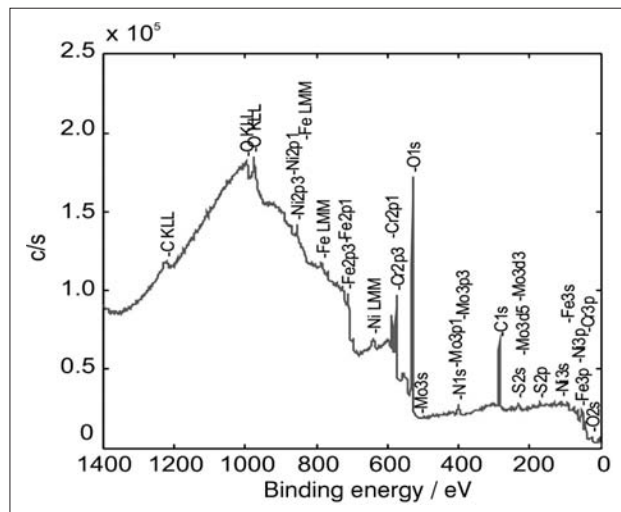


Figure 6 XPS spectrums of X2CrNiMo 17-12-2 steel samples of electropolished surface after 30 days in artificial urine

