

Pitting corrosion, Biomaterials, Urological stents, Artificial urine.

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SURFACE TREATMENT OF STAINLESS STEEL INTENDED FOR UROLOGICAL STENTS

Abstract: The work presents the influence of the surface treatment of Cr-Ni-Mo stainless steel, intended for implants applied in urogenital surgery, on their corrosion resistance. The tests were carried out in the simulated urine at the temperature $37\pm1^{\circ}$ C and pH = $6\div6,4$. In particular, the pitting corrosion resistance tests were carried out.

1. INTRODUCTION

Stents in urology are used either to eliminate narrowing of the urethra or ureter. Stent insertion to urethra, while urether was narrowed by the Bening Postatic Hyperpalsion (BPH), was described for the first time in 1980 by Fabian [3, 9]. The catheterization which is uncomfortable for patient is not necessary when we use stent. Nowadays endoscopic stent implantation method which is used to treat the BPH is also used to treat narrowing of bulbar urethra caused by instrumentation, trauma, inflammation or congenital problems [10]. Stents implantation is also recommended for narrowing or cancerous narrowing of ureter. It is especially useful for patients who are qualified to surgery but with some serious disabilities that make normal operation impossible [1, 10, 18].

Stainless steels are the most common metallic biomaterials used for stents. Almost 90% of these stents is made of steel [4 \div 6, 14, 15, 23 \div 26]. Since many years this group of biomaterials is in common use mainly as short term implants, for example in an orthopedic surgery, a dental surgery and thoracosurgery [7, 8, 12, 16, 17, 20, 21].

Very little is known about the corrosion resistance of metallic implants in a urine. This knowledge is a basic condition related with the usage of this kind of stents. It is known that the type of corrosion and its intensity depend on a chemical and phase composition of the biomaterial, stress and strain fields, geometrical features of implant and the operational technique.

The quality of the surface layer also plays important role. A qualitative and a quantitative description of corrosion processes in artificial urine will determine the efficiency and the clinical usefulness of implants and will impinge on postoperative complications. For this reasons a surface treatatment of the Cr-Ni-Mo alloy is presented in this work. The surface treatment is important because of corrosion resistance minimizing reactions and postoperative complications [2, 11].

2. MATERIAL AND METHODS

The corrosion resistance of Cr-Ni-Mo stainless steel intended for implants applied in the little invasive surgery of urogenital system was tested. The tests were carried out on samples in the form

of a rod of diameter d = 5 mm and length equal to l = 15 mm. The tested material met implantation requirements concerning the chemical composition, the structure and mechanical properties.

The tests were carried out on samples of the following surfaces: grinded – average roughness $R_a = 0.31 \mu m$, electropolished – average roughness $R_a = 0.10 \mu m$ and electropolished and chemically passivated in conditions worked by the authors – fig.1. In order to measure the roughness the Surtronic 3+ surface analyzer was applied.

The pitting corrosion tests were realized by recording of anodic polarization curves with the use of the potentiodynamic method. The VoltaLab® PGP 201 system for electrochemical tests was applied – fig. 2 [19]. The saturated calomel electrode (SCE) of KP-113 type was applied as the reference electrode. The tests were carried out in electrolyte simulating urine at the temperature of 37 ± 1 °C and pH = 6÷6,4. The electrolyte consisted of two solutions A and B mixed together in the ratio of 1:1 – table 1.

Observations of samples surfaces were carried out both before and after the corrosion tests. The observations were realized with the use of the MST ZOOM stereoscopic microscope in the magnification range from 6 to 37.

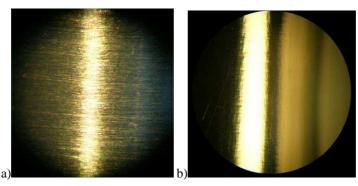


Fig. 1 View of the samples surface: a) grinded $R_a = 0.31 \ \mu m$, b) electropolished $R_a = 0.10 \ \mu m$

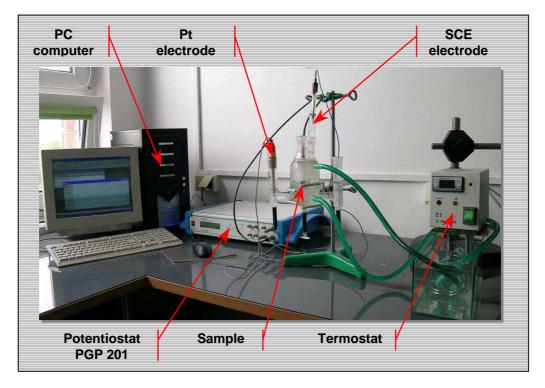


Fig. 2 Diagram of the corrosion resistance set

Ingredients A	g/l distiled water	Ingrediends B	g/l distiled water
CaCl ₂ 2H ₂ O	1.765	NaH ₂ PO ₄ 2H ₂ O	2.660
Na_2SO_4	4.862	Na ₂ HPO ₄	0.869
MgSO ₄ 7H ₂ O	1.462	Na ₃ Cit·2H ₂ O	1.168
NH ₄ Cl	4.643	NaCl	13.545
KCL	12.130		

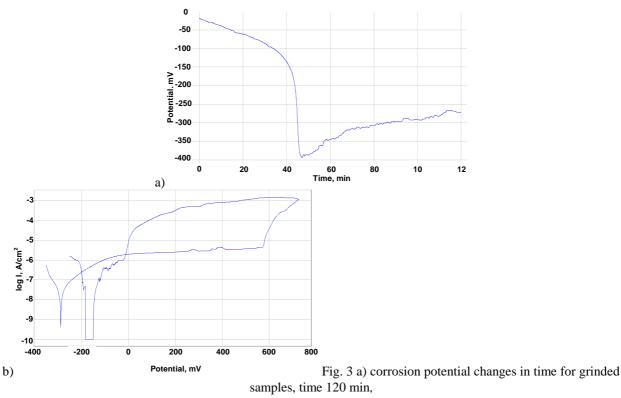
Table 1. Artificial urine (A : B= 1:1) [13]

3. RESULTS

Results of electrochemical tests have revealed the influence of surface preparation of the Cr-Ni-Mo steel on the corrosion resistance – table 2. For the grinded samples, the corrosion potential was in the range E_{kor} =-250÷-134 mV - fig. 3a. Polarization of samples caused the increase of anodic current for potentials in the range $E_B = +565 \div +657$ mV – fig. 3b. The repassivation potential was in the range E_{cp} =-22÷+272 mV. Polarization resistance of the samples was equal to R_p =536 k Ω cm².

Pitting co alloy Breakdown poten-**Polarization resis-Corrosion potential Repassivation po-**Surface preparatial tance tion method Ekor, mV tential E_{cp}, mV E_B, mV $R_{p}, k\Omega cm^{2}$ Grinded $-250 \div -134$ $-22 \div +272$ $+565 \div +657$ 536 -72 ÷ -38 $+819 \div +942$ $0 \div +140$ Electropolished 931 Electropolished and -61 ÷ -38 $+1257 \div +1296$ $-48 \div +20$ 1940 passivated

Table 2.	
prrosion resistance of Cr-Ni-Mo	a





For the electropolished samples, the corrosion potential was in the range E_{kor} =-72÷-38 mV – fig. 4a. Polarization of samples caused the increase of anodic current for potentials in the range E_B =+819÷+942 mV – fig. 4b, The repassivation potential was in the range E_{cp} =0÷+140 mV. Polarization resistance of the samples was equal to R_p = 931 k Ω cm².

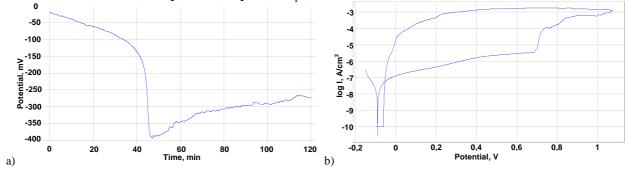


Fig. 4 a) corrosion potential changes in time for electropolished samples, time 90 min, b) anodic polarization curve for electropolished samples

For the electropolished and passivated samples, the corrosion potential was in the range E_{kor} =-61÷-38 mV – fig. 5a. Polarization of samples caused the increase of anodic current for potentials in the range E_B =+1257÷+1296 mV – fig. 5b, The repassivation potential was in the range E_{cp} =-48÷+20 mV. Polarization resistance of the electropolished and passivated samples was equal to R_p =1940 k Ω cm².

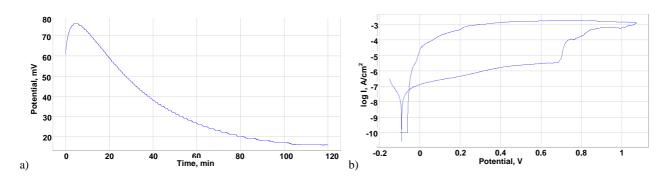


Fig. 5 a) corrosion potential changes in time for electropolished and chemically passivated samples, time 120 min, b) anodic polarization curve for electropolished and chemically passivated samples

The recorded curves of the anodic polarization were mainly characterized by the decrease of the anodic current density in the range of human body potentials ie. $0\div0.4$ V The smallest density was observed for the electropolished and passivated samples – fig. 6.

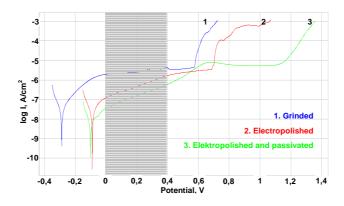


Fig. 6 Anodic polarization curves of Cr-Ni-Mo samples after diverse surface preparation

Observations of samples surfaces with the use of the stereoscopic microscope were carried out after the corrosion tests. Single pits were observed on every sample - fig. 7.

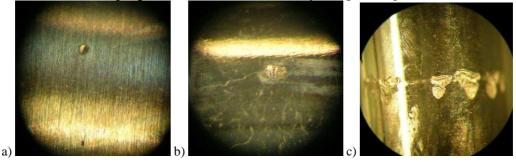


Fig. 7 Single pits on the samples surface: a) grinded specimens, b) electropolished specimens, c) electropolished and chemically passivated specimens

4. CONCLUSION

The aim of the research was the usefulness evaluation of the Cr-Ni-Mo stainless steel, commonly used for stents in operational cardiology, for application in urogenital system.

The obtained results have shown favorable influence of the applied surface treatment process on the corrosion resistance of samples made of the Cr-Ni-Mo stainless steel. The tests have revealed that the passive layer created in the electropolishing and the chemical passivation process improves the corrosion resistance of the investigated steel.

In spite of the clear influence of the surface condition on the corrosion resistance of the Cr-Ni-Mo stainless steel, further research on metallic biomaterial, appropriate for application in urogenital system, seems to be necessary.

To this end it seems to be necessary to carry out analogous corrosion resistance tests in simulated urine for other metallic biomaterials intended for stents. The tests should be completed with evaluation of susceptibility to incrustation. Ni-Ti alloys and Co-based alloys seem to be promising.

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BIBLIOGRAPHY

- BARBALIAS G.A., SIABLIS D., LIATSIKOS E.N., KARNABADITIS D., YARMENITIS S., BOUROPOLUOS K., DIMAPOULOS J.: Matal stents a new treatment of malignant urateral obstruction. J.Urol., pp.54-58, 1997, 158(1).
- [2] CHRZANOWSKI W., MARCINIAK J., SZEWCZENKO J., NAWRAT G.: Electrochemical modification of Ti₆Al₄V ELI surface. Proceeding of the 12th International Scientific Conference ,,Achievements in Mechanical and Materials Engineering 2003", pp.157-160, Gliwice-Zakopane, 2003.
- [3] FABIAN K.M.: Per intraprostatische "Partielle Katheter" (Urologische spirale). Ueologe 1980, 19, pp.236.
- [4] KAJZER W., KACZMAREK M., MARCINIAK J.: Biomechanical analysis of stent oesophagus system. The Worldwide Congress of Materials and Manufacturing Engineering and Technology COMMENT'2005, Journal of Materials Processing Technology, pp. 196-202, Vol 162-163, 15 May 2005.
- [5] KAJZER W., MARCINIAK J.: Biomechanical analysis of urological stent. XV Conference on Biomaterials in Medicine and Veterinary Medicine, pp. 141-143, Rytro, 13-16.10.2005.
- [6] KAJZER W., MARCINIAK J.: Biomechanical FEM analysis of stent-urethra system. ESB 2005 19th European Conference on Biomaterials (including the 4th Young Scientist Forum), pp. 63 and conference CD, Sorrento (Italy), 11-15.09.
- [7] KRAUZE A., KAJZER W., MARCINIAK J.: Charakterystyka biomechaniczna układu gwoździe śródszpikowekość udowa z wykorzystaniem MES. Proceeding of the 12th International Scientific Conference "Achievements in Mechanical and Materials Engineering 2003", pp.533-538, Gliwice-Zakopane, 2003.
- [8] KRAUZE, A. ZIĘBOWICZ, J. MARCINIAK: Corrosion resistance of intramedullary nails used in elastic osteosynthesis of children. The Worldwide Congress of Materials and Manufacturing Engineering and Technology COM-MENT'2005. Journal of Materials Processing Technology Vol. 162-163, pp.209-214, 15 May 2005.
- [9] LAM J.S., VOLPE M.A., KAPLAN S.A.: Use of Prostatic Stents for the Treatment of Bening Prostatic Hyperplasia in High-risk Patients, Current Science, Inc., pp.277-284, 2001, 2.
- [10]MADLANI G.H., PRESS S.M., DEFALCO A., OESTERLING J.E., SMITH A.D.: Urolume endourethral prosthesis for the treatment of urethral stricture disease: Long-term results of the North American multicenter urolume trial. Urology, pp.846-856, May 1995, Number 5.
- [11]MARCINIAK J., CHRZANOWSKI W., ŻAK J.: Modyfikacja struktury warstwy powierzchniowej stopu Ti6Al4V ELI. XIII Konferencja Naukowa "Biomateriały w medycynie i weterynarii", Rytro, 2003, Inżynieria Biomateriałów, nr 30÷33, s.56-58, 2003.
- [12]MARCINIAK J., ZIĘBOWICZ A., Krauze A.: Wyznaczenie charakterystyki biomechanicznej układu druty śródszpikowe – kość w symulowanych warunkach laboratoryjnych. Proceedings of the 9th International Scientific Conference "Achievements in Mechanical and Materials Engineering 2000", pp.367-370, Gliwice-Sopot-Gdańsk, 2000.
- [13] MULTANEN M., TALJA M., HALLANVUO S., SIITONEN A., VALIMAA T., TAMMELA T.L.J., SEPPALA J., TORMALA P.: Bacterial adherence to ofloxacin- blended polylactone- coated self- reinforced – lactic acid polymer urological stents. BJU International, pp.966-969, 86,2000.

- [14]PASZENDA Z., TYRLIK-HELD J., MARCINIAK J., WŁODARCZYK A.: Badania odporności korozyjnej stali Cr-Ni-Mo z przeznaczeniem na implanty stosowane w kardiologii zabiegowej. Proceedings of the 9th International Scientific Conference "Achievements in Mechanical and Materials Engineering 2000", pp.425-428, Gliwice-Sopot-Gdańsk, 2000.
- [15]PASZENDA Z., Tyrlik-Held J.: Badania odporności korozyjnej stentów wieńcowych ze stali Cr-Ni-Mo. Proceedings of the 10th Jubilee International Scientific Conference "Achievements in Mechanical and Materials Engineering 2001", pp.453-460, Gliwice-Kraków-Zakopane, 2001.
- [16] PASZENDA Z., TYRLIK-HELD J.: Coronary stents with passive and carbon layers. Proceedings of the 17th European Conference on Biomaterials ESB2002, pp.89, 11-14.09.2003. Barcelona.
- [17]PASZENDA Z., TYRLIK-HELD J.: Forming the physicochemical properite of coronary stents surface. 13th Conference of the European Society of Biomechanics ESB2002, pp.539-540, 1-4.09.2002, Wrocław.
- [18] PAUER W., ECKERSTORFER G.M.: Use of self-expanding permanent endoluminal stents for benign ureteral strictures: mind-term results. J.Uro., pp.319-322, 1999, 162(2).
- [19] Standard: ASTM F-746-81:1999. Standard test metod for pittiong of crevice corrosion of metallic surgical implant materiale.
- [20] SZEWCZENKO J., MARCINIAK J., CHRZANOWSKI W.: Badania procesu korozji implantów ze stali Cr-Ni-Mo w warunkach elektrostymulacji prądem sinusoidalnym. Proceedings of the 9th International Scientific Conference "Achievements in Mechanical and Materials Engineering 2000", pp.511÷514 Gliwice-Sopot-Gdańsk, 2000.
- [21]SZEWCZENKO J., MARCINIAK J., CHRZANOWSKI W.: Uszkodzenia korozyjne implantów ze stali Cr-Ni-Mo w warunkach elektrostymulacji prądem zmiennym. Proceedings of the 10th Jubilee International Scientific Conference "Achievements in Mechanical and Materials Engineering 2001", pp.543-548 Gliwice-Kraków-Zakopane, 2001.
- [22] VALIMAA T., LAAKSOVIRTA S.: Degradation behaviour of self- reinforced 80L/20G PLGA devices in vitro. Biomaterials 25, pp.1225-1232 (2004).
- [23]WALKE W., KAJZER W., KACZMAREK M., MARCINIAK J.: Analiza stanu naprężeń i przemieszczeń w warunkach angioplastyki wieńcowej. Proceedings of the 11th International Scientific Conference "Achievements in Mechanical and Materials Engineering 2002", pp. 595-600 Gliwice-Zakopane, 2002.
- [24]WALKE W., PASZENDA Z., FILIPIAK J.: Experimental and numerical biomechanical analysis of vascular stent. Journal of Materials Processing Technology, COMMENT'2005, Journal of Materials Processing Technology Vol 164-165, pp. 1263-1268, 15 May 2005.
- [25] WALKE W., PASZENDA Z., MARCINIAK J.: Corrosion resistance of Co-Cr-W-Ni alloy designer for implants used in operative cafdiology. Engineering of Biomaterials, 47-53, pp.96-99 (2005).
- [26] WALKE W., PASZENDA Z., MARCINIAK J.: Optymalizacja cech geometrycznych stentu wieńcowego z wykorzystaniem metody elementów skończonych. Proceeding of the 12th International Scientific Conference "Achievements in Mechanical and Materials Engineering 2003", s.1011-1016, Gliwice-Zakopane, 2003.