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Physicochemical properties investigations of metallic urological stent after implantation

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Materials

ABSTRACT

Purpose: : The aim of the work was to determine the surfaces as well as physicochemical properties changes of the metallic urological stent. The tested stent was made of Co-Cr-Ni-Fe-Mo-Mn alloy and was implanted during four years.

Design/methodology/approach: Electrochemical tests have been used for corrosion resistance investigations. They were carried out in the artificial urine solution at the temperature 37±1°C with the use of the VoltaLab® PGP 201 system. The evaluation of pitting corrosion was realized by recording of anodic polarization curves with the use of the potentiodynamic method. Chemical composition investigations of the surface have been carried out with the use of X-ray Photoelectron Spectroscopy (XPS). The topography of surfaces changes was observed in scanning electron microscope (SEM).

Findings: Surface observations haven't showed the signs of pitting corrosion. No decrease of corrosion resistance for metallic material was stated. Furthermore in surface layer the presence of the organic compounds was observed.

Practical implications: The time of four years of implantation didn't induce the significant changes in electrochemical properties of metallic material of the tested stent which was in contact with the natural environment of physiological fluids.

Originality/value: The results obtained concern to investigations of the metallic material of the stent, which was implanted during the period of four years in human body that mean in natural environment of human tissues and physiological fluids.

Keywords: Biomaterials; Urethral stents; XPS; Corrosion resistance

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 BPH, was described for the first time in 1980 by Fabian [1,2]. 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 - Fig.1 [3-5]. The urological stents implanted in urethra are made from Cr-Ni-Mo austenitic steel, Co and Ni-Ti alloys. The chemical composition of these alloys should ensure good biocompatibility in urine environment which contain sodium, potassium and calcium chlorides [6,18,19]. The surface treatment of stents is important factor minimizing the corrosion process and postoperative complications in consequence [6-12]. The description of corrosion processes of metallic biomaterials in artificial urine determines the efficiency and clinical usefulness of that implants. An interesting question is how the metallic urological stents behave in the environment of the soft living tissues. There is no published data concerning to that problem. For that reasons the investigations of metallic urological stent after 4 year of implantation have been undertaken in the presented paper.

2. Materials and methods

The urological UroLume stent made of Co-Cr-Ni-Fe-Mo-Mn alloy has been used for investigations – Table 1. The stent has been removed from urethra after 4 years of implantation. It belongs to the group of self expanding “mesh stents”. After earlier cutting and widening of urethra the stent remains inside and constitutes the kind of scaffold. It prevents reclosing the light of urethra, increasing its diameter and unblocking the flow of urine.

Table 1.
Chemical composition of the alloy [17]

Element	Co	Cr	Ni	Mo	Mn	Fe	C
Mass concentration,%	40	20	15	7	2	15	0.001

The UroLume stent plaited in mesh form consists of 24 wires of 0, 15 mm diameter and create the cascade having the diameter:

- in compressed state - 6 mm,
- in state after expansion - 14 mm.

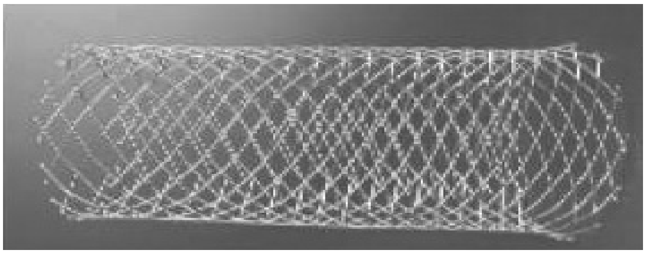


Fig. 1. Stent UroLume® [14]

Metallographic investigations have been provided for the purpose of evaluation of non-metallic inclusions as well as structure of the alloy. Observations have been performed in light microscope MEFCA of LEICA firm at 100 - 1000x magnitude.

Corrosion resistance investigations have been carried out by potentiodynamic method with the use of PGP201 potentiostate of Radiometr firm being a part of measuring set. After establishing the corrosion potential (E_{corr}) in non-current conditions the anodic polarization curves were recorded starting from the potential $E = E_{corr}$ - 100mV. Scanning rate was equal to 1 mV/s. The investigations were carried out in artificial urine environment - Table 2, at temperature +37 ± 1 °C and pH = 6. On that basis the characteristic parameters describing the corrosion resistance that is: breakdown potential E_b, repassivation potential E_{rp}, polarization resistance R_p, corrosion current density i_{corr} and corrosion rate Corr. have been determined.

Table 2.
Chemical composition of artificial urine solution [16,17]

Ingredients A	Ingredients concentration, g/l in distilled water	Ingredients B	Ingredients concentration, g/l in distilled water
$CaCl_2 2H_2O$	1.765	$NaH_2PO_4 2H_2O$	2.660
Na_2SO_4	4.862	Na_2HPO_4	0.869
$MgSO_4 7H_2O$	1.462	Na_2 Cit $2H_2O$	1.168
NH_4Cl	4.643	NaCl	13.545
KCl	12.130	-	-

The observations of topography of stents surface have been conducted in electron scanning microscope OPTON DSM 940 at magnifications in the range of 40 - 1000x.

X-ray photoelectron spectroscopy (XPS) was used to identify elements and their chemical states. Measurements were performed on Multitechnique Electron Spectrometer PHI 5700/660 from Physical Electronics using monochromatized $Al_{K\alpha}$ radiation with energy 1486 eV. The urological stents were sputtered with argon ions at energy of 4 keV. Calculations were done using the Multipak programme. XPS method belong to surface-sensitive methods because mean free path of electrons in solid material is only equal to tents of Å. Parts of stents of about 2 mm length were analyzed.

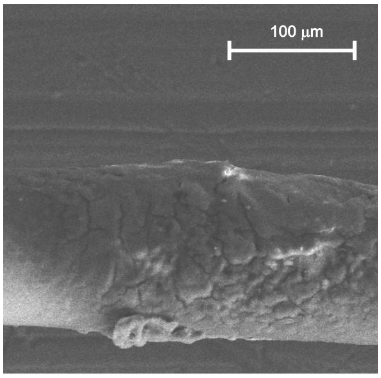
3. Results

Metallographic investigations have showed small amount of non-metallic inclusions in the structure of Co-Cr-Ni-Fe-Mo-Mn alloy.

Microscopic observation revealed the presence of fine grain austenitic structure in strain hardened state after plastic deformation. Surface observation of the stent which has been removed after 4 years from the patient urethra didn’t show the signs of pitting corrosion. On the basis of carried out observations in scanning microscope there were only stated local surface changes. The largest concentrations of changes on the stent surface appeared in the points of contact of particular wires, resulting from mesh form of stent construction and places of cross-linking of sequential parts of wires of which the stent was made of – Fig. 2a,b,c. The changes observed had therefore /accordingly local character and were repeated in periodical distances. They form discontinuous layer which increases significantly the roughness of the layer. In the rest part of observed sections the smooth surface of stents wires was stated – Fig. 2d.

Potentiodynamic investigations of corrosion resistance realized in artificial urine have showed comparable results and similar character of run of anodic polarization curves for all tested samples that were cut from urological stent – Table3.

Corrosion tests showed that the values of corrosion potentials were in the range of E_{corr} = -269 – -180 mV. Sudden increase of anodic current density was observed in the range of potentials E_b= +990 – +1080 mV, after polarization of tested specimens in the a)



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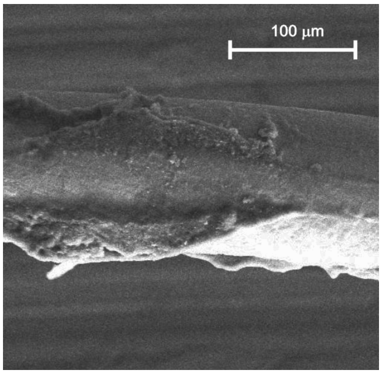

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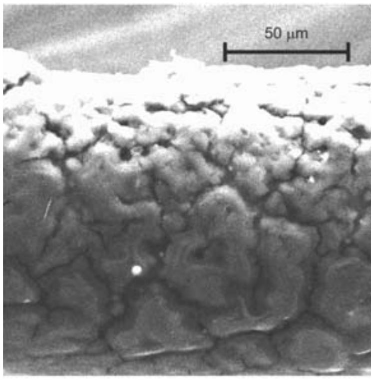

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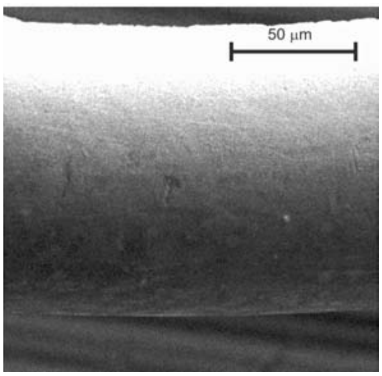

Fig. 2. Surface images of UroLume stent

positive values direction. Direction of polarization was changed after achieving the current density equal to 1mA/cm^2. The repassivation potential E_{cp} determined in that way had values from the range +850 – +860 mV. The curves recorded were characterized by a hysteresis loop – Fig. 3.

Table 3.
Results of pitting corrosion resistance investigations

Sample no	E_{corr}, mV	E_b, mV	E_{cp}, mV	i_{corr}, nA/cm^2	R_p, kΩcm^2	Corr., µm/year
1	-180	+1080	+850	4.33	6010	0.05
2	-249	+1010	+855	13.61	1910	0.15
3	-269	+990	+860	42.34	614	0.46

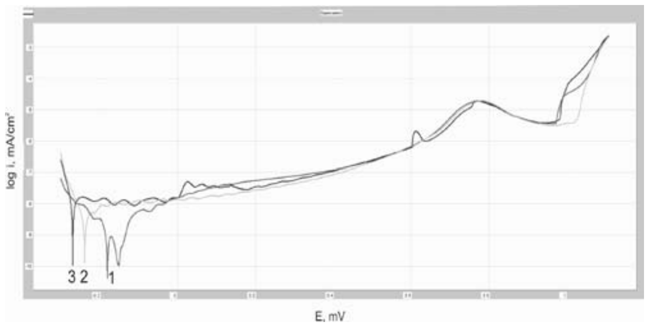

Fig. 3. Anodic polarization curves recorded for specimens cut from the UroLume® stent after 4 year of implantation

Only elements from organic compounds were identified on the surface of stent using XPS method. Metals from stent were revealed in the spectra after argon sputtering (Fig. 4). XPS lines of metals were split into two parts corresponded to two different chemical states. The first one at lower binding energy comes from pure metal whereas the second one at higher binding energy comes from oxidized metal. At longer time of sputtering higher contribution of pure metal line was observed.

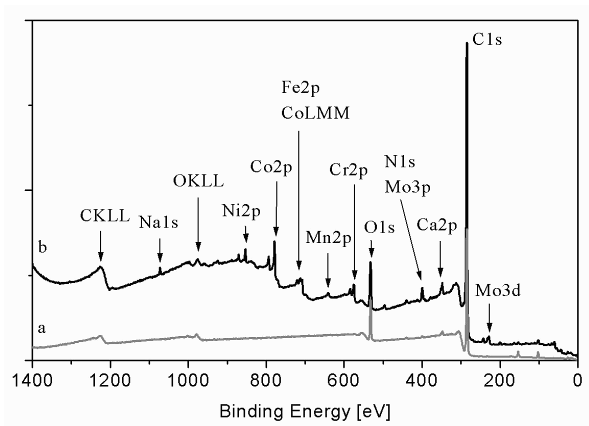

Fig. 4. XPS spectrum of a stent before argon sputtering (a) and after 4 keV argon sputtering for 4 minutes

4. Conclusions

The investigations of physicochemical properties of metallic biomaterials are carried out to asses their biocompatibility. The tests are realized in general majority in *in vitro* conditions. Interesting research materials provides the implants which were left in the human body for a longer time and were in direct contact with natural environment of human tissues and physiological fluids.

The investigated urological stent made of Co-Cr-Ni-Fe-Mo-Mn alloy was implanted in urethra during four years. The results of carried out investigations showed that metallic biomaterial of the stent after that time of implantation is still showing a good corrosion resistance. The values of breakdown potentials and other parameters related to pitting corrosion resistance are similar to the values describing the corrosion resistance of Co alloy (L605) which have close chemical composition and was tested in initial state that mean before implantation [20]. Surface observations in scanning microscope didn't reveal the signs of corrosion run and the changes which have been locally seen were connected with accumulating of the organic compounds on the surface of stent. It was confirmed by XPS investigations. Nevertheless in surface layer after longer time of sputtering higher contribution of pure metal lines were observed. It points out that surface reactions occur on the metal-tissue interface. Further investigations for explaining that processes are required.

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