

Surface modification and corrosion resistance of Ni-Ti alloy used for urological stents

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Materials

ABSTRACT

Purpose: The work presents the influence of the surface treatment of Ni-Ti alloy, intended for implants applied in urogenital surgery, on their corrosion resistance. The tests were carried out in the simulated urine at the temperature $37\pm 1^\circ\text{C}$ and $\text{pH} = 5.6\div 6.4$. In particular, the pitting and crevice corrosion resistance tests were carried out.

Design/methodology/approach: The 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. The tests were carried out in electrolyte simulating urine ($\text{pH} = 5.6 \div 6.4$) at the temperature of $37\pm 1^\circ\text{C}$.

Findings: Surface condition of metallic biomaterial determines its corrosion resistance.

Research limitations/implications: The obtained results are the basis for the optimization of physicochemical properties of the Ni-Ti alloy.

Practical implications: On the basis of the obtained results it can be stated that Ni-Ti alloy can be applied in urology.

Originality/value: The paper presents the influence of the surface treatment on corrosion resistance of Ni-Ti alloy.

Keywords: Metallic alloys; Biomaterials; Corrosion

1. Introduction

A great progress has been observed in last years in development of materials with varying and specific applications in medicine and biology [13]. Metallic biomaterials are commonly used in reconstruction in the orthopedic and dental surgery, operative cardiology and urology.

Many years' clinical experiences and evaluation of the organism's reaction to implants from the metallic biomaterials have been the basis for modifications of their chemical and phase compositions, both quantitative and qualitative. Some alloys were chosen, that may be safely employed for implants within a given time span, stipulating additionally for the particular physical and chemical properties of the implants surfaces. The corrosion resistance of the biomaterial decides the reactivity of implants in the environment of tissues and organism fluids. There is a strong correlation between the corrosion resistance and the biocompatibility. Good biocompatibility is observed for metal and alloys with the high anode potential [1, 2].

The metallic implants corrode. Corrosion type and its intensity depend on the chemical composition of the material, load type, implants geometrical shape, and the operation technique [19, 20]. One may distinguish the following corrosion types: pitting, crevice, stress and fatigue corrosion. All efforts of statistical systematizing of the corrosive determination of implants and distinguishing of corrosion types as for their usable form and the implant's chemical composition still evoke controversy [13].

Differences are shown in the corrosion development in particular zones of the same implant. The corrosion dynamics is decided by the chemical composition, homogeneity of structure, local strengthening state or stress state. Evaluation of the corrosion process is made difficult without the initial analysis of the physical and chemical quality of the implant's surface and also evaluation of the stress and strain states introduced during the operation [13].

Stents in urology are used either to eliminate narrowing of the urethra or ureter. Stent insertion to urethra, while urethra was

narrowed by the Benign Prostatic Hyperplasia (BPH), was described for the first time in 1980 by Fabian [3, 4]. 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 [5÷7].

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 treatment of the Ni-Ti alloy is presented in this work. The surface treatment is important because of corrosion resistance minimizing reactions and postoperative complications [8÷12, 14].

2. Material and methods

The corrosion resistance of Ni-Ti alloy 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 15x10x1 flat bar. 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 $R_a = 0,31 \mu\text{m}$, electropolished - average roughness $R_a = 0,10 \mu\text{m}$ and electropolished and chemically passivated, with carbon layer, electropolished and chemically passivated after sterilization, electropolished and chemically passivated after "in vitro" test in conditions worked by the authors. 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 [15]. 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 $37 \pm 1 \text{ }^\circ\text{C}$ and pH = 5,6÷6,4. The electrolyte consisted of two solutions A and B mixed together in the ratio of 1:1 [17, 18].

Crevice corrosion resistance was carried out in accordance to the ASTM G5-94:1999 standard [16]. The samples were polarized in the potential of 0,8 V for 900 seconds.

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.

3. Results

3.1. Pitting corrosion resistance tests results

Table 1 presents results of pitting corrosion resistance of Ni-Ti samples with differently modified surfaces. Furthermore, pitting corrosion tests were carried out for electropolished and passivated samples with deposited carbon layer, electropolished and passivated in sterilization process and samples after six month exposition in simulated artificial urine. The average value of the

ground samples tested in the artificial urine was $E_{\text{cor av}} = -196 \text{ mV}$. The process of electropolishing and chemical passivation increased the corrosion potential up to $E_{\text{cor av}} = -51 \text{ mV}$ for the electropolished samples and $E_{\text{cor av}} = +108 \text{ mV}$ for the passivated samples. The corrosion potential for the samples with carbon layer was equal to $E_{\text{cor av}} = -145 \text{ mV}$ and for the sterilized samples was $E_{\text{cor av}} = +47 \text{ mV}$. Furthermore, a significant decrease of the corrosion potential was observed for the passivated samples after "in vitro" tests ($E_{\text{cor av}} = -394 \text{ mV}$). The corrosion potential of the analysed samples was fixed in 15 – 120 minutes – fig. 1.

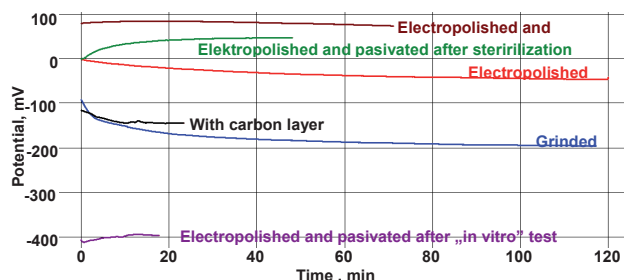


Fig. 1. Corrosion potential changes in time

The transpassivity potentials were diverse for the differently modified surfaces. For the ground samples tested in the artificial urine the average value of the transpassivity potential was equal to $E_{\text{tr}} = +1385 \text{ mV}$. The transpassivity potentials for the electropolished, the passivated samples and the samples with the carbon layer were equal to $E_{\text{tr}} = +1373 \text{ mV}$, $E_{\text{tr}} = +1470 \text{ mV}$ and $E_{\text{tr}} = +1470 \text{ mV}$ respectively.

For the sterilized samples the decrease of the transpassivity potential was observed $E_{\text{tr}} = +1261 \text{ mV}$.

For the "in vitro" tested samples the average transpassivity potential was equal to $E_{\text{tr}} = +1455 \text{ mV}$. The change of polarization caused the decrease of the anodic current density. The recorded curves were characterized by the small hysteresis loop that shows good corrosion resistance of the Ni-Ti alloy.

Comparative analysis of the anodic current density showed that the electropolishing and the passivation process reduced the density with the reference to the ground samples for the potentials up to +0,6 V – table 2, fig. 2. The electropolishing and the passivation process of the Ni-Ti alloy increased the polarization resistance to the value of $R_p = 1509 \text{ k}\Omega\cdot\text{cm}^2$ (with reference to the ground samples $R_p = 340 \text{ k}\Omega\cdot\text{cm}^2$). For the samples with carbon layer the increase of the anodic current density as well the decrease of the polarization resistance ($R_p = 194 \text{ k}\Omega\cdot\text{cm}^2$) with reference to the electropolished and the passivated samples were observed.

For the sterilized samples the decrease of the polarization resistance ($R_p = 839 \text{ k}\Omega\cdot\text{cm}^2$) with reference to the passivated samples was observed. For the "in vitro" tested samples the further decrease of the polarization resistance ($R_p = 320 \text{ k}\Omega\cdot\text{cm}^2$) with reference to the passivated samples was observed – table 3. For all samples the significant decrease of the corrosion rate was observed. The corrosion rate for the ground, the electropolished, the passivated and the carbon coated samples was equal to 1137 mm/year, 722 mm/year, 425 mm/year i 6 mm/year respectively. For the sterilized and the "in vitro" tested samples the corrosion rate was equal to 346 mm/year and 1262 mm/year respectively.

Table 1.
Pitting corrosion resistance of Ni-Ti alloy

Surface preparation method	Corrosion potential E_{cor} , mV	Average corrosion potential $E_{cor,av}$, mV	Transpassivation potential E_{tr} , mV	Average transpassivation potential $E_{tr,av}$, mV
1	2	3	4	5
grinded	-198 ÷ -194	-196	+1377 ÷ +1393	+1385
electropolished	-55 ÷ -48,	-51	+1346 ÷ +1401	+1373
electropolished and passivated	+73 ÷ +143	+108	+1442 ÷ +1445	+1443
carbon layer	-188 ÷ -102	-145	+1445 ÷ +1495	+1470
passivated after sterilization	+39 ÷ +55	+47	+1224 ÷ +1298	+1261
passivated ofert „in vitro” test	-415 ÷ -373	-394	+1438 ÷ +1478	+1455

Table 2.
Pitting corrosion resistance of Ni-Ti alloy

Surface preparation method	Current density, $\mu\text{A}/\text{cm}^2$				Polarization resistance R_p , $\text{k}\Omega\text{-cm}^2$	Corrosion intensity, mm/rok
	0 V	0,2 V	0,4 V	0,6 V		
1	2	3	4	5	6	7
grinded	0,0001	340	1137	0,0300	340	1137
electropolished	0,0001	490	722	0,0004	490	722
electropolished and passivated	0,0001	1509	425	0,0001	1509	425
carbon layer	0,0010	194	6	0,0019	194	6
passivated after sterilization	0,0006	839	346	0,0001	839	346
passivated ofert „in vitro” test	0,0045	320	1262	0,0117	320	1262

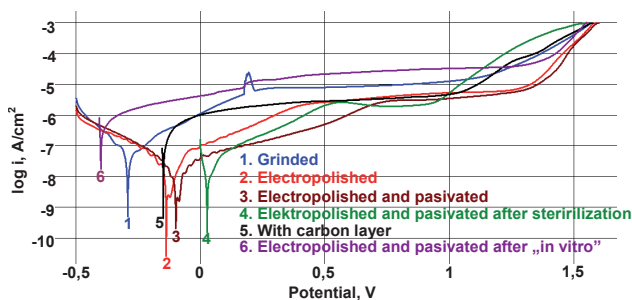


Fig. 2. Anodic polarization curves of Ni-Ti samples after diverse surface preparation

3.2. Crevice corrosion resistance results

Crevice corrosion tests were carried out for the ground, electropolished, passivated and carbon coated samples. The corrosion potentials for the ground, electropolished, passivated and carbon coated samples were equal to -174 mV, -99 mV, -99 mV and +20 mV respectively. Anodic current intensity for the $E=+800$ mV potential reached very small values for the

electropolished, passivated and carbon coated samples. The tests revealed that the ground and the electropolished samples are not resistant to crevice corrosion. The corrosion damage of these samples appeared in the potential range +100 do +800 mV. The passivated and the carbon coated samples are resistant to crevice corrosion – fig. 3.

4. Conclusions

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

Furthermore, the electropolished and the passivated samples showed lesser values of the anodic current density in the potential range 0 ÷ 400 mV. Also the sterilization process didn't changed unfavorably the anodic current density in the analyzed potential range (with reference to the passivated samples).

It was observed that deposition of the carbon layer on the electropolished surface caused the increase of current density in the potential range 0 ÷ 400 mV (with reference to the

electropolished samples). The most unfavorable influence on the current density was observed for the long-term exposure to the artificial urine.

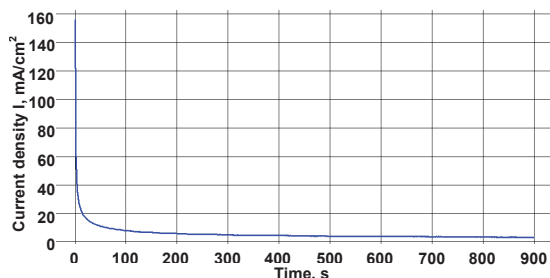


Fig. 3. Change of anodic current in a function of time for electro-polished and chemically passivated with carbon layer samples

It was observed that deposition of the carbon layer on the electropolished surface caused the increase of current density in the potential range 0 ÷ 400 mV (with reference to the electropolished samples). The most unfavorable influence on the current density was observed for the long-term exposure to the artificial urine.

No corrosion pits were observed in the analyzed samples which proves good corrosion resistance of Ni-Ti alloy in the artificial urine.

The crevice corrosion tests revealed that the ground and the electropolished samples are not resistant to this type of corrosion. Further modifications of surface, e.i. passivation and carbon deposition, make the alloy resistant to crevice corrosion in the artificial urine.

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

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