



Surface modification and corrosion behavior of Ni-Ti alloy used for urological implants

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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. 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 $37 \pm 1^\circ\text{C}$. The tests were carried out on samples of the following surfaces: grinded – average roughness $R_a = 0,16 \mu\text{m}$ and electropolished and chemically passivated average roughness $R_a = 0,10 \mu\text{m}$.

Findings: Surface condition of Ni-Ti alloys 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

MATERIALS

1. Introduction

The latest trends of research in biomedical engineering centers are focused on problems connected with surface engineering of implants. Surface treatment method that ensure minimal postoperative complications are developed. Biocompatibility of implants in tissue environment is determined by inseparable biochemical, biomechanical and bioelectronic factors. Biological reactions are analyzed with respect to metabolic, bacteriological, immunological and oncological processes [1].

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 [2].

The metallic implants corrode [3-5]. 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. Corrosion products infiltrate tissues. This process is called metalosis [1]. Phatomorphological changes, dependent on the type and concentration of elements, occur in

tissues close to implant. Histopathological changes are observed in the detoxication organs (liver, kidneys, spleen) [1].

Therefore, corrosion tests in simulated body fluids are the basis for searching optimal fields of usage and improvement of existing solutions.

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 [1].

In urology metallic biomaterials are mainly applied to produce catheters and urethral stents. For the first time these types of stents were introduced by Fabian [6-8] in 1980 and were applied to treat strictures caused by Benign Prostatic Hyperplasia (BPH). Nowadays metallic urethral stents are used in treatment of obstructions caused by tumor, intermittent urethrostenosis, trauma, inflammations or chronic diseases. Due to high percentage of complications related to usage of urological stents this method of treatment is applied in patients who are not suitable for surgical procedures (bad condition of health). Urological stents are also applied in older patients in order to improve the quality of life. Schematic implantation of urethral stent depending on disease was presented in Fig. 1 [9-11].

In order to improve positive effects of stents applied in urethrostrictures there is a need to search for new metallic biomaterials as well as methods of surface treatment (in order to increase their biocompatibility).

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 [12-15].

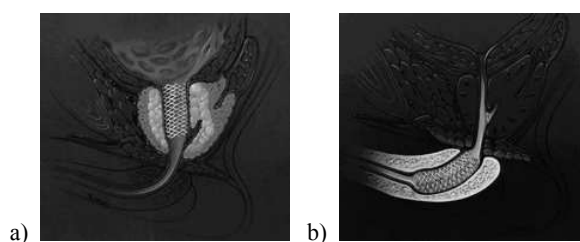


Fig. 1. Urolume® Urethral Stent implanted to: a) prostatic urethra, b) bulbar urethra [19]

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 specimens in the form of 15x10x1 flat bar. The tested material met implantation

requirements concerning the chemical composition, the structure and mechanical properties [16].

The tests were carried out on specimens of the following surfaces: grinded – average roughness $R_a = 0,16 \mu\text{m}$, 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 – Fig.2. 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. 3 [17]. 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 $\text{pH} = 5,6 \div 6,4$. The electrolyte consisted of two solutions A and B mixed together in the ratio of 1:1 – Table 1.

Crevice corrosion resistance was carried out in accordance to the ASTM G5-94:1999 standard [18]. 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 and with the use of the DSM 940 OPTON scanning microscope in the magnification range from 50 to 2000x.

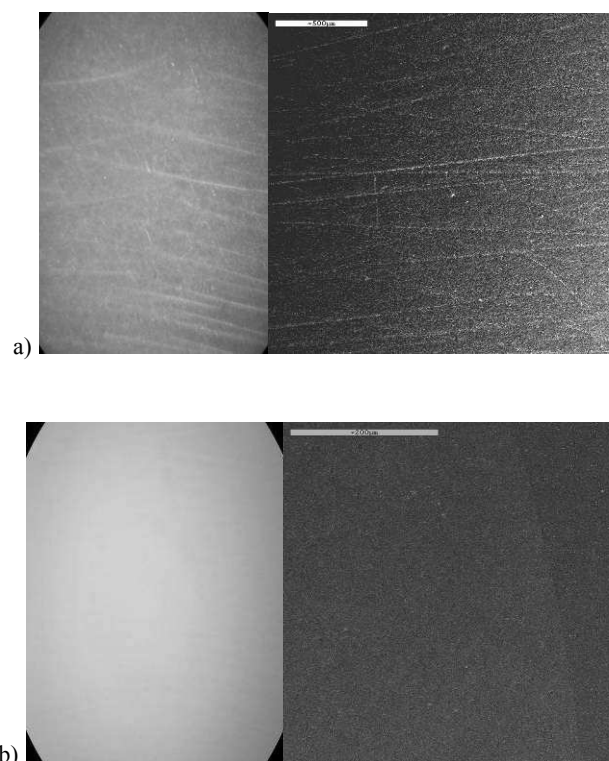


Fig. 2. View of the specimens surface: a) ground, b) electropolished

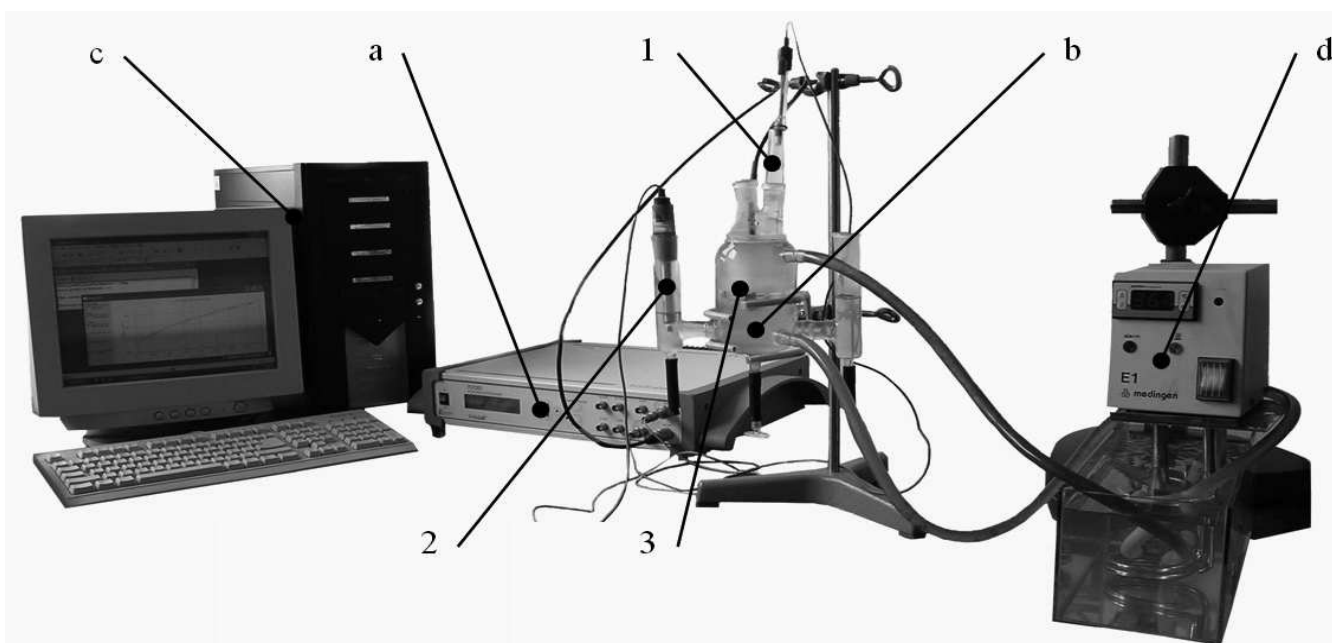


Fig. 3. Diagram of the corrosion resistance set: a) potentiostat VoltaLab® PGP201, b) electrochemical cell: 1 – SCE electrode, 2 – Pt electrode, 3 – sample, c) computer, d) thermostat Medlingen

Table 1.
Artificial urine (A : B= 1:1) [20, 21]

Ingredients A	g/l distilled water	Ingredients B	g/l distilled water
CaCl ₂ ·2H ₂ O	1.765	NaH ₂ PO ₄ ·2H ₂ O	2.660
Na ₂ SO 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		

3. Results

3.1. Pitting corrosion resistance tests results

Table 2 presents results of pitting corrosion resistance of Ni-Ti specimens with differently modified surfaces. Furthermore, pitting corrosion tests were carried out for electropolished and passivated specimens with deposited carbon layer, electropolished and passivated in sterilization process and specimens after 180 days exposition in simulated artificial urine. The value of the corrosion potential for ground specimens tested in the artificial urine was $E_{\text{cor}} = -198 \div -194$ mV. The process of electropolishing and chemical passivation increased the corrosion potential up to $E_{\text{cor}} = -55 \div -48$ mV for the electropolished specimens and $E_{\text{cor}} = +73 \div +143$ mV for the passivated specimens. The corrosion potential for the specimens with carbon layer was equal to $E_{\text{cor}} = -188 \div -102$ mV and for the sterilized specimens was $E_{\text{cor}} = +39 \div$

$+55$ mV. Furthermore, a significant decrease of the corrosion potential was observed for the passivated specimens after “in vitro” tests ($E_{\text{cor}} = -415 \div -373$ mV). The corrosion potential of the analysed specimens was fixed in 15 – 120 minutes – Fig. 4.

The transpassivity potentials were diverse for the differently modified surfaces. For the ground specimens tested in the artificial urine the average value of the transpassivity potential was equal to $E_{\text{tr}} = +1377 \div +1393$ mV. The transpassivity potentials for the electropolished, the passivated specimens and the specimens with the carbon layer were equal to $E_{\text{tr}} = +1346 \div +1401$ mV, $E_{\text{tr}} = +1442 \div +1445$ mV and $E_{\text{tr}} = +1445 \div +1495$ mV respectively. For the sterilized specimens the decrease of the transpassivity potential was observed $E_{\text{tr}} = +1224 \div +1298$ mV. For the “in vitro” tested specimens the transpassivity potential was equal to $E_{\text{tr}} = +1438 \div +1478$ mV. Anodic polarization curves of the specimens with modified surfaces tested in the artificial urine were presented in Fig. 5. 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. Fig. 6 presents surfaces of the Co alloy after electrochemical tests.

Comparative analysis of the anodic current density showed that the electropolishing and the passivation process reduced the density with the reference to the ground specimens for the potentials up to $+0,6$ V – Table 3, Fig. 7. The electropolishing and the passivation process of the Ni-Ti alloy increased the polarization resistance to the value of $R_p = 884 \div 993$ k Ω ·cm² (with reference to the ground samples $R_p = 359 \div 441$ k Ω ·cm²). For the specimens with carbon layer the increase of the anodic current density as well as the decrease of the polarization resistance ($R_p = 98 \div 164$ k Ω ·cm²) with reference to the electropolished and the passivated samples were observed.

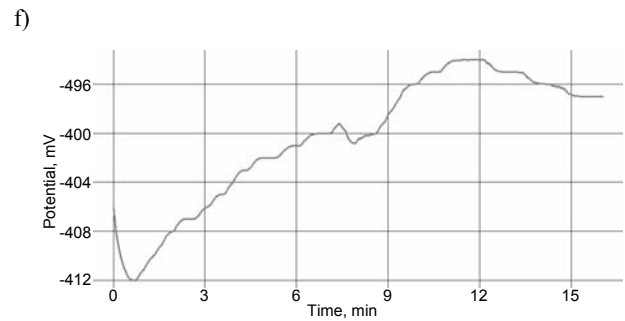
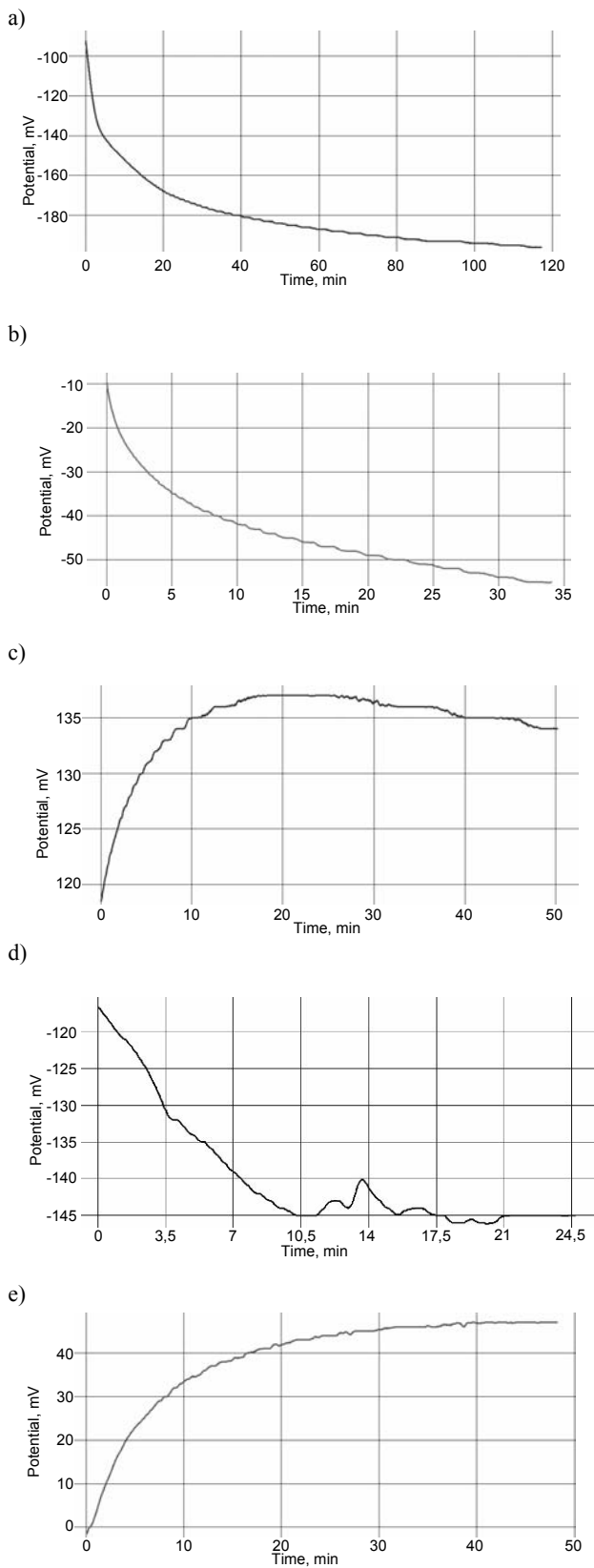


Fig. 4. Corrosion potential changes in time: a) grinded, b) electropolished, c) electropolished and passivated, d) electropolished and passivated with carbon layer, e) electropolished and passivated after sterilization, f) electropolished and passivated after "in vitro" test

For the sterilized samples the decrease of the polarization resistance ($R_p = 884 \div 993 \text{ k}\Omega\cdot\text{cm}^2$) with reference to the passivated samples was observed. For the "in vitro" tested samples the further decrease of the polarization resistance ($R_p = 320 \div 411 \text{ k}\Omega\cdot\text{cm}^2$) with reference to the passivated samples was observed – Table 3.

For all specimens 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 $373 \div 425 \text{ nm/year}$, $28 \div 59 \text{ nm/year}$, $5382 \div 5836 \text{ nm/year}$. For the sterilized and the "in vitro" tested specimens the corrosion rate was equal to $55 \div 66 \text{ nm/year}$ and $1262 \div 1322 \text{ nm/year}$ respectively.

3.2. Crevice corrosion resistance results

Crevice corrosion tests were carried out for the ground, electropolished, passivated and carbon coated specimens. The corrosion potentials for the ground, electropolished, passivated and carbon coated specimens were equal to -174 mV, -99 mV, -99 mV and +20 mV respectively. Anodic current intensity for the $E = +800 \text{ mV}$ potential reached very small values for the electropolished, passivated and carbon coated specimens – Fig. 2b and c. The tests revealed that the ground and the electropolished specimens are not resistant to crevice corrosion. The corrosion damage of these specimens appeared in the potential range +100 do +800 mV – Fig. 8a. The passivated and the carbon coated specimens are resistant to crevice corrosion – Fig. 8 b and c.

4. Conclusions

The results showed positive influence of the proposed method of surface treatment on the corrosion resistance in the simulated artificial urine. Both, electropolishing and deposition of carbon layer (in CVD process) caused the improvement of the main corrosion parameters in relation to the ground samples. Only the sterilization process of the tested biomaterial decreased the transpassivation potentials to levels even lower than obtained for the ground samples. The proposed surface modifications also decreased the anodic current density in the analyzed range of potentials (0 to 400 mV). The decrease of densities was observed for electropolished samples, electropolished and passivated samples before and after the sterilization. The values of anodic

current density for the samples with carbon layer were also lower than for the ground samples. Only in vitro tested samples were characterized by significant increase of anodic current densities in the analyzed potential range.

In general it can be stated that both the electropolishing, the passivation, the deposition of carbon layer and sterilization process improve the biocompatibility of the NiTi alloy intended for implants applied in urology. For implants made of the analyzed biomaterial of electropolished and passivated surface exposed to the artificial urine for a long time, the insignificant deterioration of biocompatibility can be observed (good pitting corrosion resistance is kept).

Microscopic observations of the samples' surfaces revealed pits only on the ground samples. Other samples of diverse surface modification no corrosion pits were observed.

Additional crevice corrosion tests revealed that the NiTi alloy of ground and electropolished surface is not resistant to this type of corrosion. It should be stated that the analyzed biomaterial of the electropolished surface only should not be used in the clinical practice. It is necessary to passivate the alloy. Another surface treatment that can be applied to increase the crevice corrosion resistance is deposition of carbon layer.

In order to fully characterize the corrosion resistance of the NiTi alloy intended for implants applied in urology, another simulated urine solutions should be applied. It seems to be necessary because of the lack of a standardized chemical composition of the simulated urine (there are at least several solutions used for testing urological implants).

Furthermore, a chemical composition examination of the surface layer (generated in the electropolishing and the passivation process) before and after in vitro tests should be carried out. This information would be of great importance in order to fully understand physiochemical properties of the Ni-Ti alloy as a biomaterial applied in urogenital system.

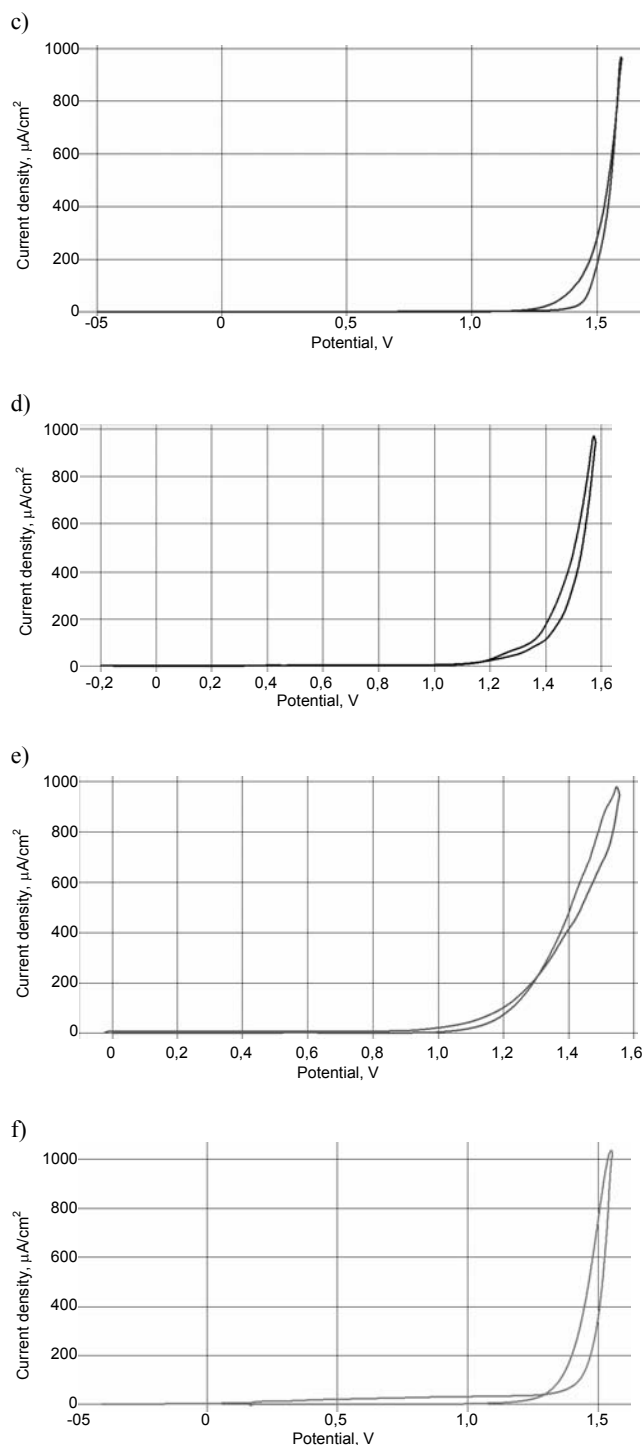
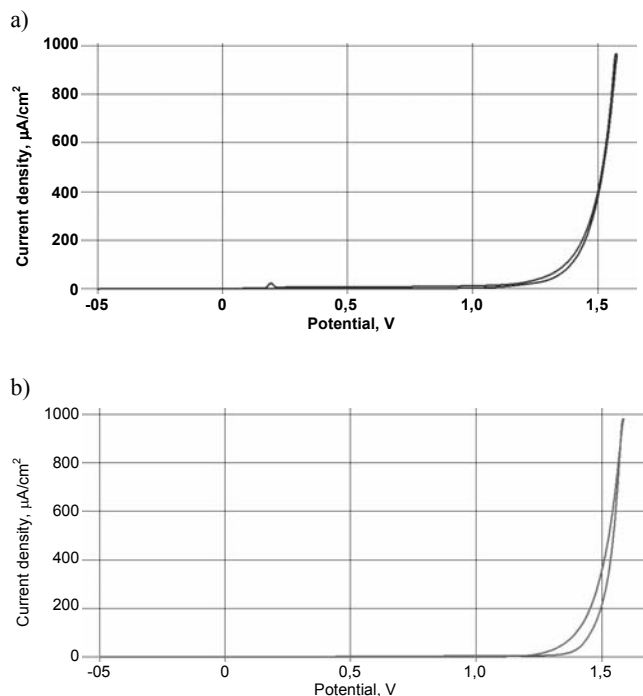


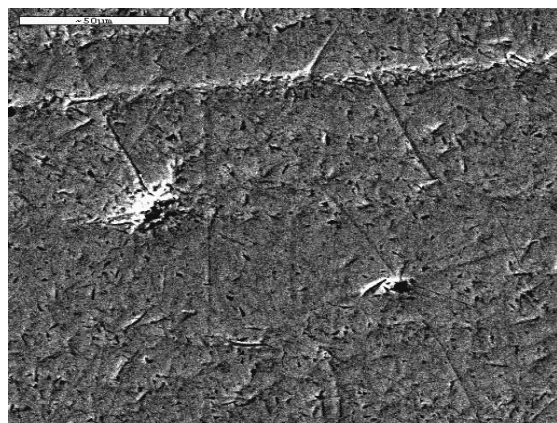
Fig. 5. Example of the anodic polarization curve of Ni-Ti specimens after diverse surface modification: a) ground, b) electropolished, c) electropolished and pasivated, d) electropolished and pasivated with carbon layer, e) electropolished and pasivated after sterilization, f) electropolished and pasivated after "in vitro" test

Table 2.
Pitting corrosion resistance of Ni-Ti alloy

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

Table 3.
Pitting corrosion resistance of Ni-Ti alloy

Surface preparation method	Current density, $\mu\text{A}/\text{cm}^2$			Polarization resistance R_p , $\text{k}\Omega \cdot \text{cm}^2$	Corrosion intensity, nm/rok
	0,2 V	0,4 V	0,6 V		
1	2	3	4	5	6
ground	30,0 ÷ 31,7	7,0 ÷ 10,8	9,0 ÷ 13,1	359 ÷ 411	373 ÷ 425
electropolished	0,4 ÷ 0,5	2,0 ÷ 2,3	3,0 ÷ 3,8	954 ÷ 1128	167 ÷ 199
electropolished and passivated	0,1 ÷ 0,2	0,2 ÷ 0,3	0,9 ÷ 1,0	884 ÷ 993	28 ÷ 59
electropolished and with carbon layer	1,9 ÷ 2,1	2,6 ÷ 2,6	3,0 ÷ 3,4	98 ÷ 164	5382 ÷ 5836
electropolished and passivated after sterilization	0,1 ÷ 0,3	0,8 ÷ 1,7	2,5 ÷ 4,6	884 ÷ 993	55 ÷ 66
electropolished and passivated ofert „in vitro” test	11,7 ÷ 13,5	18,2 ÷ 22,4	23,7 ÷ 24,8	320 ÷ 411	1262 ÷ 1322



Rys. 6. View of the ground specimens surfach after pitting corrosion test

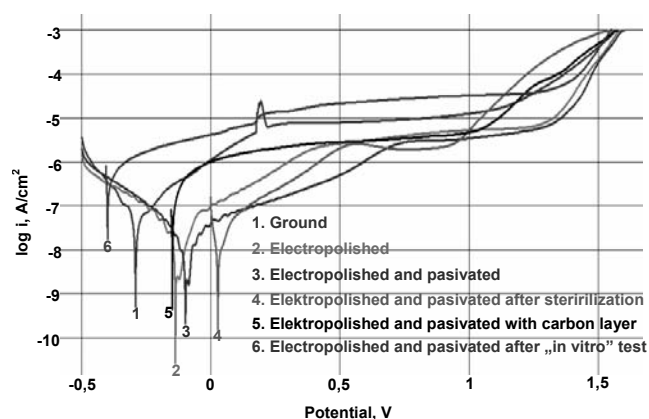


Fig. 7. Anodic polarization curves of Ni-Ti specimens after diverse surface preparation

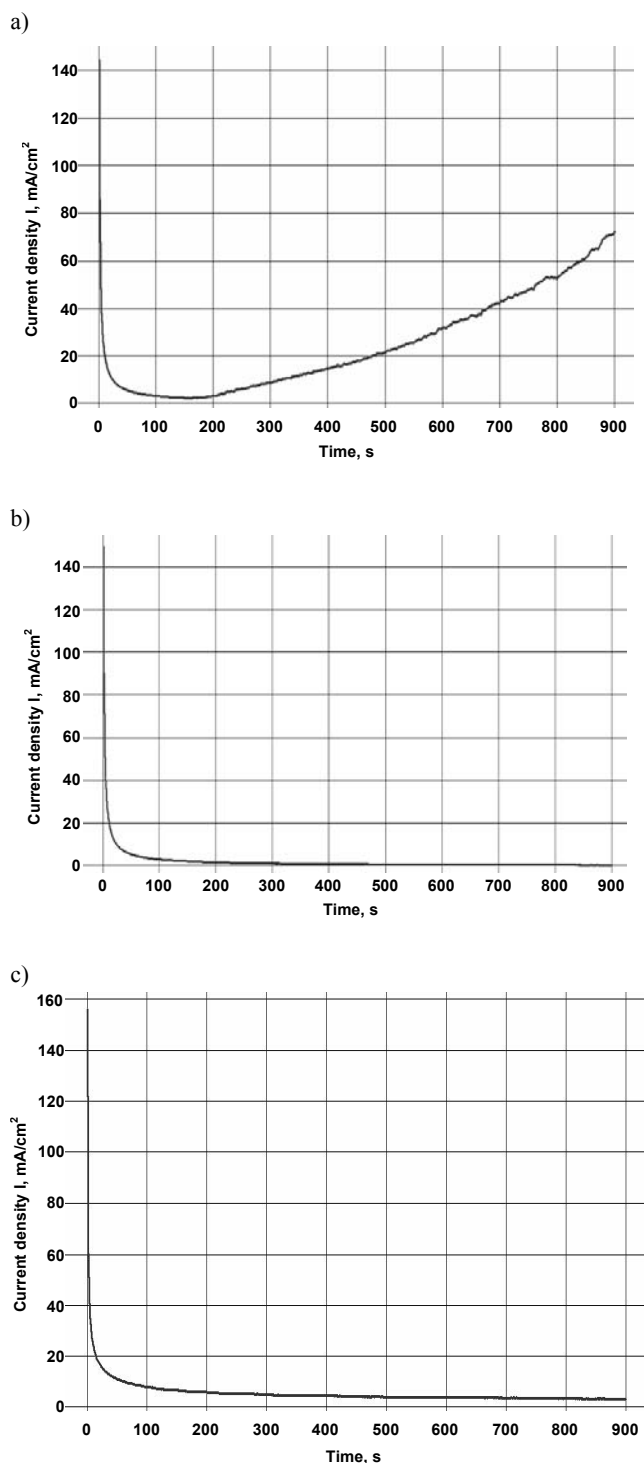


Fig. 8. Change of anodic current in a function of time for Ni-Ti specimens: a) electropolished $E = +100$ mV, b) electropolished and chemically passivated, $E = +800$ mV, c) electropolished and chemically passivated with carbon layer $E = +800$ mV

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