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Crevice corrosion resistance of NiTi alloy after various surface treatments

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ABSTRACT

Purpose: The aim of the work was determination of crevice corrosion resistance of NiTi alloy after various surface treatments.

Design/methodology/approach: The evaluation of the electrochemical behavior of NiTi alloy was realized by recording of anodic polarization curves with the use of the potentiodynamic method in the presence of a crevice former. Tests were carried out in Tyrode's physiological solution.

Findings: Surface condition of metallic biomaterial determines its corrosion resistance. In the course of the work it was observed that only ground samples showed no resistance to crevice corrosion. Suggested surface modifications ensure good crevice corrosion resistance.

Practical implications: On the basis of the obtained results it can be stated that the suggested surface treatment can be applied for medical implants due to increase of the crevice corrosion resistance and in consequence increase of biocompatibility.

Originality/value: The paper presents the influence of various methods of surface treatment on crevice corrosion resistance of the NiTi alloy. The suggested methods can be applied in treatment of the material intended for medical applications especially as reduced and complex shape implants (contact of metallic material with human body fluids in a small and occluded space).

Keywords: Metallic material; Biomaterials; Corrosion; Potentiodynamic tests

MATERIALS

1. Introduction

Metallic materials are important class of implant materials because of the combination of strength and ductility (on the contrary to polymers and ceramics respectively). On the other hand, metallic materials are less corrosion resistant compared with the other two classes of implant materials. Corrosion reduces strength and causes premature failure of implants [1-3] and may also impose harmful effects on the surrounding tissues [3-7]. Stainless steels, titanium alloys and cobalt alloys are commonly used as biomaterials [8-13]. Shape memory alloys (SMA) are relatively new group of metallic biomaterials.

Extraordinary properties of NiTi shape memory alloys are widely used in medical applications (orthodontics, cardiovascular, orthopaedics, urology, etc.) due to their unique shape memory effects, superelasticity and good corrosion resistance [27]. However, several studies reported that NiTi exhibits poor resistance to localized corrosion in chloride-containing environments [14-15].

Furthermore, toxicity and carcinogenesis of Ni ions released from NiTi alloy are a very concerned problem [17-18]. Therefore, it is necessary to modify the surface of NiTi alloys to improve their corrosion resistance and impede the Ni ions release. Thus different surface treatments were proposed to modify the surface of the alloys to improve the corrosion and biocompatibility. These methods include chemical and electrochemical passivation, thermal oxidation, nitriding, laser surface melting, ion-beam treatment, and sol–gel [19-28].

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2. Material and methods

NiTi alloy, intended for implants, was investigated in the study. The NiTi alloy was tested in the parent (austenitic) phase. The chemical composition of the alloy (Ni – 55,5%, Ti – balance) met the requirements of the ASTM 2063 standard. The tests were carried out on samples in the form of a flat bar (length l = 21 mm, width w = 16 mm and thickness equal to 1 mm). In order to evaluate the influence of diverse methods of surface modification on the crevice corrosion resistance of the alloy, the following surface treatments were applied:

- grinding (SiC, #800),
- electropolishing – previously ground samples (#800) were electropolished in the HF-based solution worked out by the author. Current densities were in the range 5 – 50 A/dm^2,
- passivation – the passivation process was carried out in boiling water for 1 hour,
- deposition of carbon layer – the carbon layer was deposited with the use of RF PCVD (Radio Frequency Plasma Chemical Vapour Deposition) method.

The aim of the research was determination of crevice corrosion resistance of NiTi samples of modified surfaces in Tyrode's physiological solution – Table. 1.

Table 1.
Chemical composition of the Tyrode's physiological solution

	Components	Concentration, g/l
Tyrode's solution	NaCl	8.0
	$CaCl_2$	0.2
	KCl	0.22
	$NaHCO_3$	1.0
	NaH_2PO_4	0.05
	$MgCl_2$	0.2

The ASTM F746 standard test method was applied to assess crevice corrosion resistance. According to the standard, stimulation of localized corrosion is marked by one of the following conditions: the polarization current density exceeds 500 μA/cm^2 instantly; the current density does not exceed 500 μA/cm^2 within 20 s, but is increasing in general; these two conditions are not met in the first 20 s, but are met in a period of 15 min.
The saturated calomel electrode (SCE) was applied as the reference electrode and the auxiliary electrode was a platinum foil. The tests were conducted at the temperature of 37^{o}C. The corrosion potential of the sample was continuously monitored for 1 h, starting immediately after immersion in the electrolyte. According to the ASTM standard, damage of the passive film is performed electrochemically by applying a potential of +800 mV versus SCE for durations up to 15 min on a creviced sample. If during 15 min localized corrosion is not stimulated the test is terminated and the material is considered resistant to localized corrosion, otherwise a voltage step back to a preselected potential is conducted. The test consists of alternating steps between stimulation at +800 mV and repassivation to a preselected potential up to a critical potential, for which repassivation does not take place, is attained (the increase of the preselected potential value between the steps is 50 mV).

It should be mentioned that according to the ASTM F746 standard the crevice conditions have to be produced by fitting PTFE tapered collars on cylindrical specimens, in the present study the crevice conditions were achieved by fitting the PTFE collar on the flat sample. Schematic view of the applied collar is presented in Fig. 1.

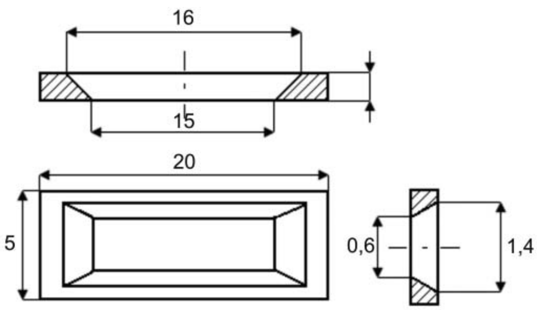

Fig. 1. Schematic view of the applied PTFE collar

3. Results

The electrochemical tests carried out in the Tyrode's physiological solution showed diverse resistance of NiTi alloy to crevice corrosion depending on the applied surface treatment.
Results of the crevice corrosion resistance for the ground, electropolished, passivated and carbon coated samples as well as characteristic values of the corrosion potential E_{corr} for various samples tested in the Tyrode's physiological solution are presented in Table 2. The critical potential E_{cc} is the noblest potential (within a step of 50 mV) that a material can repassivate after the stimulation step.

Table 2.
Crevice corrosion resistance of the NiTi alloy depending on the applied surface treatment

Surface	E_{corr}, mV	E_{cc}, mV	Crevice corrosion resistance
Ground	- 248	+ 450	—
Electropolished	- 193	> + 800	+
Passivated	- 186	> + 800	+
Carbon coated	+ 74	> + 800	+

Typical plots for the current density as a function of time are presented in Figs. 2-5.

The ground samples were characterized by the lowest value of corrosion potential in comparison to the surface treated samples. The average value of the corrosion potential was equal to E_{corr} = - 248 mV. For the ground samples it was also observed that during the first stimulation step, the current densities exceeded the critical value of 500 μA/cm^2. None of the tested ground samples reached the value of + 800 mV. The critical potential value was equal to E_{cc} + 450 mV.

The average value of the corrosion potential for the electropolished, the passivated and the carbon coated samples was equal to E_{corr} = - 193 mV, - 186 mV and + 74 mV respectively.

For all the samples the critical potential E_{cc} exceeded the value of + 800 mV and no increase of anodic current density in the period of 900 seconds was observed. Microscopic observations revealed no corrosion pits on the analyzed surfaces.

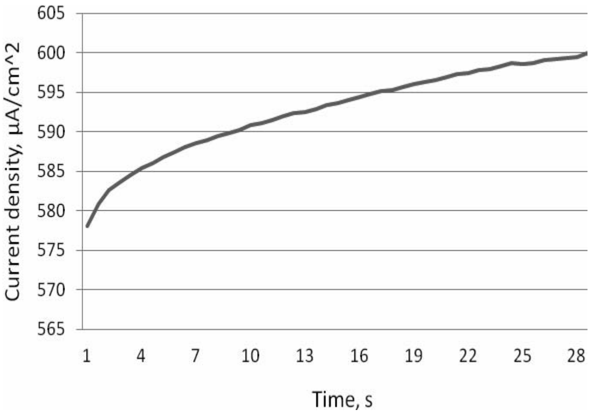

Fig. 2. Typical plot of current density as a function of time for the ground samples polarized at + 800 mV

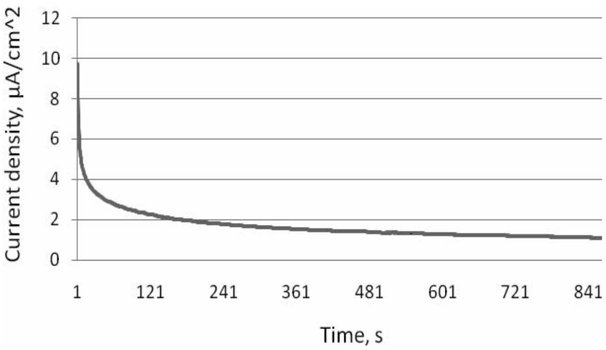

Fig. 3. Typical plot of current density as a function of time for the electropolished samples polarized at + 800 mV

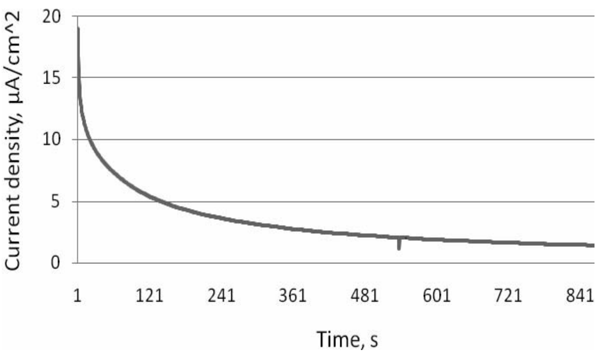

Fig. 4. Typical plot of current density as a function of time for the passivated samples polarized at + 800 mV

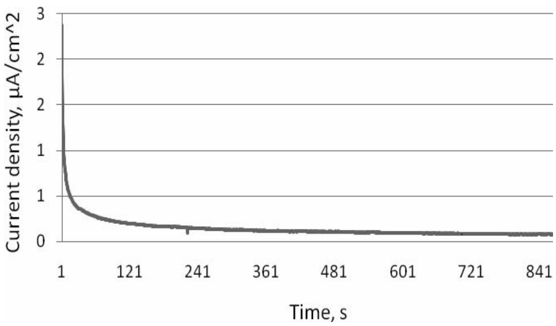

Fig. 5. Typical plot of current density as a function of time for the carbon coated samples polarized at + 800 mV

4. Conclusions

The electrochemical tests carried out in the Tyrode's physiological solution showed diverse resistance of NiTi alloy to crevice corrosion depending on the applied surface treatment. Grinding does not assure resistance to crevice corrosion. Only electrolytical polishing, passivation and deposition of carbon layer assures resistance of NiTi alloy to crevice corrosion in Tyrode's physiological solution. For all these samples no signs of crevice corrosion were observed on their surfaces.

Suggested surface modifications ensure resistance of NiTi alloy to crevice corrosion.

Acknowledgements

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