

Investigation of Functional Properties of Corrosion-Resistant Coatings on TiNi Implants

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Abstract

Nitinol alloy is a widely used material for medical implants, but it can cause some dangerous side effects when nickel is released into the patient body. In order to prevent this, the protective coatings prepared by the method of oxidation in electrolytic plasma were investigated. Coatings were exposed to an alternative anodic-cathodic mode with a predominance of the anodic one with durations from 15 to 60 minutes. The quality of coatings prepared in different modes was tested in different electrolytes by analyzing of their mechanical properties, as well as by detecting nickel ions in physiological saline (0.9 mass % NaCl in water) after 32 days during 37 °C, which imitated the environment inside the human body. The modes of preparing dense protective coatings with high adhesion, ensuring the absence of nickel ion emission were determined. The microhardness of coatings deposited under optimal conditions is HV 240–260, their thickness is 18–20 μm.

Keywords

Coating; electrolytic plasma oxidation; implants; Nitinol; TiNi.

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Introduction

To perform its functions, any medical implant must have the necessary mechanical properties: high strength (static and fatigue) and stiffness. As a rule, the laparoscopic process of delivering an implant to the place of its fixation requires quite opposite properties; in particular, the material must withstand large reversible (elastic) deformations. But this is not a complete list of requirements for the material. An implant inside an organism is exposed to an aggressive environment; therefore, firstly, the material must resist both general corrosion and stress corrosion cracking throughout its entire service life (which is literally decades); and, secondly, it must not emit harmful and dangerous substances into the surrounding implant environment. From the point of view of corrosion resistance and biocompatibility, pure titanium is an ideal material for implants, but it cannot provide the necessary combination of strength and elasticity. Titanium alloying can significantly increase its strength characteristics, but at the same time it increases the elastic limit, which complicates the implant delivery.

Modern implantology uses a wide range of titanium-based alloys for various purposes. One of them, Nitinol (near-equiatomic alloy of Ti and Ni), is characterized by a unique combination of the required mechanical properties, including high strength and high reversible deformation, as well as low effective elastic modulus. This behavior of the alloy is due to reversible martensitic transformation, which results in the so-called “pseudo elasticity”. Pseudo elastic reversible transformation in the Nitinol after special thermal and mechanical pretreatment [1, 2] can give up to 7 % of reversible deformation, and thus it provides delivering of the implant to any necessary place inside the human body.

Titanium is a very chemically active element; therefore, its surface and the surface of its alloys are always covered with an oxide film. On pure titanium this TiO₂ film is protective, i.e., it is dense and chemically resistant in organic environments. The properties of the film, covering titanium-based alloys are determined by the alloying elements. Films, which are formed during the interaction of the Nitinol

and natural environments, are usually protective for the alloy. However, there is one significant problem, which solution is the purpose of the present work.

Interaction of the intermetallic compound TiNi with organic liquids inside the body results in the formation of the surface film, which does not completely prevent the infiltration of Ni ions from the alloy to the environment. The high concentration of nickel in the area of implant's site can cause allergic reactions [3], local toxicity, DNA damage, carcinogenesis, and provoke the formation of oxygen radicals and inflammation [4 – 8].

There are many techniques to cover metallic materials by protective films [9, 10] and to evaluate its mechanical and adhesive properties (standardized according to GOST 9.302–88 [11] and innovative, for example, [12]). One of the methods to cover metallic materials is electrolytic plasma oxidation. This method is effective, ecological and relatively easily controlled one [13]. Most dense protective layers can be formed during alternative anodic/cathodic mode of electrolytic plasma processing with a predominance of anodic component [14].

Materials and methods

The present study focused on the procedure of applying of the anticorrosion layer on the medical implants made of TiNi alloy (50.4 at. % Ni and 49.6 at. % Ti) produced by Matex Ltd. The anti-corrosion coating was deposited by the plasma electrolytic oxidation (PEO) method with Microplasma 205 equipment. The PEO was realized in an anode-cathode system primarily in the anodic mode with the varying bath-sample polarity. The varying parameters were the anode potential, the cathode potential and the oxidation time. Several electrolytes of different chemical composition (electrolyte composition and procedure parameters are included in Table 1) were used in the process and that made it possible to control the chemical composition of the surface layer [15] formed by oxidation.

Corrosion resistance was tested with the samples placed for 32 days in the corrosive medium (physiological saline, i.e. aqueous solution with 0.9 mass. % of NaCl, test temperature 37 °C) simulating aseptic inflammation caused by the implant. The following coating characteristics were measured: coating thickness (using optical microscope MKM UNION 7384, $\times 500$), micro hardness HV (using Struers Duramin-2 by Vickers method at 0.4903 H load and 10-second exposure), and bending strength of coating-to-base metal bond.

The quality of the surface layer was evaluated by visual examination of surface defects and surface condition after the bending test (bend-to-break test) – the fracture was checked for coating separation. Separation and crumbling of the surface layer was regarded as a unsatisfactory quality of the coating.

The through-coating porosity (presence of Ni ions in the milieu) was evaluated based on the results of 12h test during which we determined a color of the complex solution produced from 0.9 mass. % NaCl aqueous solution after corrosion tests, 1 mass. % dimetilglyoxime ($C_4H_8N_2O_2$) ethanol solution, and 10 mass. % NH_3 aqueous solution with equal volumes. The presence of Ni ions was determined by the change of solution color.

Discussion

The study of the PEO coating of the samples demonstrated that the quality of the surface oxide layer depends on electrolyte composition, oxidation electrical parameters (mode), and oxidation time (Table 2). The good quality surface was produced in electrolyte 1, where the surface layer composed mainly of aluminium phosphate and aluminium oxides was formed, was observed at anode voltage 220 V (mode 1.1, oxidation time 60 minutes) and at anode voltage 210 V (mode 1.2, oxidation time 15-60 minutes).

The good quality surface produced in electrolyte 2, which forms the surface layer composed mainly of titanium oxide [15], was observed at cathode voltage 70V and oxidation time in the range of 15–60 minutes. The results are given in Table 2. No proper quality surface was observed in electrolyte 3 forming the surface layer composed mainly of titanium oxide and aluminium oxide [15] with etching effect noticed on several samples. Testing the strength of coating-to-base metal bonding resulted in coating separation on the samples produced by PEO modes 1.1 (oxidation time 60 minutes) and 1.2 (oxidation time 15–60 minutes) as well as mode 2 (oxidation time 15 minutes).

The thickness values of coatings formed by modes producing good quality surface are included in Table 3. The increase in the PEO time resulted in a thicker surface layer; treatment with electrolyte containing water solution of $NaAlO_2$, liquid glass $Na_2O \cdot 2.9 \cdot SiO_2 \cdot 9H_2O$, $(NaPO_3)_6$, $C_4H_8N_2O_2$ resulted in a thicker surface layer compared with the one produced by electrolyte containing water solution of NaOH and $(NaPO_3)_6$. The HV surface layer behaved similarly – it increased with the increase in the surface layer thickness (microhardness of non-oxidized sample was (400 ± 31) HV) that obviously indicated that the coating porosity decreased with the increase in the oxidation time (Table 3).

Table 1

Electrolyte composition and PEO parameters

Mode	Electrolyte type*	Anode potential, V	Cathode potential, V
1.1	Aqueous solution containing NaAlO ₂ , liquid silica glass Na ₂ O·2.9·SiO ₂ ·9H ₂ O, (NaPO ₃) ₆ , C ₄ H ₈ N ₂ O ₂	220	80
1.2		210	100
1.3		140	80
2.0	Aqueous solution containing NaOH, (NaPO ₃) ₆	210	70
3.0	Aqueous solution containing NaAlO ₂ , NH ₄ F	210	70

Table 2

Quality evaluation of PEO coating on TiNi alloy samples

Mode	Oxidation time (minutes)							
	15		30		45		60	
	Coating quality	Adhesive strength	Coating quality	Adhesive strength	Coating quality	Adhesive strength	Coating quality	Adhesive strength
1.1	n/s		n/s		n/s		sat.	
1.2	sat.	n/s	sat.	n/s	sat.	n/s	sat.	n/s
1.3	n/s		n/s		n/s		n/s	
2.0	sat.	n/s	sat.	sat.	sat.	sat.	sat.	sat.
3.0	n/s		n/s		n/s		n/s	

Note: n/s – not satisfactory; sat. – satisfactory.

Table 3

Coating thickness* and microhardness of surface layer in TN1 alloy samples after PEO

Mode	Oxidation time (minutes)							
	15		30		45		60	
	Coating thickness, μm	Micro-hardness, HV	Coating thickness, μm	Micro-hardness, HV	Coating thickness, μm	Micro-hardness, HV	Coating thickness, μm	Micro-hardness, HV
1.2			–				24.5	268 ± 10
2.0	6.0	222 ± 14	11.0	236 ± 13	18.5	245 ± 12	20.0	256 ± 17

*Minimum values of all measured samples for each mode.

Table 4

Evaluation of the surface layer quality and bonding strength in TN1 alloy samples after corrosion tests

Mode	Oxidation time (minutes)							
	15		30		45		60	
	Coating quality	Adhesive strength	Coating quality	Adhesive strength	Coating quality	Adhesive strength	Coating quality	Adhesive strength
1.2			–				n/s	–
2.0	n/s	–	n/s	n/s	sat.	sat.	sat.	sat.

Note: n/s – coating quality is not satisfactory (separation and/or through-coating porosity); sat. – satisfactory coating quality (no separation, no through-coating porosity).

The resistance to through-coating porosity was tested on the samples oxidized under modes 1.2 (oxidation time 60 minutes) and 2 (oxidation time 15–60 minutes). The colour of solutions containing samples with the coating produced under modes 1.2 (oxidation time 60 minutes) and mode 2 (oxidation time 15 and 30 minutes) turned pale pink. Solutions containing samples with the coating produced under modes 2 (oxidation time 45 and 60 minutes) did not change their color, which testifies to the absence of Ni ions in the solution.

Corrosion resistance was tested for all above mentioned modes. Testing established that the surface layer on samples pretreated under modes 1.1 – 1.3 and 3 with oxidation times 15–60 minutes separated completely; the surface layer on samples pretreated under mode 2 with PEO time 15 minutes separated only partially while the coating obtained in mode 2 with PEO time 30 minutes separated just slightly. The samples treated under mode 2 with PEO time 45 and 60 minutes have shown no separation of the coating (Table 4).

After corrosion tests, the samples treated under PEO mode 2 with the oxidation time 30–60 minutes were subjected to bending test. Coating separation was revealed on the samples that were given 30 minutes of PEO treatment.

Thus, the PEO mode 2 with the oxidation time from 45 to 60 minutes ensuring the absence of Ni ions was an optimal procedure for treatment of medical implants made of TN1 Ti-Ni alloy.

Conclusions

The effect of different electrolyte compositions and electrolytic plasma oxidation modes on corrosive properties of Ti-Ni alloy implants was observed.

It was confirmed that the corrosion resistance of medical Ti-Ni implants with oxide coating was the function of coating thickness and composition with the optimal coating composition was composed primarily of titanium oxide.

The mode for a proper quality surface layer preventing the release of Ni ions into the working environment of Ti-Ni alloy implants was determined.

Acknowledgments

The author is deeply grateful to Professor A.G. Rakoch (NUST "MISiS") for help and advice.

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