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Influence of Surface Modification of Nitinol with Silicon Using Plasma-Immersion Ion Implantation on the Alloy Corrosion Resistance in Artificial Physiological Solutions

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Abstract. Cyclic voltammetry and potentiostatic polarization have been applied to study electrochemical behavior and to determine corrosion resistance of nitinol, which surface was modified with silicon using plasma-immersion ion implantation, in 0.9% NaCl solution and in artificial blood plasma. It was found out that continuous, and also homogeneous in composition, thin Si-containing layers are resistant to corrosion damage at high positive potentials in artificial physiological solutions due to formation of stable passive films. Breakdown potential E_b of Si-modified NiTi depends on the character of silicon and Ni distribution at the alloy surface, E_b values amounted to 0.9–1.5 V (Ag/AgCl/KCl sat.) for the alloy samples with continuous Si-containing surface layers and with decreased Ni surface concentration.

INTRODUCTION

Nitinol and alloys on its basis are widely used in medicine as materials for implants. Despite a considerable part of toxic nickel in NiTi (about 50 at %) medical applications of nitinol are caused by its high strength and plastic properties, shape memory effects, pseudo-elasticity, damping, good biocompatibility [1]. To decrease toxic, cancerogenic and allergenic influence of nickel on living tissues [2] the surface of the alloy products are treated using mechanical, chemical, electrochemical, thermal, etc. methods [3]. Mechanical treatment (sandblasting, mechanical polishing, etc.) does not permit to achieve satisfactory corrosion resistance in physiological solutions. Chemical and electrochemical methods of NiTi treatment (chemical etching in acid mixtures, thermal oxidation, autoclaving in boiling water, electropolishing) lead to higher values of breakdown potential E_b up to 0.8–1.3 V which means rather high corrosion stability of the alloy. At the same time, such passivating layers often have the lowered stability and don't prevent corrosion destruction of the material [3, 4].

The ion-beam and plasma-immersion methods of NiTi surface implantation in combination with chemical etching and electropolishing are prospective ways to prevent nitinol corrosion in physiological solutions are. Non-metal ion-beam implantation (B, C, N, O) leads to the formation of thin (30–70 nm) surface layers with high hardness and high corrosion resistance ($E_b = 1.0$ – 1.2 V) [5, 6]. Si, Ti, Zr, Hf or Mo ion beams (fluence up to 2×10^{17} ion/cm²) improve corrosion resistance, and also significantly improve alloy biocompatibility [7, 8]. For example [5], implantation of nitrogen leads to formation of thin nitride TiN layer which significantly increases microhardness in ~ 2 times, improves corrosion resistance in artificial blood plasma ($E_b = 1.1$ V) and osteoblasts proliferation. Plasma-immersion implantation of NiTi with oxygen leads to significant reduction of Ni content (1.6–7 at %) at the surface layer to the depth of 10 nm. In contrast, treatment with helium under similar conditions [5] leads to the formation of a porous surface layer (He does not form solid solutions or compounds with metals), which reduces the mechanical strength and degrades alloy hemocompatibility.

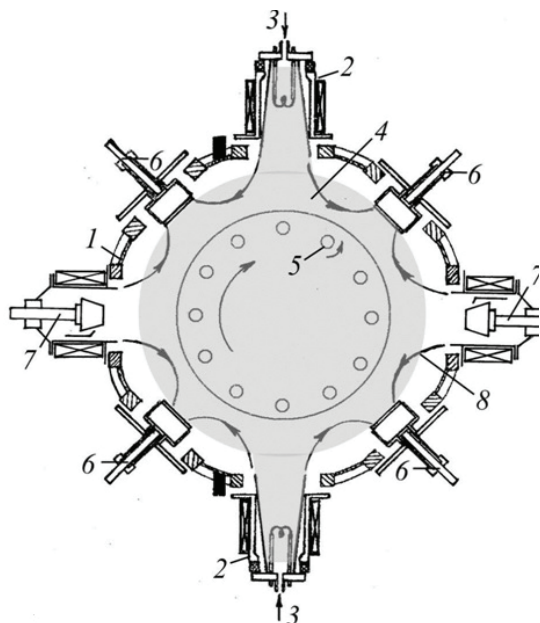


FIGURE 1. Structure scheme of the plasma-immersion ion implantation device: 1—vacuum chamber; 2—cathode parts of the gas-discharge plasma generators; 3—gas inlet; 4—plasma; 5—samples; 6—magnetron sputtering system; 7—arc evaporator; 8—magnetic field lines

TABLE 1. NiTi specimen designation and conditions of the alloy surface treatment

| Specimen | Conditions of treatment |
|----------|--|
| 00 | Mechanical polishing |
| 0 | Electrolytic polishing |
| 17 | Electropolishing and Ar-plasma exposure |
| 18 | Electropolishing and Si-plasma-immersion implantation: Visible superficial Si-layer |
| 20 | Electropolishing and Si-plasma-immersion implantation: Homogeneous Si-containing superficial layer |
| 21 | Electropolishing and Si-plasma-immersion implantation: Inhomogeneous (discontinuous) Si-containing superficial layer |

It should be pointed out that corrosion resistance of NiTi with the implanted surface layers have not been adequately studied. In this regard, the aim of the present work was to study the corrosion parameters of nitinol modified with silicon in artificial physiological solutions.

MATERIALS AND INVESTIGATION PROCEDURE

As NiTi samples (industrial alloy $\text{Ni}_{50.9}\text{Ti}_{49.1}$ of technical purity) were used plates $50 \times 10 \times 1 \text{ mm}^3$. Before plasma-immersion ion implantation (PIII) the surface of NiTi was mechanically polished using sandpaper with decreasing grain size of abrasive material, chemically etched in the acid mixture HNO_3 (65 wt %) : HF (50 wt %) = 3 : 1 (v.u.), and then electrolytically polished in the acid mixture CH_3COOH (97%) : HClO_4 (70%) = 3 : 1 (v.u.) at $U = 30 \text{ V}$. The treated NiTi samples were fixed in a special holder (the framework) and placed on the desktop of vacuum-plasma unit SPRUT, designed and manufactured at Tomsk State University. The scheme of the PIII-setup is presented in Fig. 1.

During the plasma-immersion procedure the samples were rotated at a speed of 2 rpm, the holders with samples were also rotated around its own axis. To treat the samples the unbalanced magnetrons were used having pure Si cathodes, and one plasma torch with a thermionic cathode for generating a discharge plasma in argon of high purity (99.99%). The implantation regimes are listed in Table 1. There was applied DC or pulsed negative bias voltage with frequency up to 50 kHz and with a step increase in amplitude from 50 to 1000 V. Cleaning of the surface of the alloy samples by bombardment with argon ions caused sputtering of the surface layers.

Morphology, composition and structure of the obtained NiTi samples were studied by means of profilometry (New View 5000), Auger spectroscopy (Shkhuna-2), optical microscopy (Axiovert 200 MAT), scanning and transmission electron microscopy (Philips SEM-150 with EDS analyzer, EM-125 K), X-ray diffraction (Shimadzu XRD 6000).

Electrochemical behavior of the alloy samples was studied using pulse potentiostat/galvanostat PI-50-1.1 in solutions under natural aeration or deaerated by bubbling nitrogen of high purity. Measurements were performed in a thermostated three-electrode cell with separated electrode space. The reference electrode was a saturated silver

chloride electrode (Ag/AgCl/KCl sat.), graphite served as auxiliary electrode with surface area of $\sim 20 \text{ cm}^2$. The surface of the NiTi samples was pre-treated with acetone, ethyl alcohol, and then washed with distilled water. The electrolytes were physiological solution 0.9% NaCl, and artificial blood plasma (NaCl—6.8; NaHCO_3 —2.2; NaH_2PO_4 —0.026; Na_2HPO_4 —0.126; NaH_2PO_4 —0.026; KCl—0.4; CaCl_2 —0.2; MgSO_4 —0.1 g/l) [9]. All the solutions were prepared using reagents of analytical grade without additional purification, and distilled water. Parameters of electrode processes: stationary (corrosion) potential E_{cor} , breakdown (pitting) potential E_b , potential of repassivation E_{re} , corrosion current i_{cor} were determined according to standard methods [9].

RESULTS AND DISCUSSION

According to the profilometry results the surface topography of mechanically polished NiTi specimens (sample 00, Table 1) depends on the mechanical loading intensity during polishing. The roughness parameter may vary in a wide range. The surface morphology of electrolytically polished (sample 0, Table 1) specimens has a quasi-periodic distribution of convex and concave regions with an average spacing of 5–10 μm . The elemental composition of the surface layer of mechanically polished NiTi is characterized by the ratio of major alloy components Ti : Ni close to equiatomic. For freshly polished samples NiTi oxygen content decreases from 50 to 10 at % in a relatively narrow range of the oxidized layer thickness from 8 to 10 nm. Chemical etching and electrolytic polishing lead to change in the element ratio Ti:Ni: concentration of Ti increases from the surface to 80–100 nm depth because of selective removal of nickel. The main component of the surface oxide film $\sim 20 \text{ nm}$ thick is Ti oxide which composition is close to TiO_2 .

Exposure of the electropolished NiTi samples to argon plasma (specimen 17, Table 1) leads to the removal of the surface layer $\sim 7 \text{ nm}$ formed during electrolytic polishing (Fig. 2). Plasma-immersion treatment of nitinol with silicon ions (regime 18, Table 1) leads to the formation of coatings consisted of almost pure silicon with thickness up to 300 nm. Between the coating and the base of the material there is transition layer with thickness about 50 nm, in which concentration of Si decreases and concentrations of Ni and Ti increase (Fig. 2). The main material TiNi, underlying the transition layer, consists of two phases—B2- and R-phase, about 1 μm thick.

During the implantation of Si ions under the regime 20 (Table 1) the continuous Si-containing superficial layer is formed, distribution of elements in the layer depends on the thickness. Microstructure and phase composition of the surface layer is similar to sample 18. Surface layer of sample 21 of 80 nm thick has non-uniform distribution of Si by depth and surface.

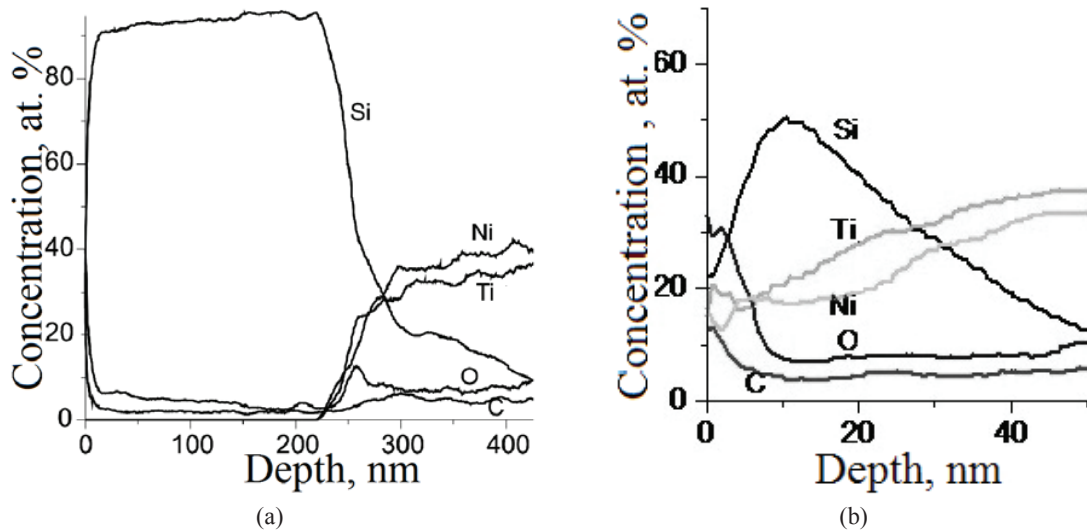


FIGURE 2. Concentration profiles of the elements at the superficial layers of NiTi samples, treated in the plasma-immersion implantation setup, according to Auger spectrometry: (a) Si-plasma, formation of continuous silicon coating (sample 18); (b) Si-plasma, formation of silicon-containing superficial layer (sample 20)

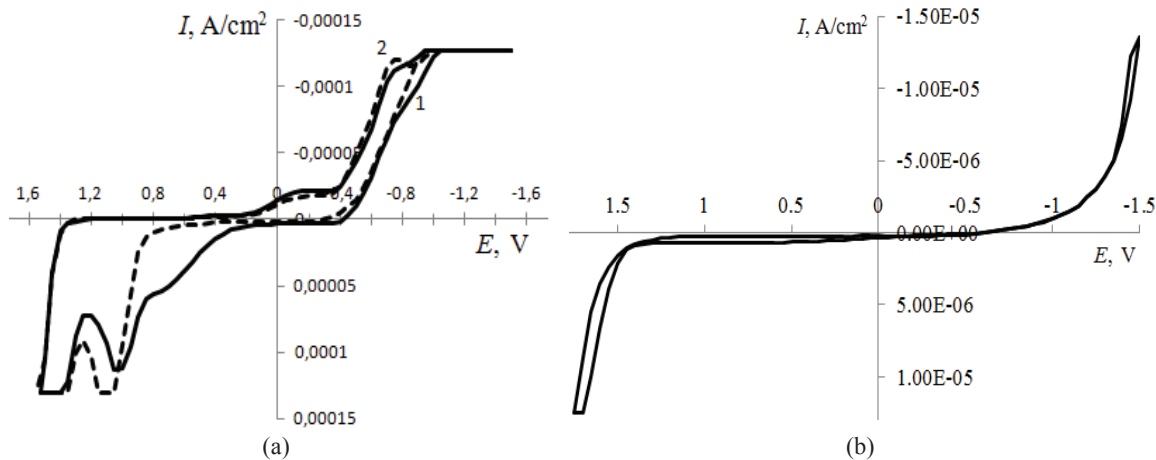


FIGURE 3. Cyclic voltammograms of NiTi sample 17 (a) and 18 (b) in artificial blood plasma (air atmosphere, $E_{in} = -1.6$ V, $w = 10$ mV/s, 1, 2—sequence curves recorded without renewing the sample surface)

Influence of element composition of NiTi surface layers, treated under different conditions of the plasma-immersion implantation, on the alloy electrochemical behavior and on its corrosion resistance is studied in the artificial biology solutions using potentiostatic and potentiodynamic polarization. According to cyclic voltammetry (CVA) TiNi sample 17, which surface after preliminary chemical etching and electropolishing was exposed to Ar-plasma, reveals poor corrosion resistance in Cl^- -containing solutions unlike samples 18 and 20, which surface contains silicon. Potentiodynamic voltammograms are presented in Fig. 3.

Low corrosion resistance of sample 17 is caused by removing the surface oxide layer during preliminary treatment in Ar-plasma. Interval of potentials of the passive state of the sample is quite narrow $-0.4 \div 0.2$ V. Further increase of potentials leads to intensive anodic oxidation at $E \geq 0.2$ V (Fig. 4). At $E = 1.0$ V there occurs selective anodic oxidation of nickel in the surface layer of the alloy. Maximum of cathodic current on voltammograms at $E = -0.8$ V corresponds to reduction of oxidized nickel species (oxide-hydroxide films) formed during anodic oxidation. The obtained electrochemical data are clearly coincides with results of Auger spectrometry: superficial oxide layer of sample 17 is too thin to be a resistant surface passive film to prevent breakdown at high positive potentials.

Cyclic voltammograms of NiTi sample 18, which surface was exposed to Si-plasma resulted in depositing the continuous silicon coating of 300 nm thick, reveal the best corrosion resistance as compared with the other samples (Fig. 3). In contrast to CVA of sample 17, the passive state of the alloy in wide potential range $-0.5 \div 1.5$ V remained after repeated cyclic scanning of potentials without renewing the sample surface. At high positive potentials $E > 1.5$ V (Fig. 3) there occurs oxidation of the medium species (water, chloride-anions). Backward scan of potentials in the negative direction does not reveal any special reduction processes unlike sample 17, which evidences the absence of Ni at the surface layer contacting with solution. NiTi sample 20, which surface consists of silicon-containing layer of 80 nm thick with maximum Si-concentration 50 at % at 5–6 nm depth, behaved like sample 18; as for sample 21 with discontinuous (inhomogeneous) Si-containing layer, redox processes are similar to those of sample 17.

In Fig. 4 the potentiostatic curves are shown; it follows from the graph, that the main corrosion parameters – corrosion and breakdown potentials—definitely depend on the method of the alloy surface treatment. Sample 00 is characterized by the lowest pitting potential (≈ 0.0 V) and by the value $E_{cor} = -0.43$ V (Fig. 4). Decrease of Ni concentration at the alloy surface, and formation of continuous passive layer after PIII lead to considerable shift of the potentials to positive direction (samples 17 and 20). Discontinuous superficial Si-containing layer (sample 21) is less stable in the solution medium.

Influence of the method of the alloy surface treatment on resistance to Ni selective oxidation, and its ions emission to solutions were studied using potentiostatic polarization of the alloy samples at breakdown potential E_b , and EDX-analysis (Table 2). It follows from the obtained data that samples with Si-modified surface are much more stable in Cl^- -containing medium at positive potentials. Implantation with Si allows to raise E_b and to minimize emission of Ni from the alloy surface to environment.

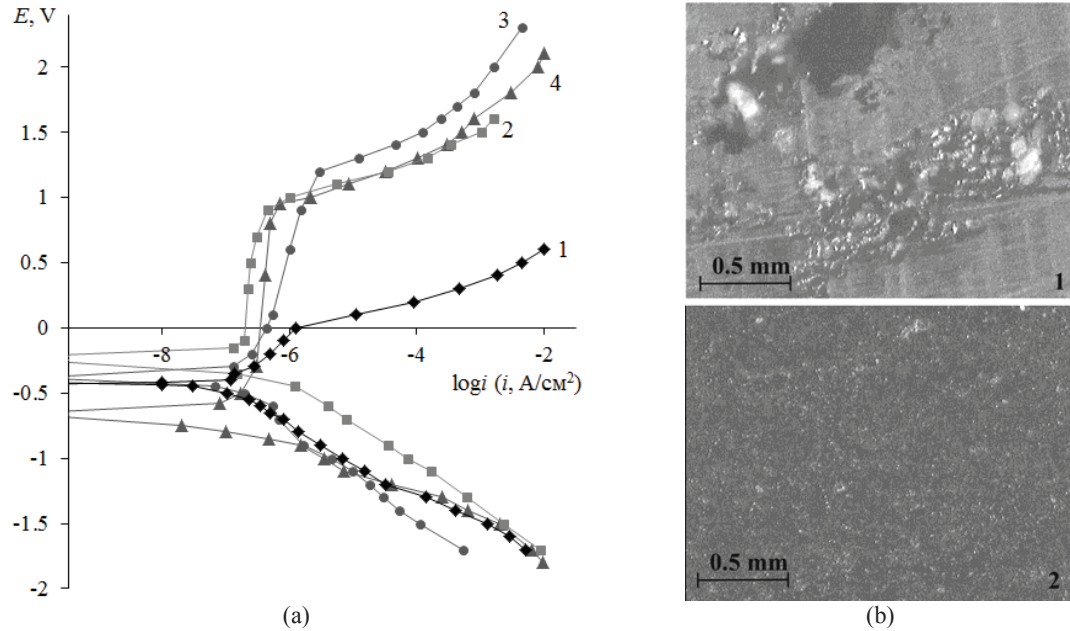


FIGURE 4. Potentiostatic polarization curves of NiTi samples (a) with treated surfaces (artificial blood plasma, N_2 atmosphere, $t = 37^\circ C$): 00 (1); 17 (2); 20 and 21 (3, 4), respectively; (b) micrographs of NiTi samples surface after two sequential potential scans in the interval $-1.5 \div 2.0$ V in artificial blood plasma: 00 (1); 20 (2)

Morphology of NiTi samples surface after polarization tests in solutions was studied using optical and electron microscopy. Optical micrographs are presented in Fig. 4. Analysis of the micrographs has shown that the method of surface treatment influences the character of corrosion damage of the alloy surface layer in artificial physiological solutions. At the surface of mechanically polished NiTi sample after sequential potential scans the protective passivation layer does not form; the corrosion damage of the alloy surface accompanies with significant Ni emission from the surface layer to solutions. Formation of thin silicon-containing layers under PIII conditions caused a substantial increase in corrosion resistance of the alloy (Fig. 4). The obtained microscopy data are in good agreement with the results of electrochemical measurements.

CONCLUSION

Plasma-immersion ion implantation of NiTi surface with silicon allows to form thin Si-containing surface layers up to 80 nm thick with maximum Si concentration up to 50 at % at depth of 5–6 nm, and also thin silicon coating up to 300 nm thick.

Nitinol, which surface was modified with silicon under conditions of the plasma-immersion ion implantation, is characterized by increased corrosion resistance in artificial physiological solutions, as compared with mechanically polished alloy samples, which is consisted in increase of potentials of intensive anodic oxidation up to 0.9–1.5 V (vs. Ag/AgCl/KCl sat.).

TABLE 2. Corrosion parameters and composition of the surface of NiTi samples (artificial blood plasma, $t = 37^\circ C$, N_2 atmosphere)

| Specimen | Surface treatment | Potential, V | | Element concentration at the surface layer, at % | | | | | | | |
|----------|-----------------------|--------------|-------|--|----|----|------------------------------------|----|----|----|----|
| | | | | Initial state | | | After exposure at E_b for 30 min | | | | |
| | | E_{cor} | E_b | Ti | Ni | O | Si | Ti | Ni | O | Si |
| NiTi | Mechanical polishing | -0.43 | 0.0 | 38 | 39 | 23 | – | 23 | 8 | 69 | – |
| NiTi-Si | Ion-beam implantation | -0.35 | 0.9 | 39 | 41 | 19 | 1 | 39 | 41 | 18 | 2 |

Long-term exposure to anodic polarization at high positive potentials in Cl⁻-containing solutions did not cause pitting of the modified alloy surface; concentration of Ni in the alloy surface layer under polarization conditions practically was not changed because of the protective Si-containing layers.

The corrosion pattern for the Si-modified nitinol depends on the character of Si distribution at by the alloy surface and by depth: continuous, and also homogeneous in composition, thin Si-containing layers are resistant to corrosion damage due to formation of stable passive films in Cl⁻-containing media.

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