Corrosive researches of nonnickel shape memory alloy

M A Sevostyanov¹, M Losertova², E O Nasakina¹, O G Kuznetsova¹, A M Levin¹, A A Kirsankin¹, K V Sergiyenko¹, S V Konushkin¹, M I Baskakova¹, A V Leonov¹, M A Sudarchikova¹, I M Fedyuk¹, M A Kaplan¹, L A Shatova¹ and A G Kolmakov¹

¹ Baikov Institute of Metallurgy and Material Sciences, 49 Leninsky Avenue, Moscow, Russia
² ŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic
³ Voronezh State Technical University, st. 20-letiya Oktyabrya, 84/4, Voronezh, Russia

E-mail: nacakina@mail.ru

Abstract. Corrosion resistance of a nickel-free shape memory alloy TiNbTaZr of several compositions were studied. The structure and composition of the materials were determined using SEM, atomic emission spectrometry and Auger electron spectrometry. Electro-chemical parameters and alloy dissolution in physiological modeling media were investigated. It has been shown that the alloys are quite corrosion-resistant: no dissolution and high Ebd potential.

1. Introduction

Materials with shape memory effect (SME) are widely used in the modern world and are considered the best candidates for creating medical implants used in noninvasive endoscopic surgery, due to plastic deformation in a chilled state to an extremely compact form, contributing to easier and less traumatic delivery to the necessary part of the body without abdominal surgery, and independent adoption of a functional form in specified operating conditions without additional exposure [1–2]. The most famous medical material from this class is nitinol, endowed with mechanical characteristics similar to the behavior of living tissues, which helps it to adapt to physiological loads [1–7]. However, in addition to the positive mechanical characteristics, this alloy is endowed with a number of disadvantages: difficulty of processing in the manufacture of products, a high content of toxic element [8–10], a controversial level of biocompatibility and corrosion resistance [3, 11–22], which limits its applicability.

At the same time, SME and superelasticity are also found in other materials — alloys and polymers. These include titanium nickel-free alloys, which, due to the corrosive and biological properties of their elements, perfectly meet medical requirements. Unfortunately, at the moment, these alloys are inferior to nitinol in the manifestation of these unique mechanical characteristics. In addition, the technology for obtaining thin wire or other geometrical objects, which are suitable for the production of minimally invasive implants, has not yet been developed. At the same time, the configuration and the state of the surface of an object, defined by the production process, strongly influence the manifestation of all material properties.
This work is devoted to a long-term study of the dissolution of shape memory alloys of the composition Ti-(20–30)Nb-(10–13)Ta-5Zr in the form of a thin wire in media that simulate physiological, in static conditions.

2. Materials and methods
The object of the research was wire with a diameter of 280 μm and a length of 80 mm from Ti-20Nb-10Ta-5Zr; Ti-20Nb-13Ta-5Zr; Ti-25Nb-10Ta-5Zr; Ti-25Nb-13Ta-5Zr; Ti-30Nb-10Ta-5Zr, Ti-30Nb-13Ta-5Zr in the initial state (after drawing) and after grinding the surface. In order to improve the quality of the surface, wires in the initial state were subjected to successive grinding of the surface with emery paper of grit from 180 to 1000 and final processing with diamond paste to a mirror surface.

The morphology and layered elemental composition (including using transverse thin sections) of the surfaces of the materials were examined with a TESCAN VEGA II SBU scanning electron microscope (SEM) equipped with an INCA Energy dispersive energy analyzer, which also carried out fractographic studies of the samples, and electronic Auger spectrometer JAMP-9500F company JEOL in combination with ion etching when bombarded with argon at an angle of 30°.

The corrosion dissolution of the material was studied under static conditions by the method of immersion in solutions of various acidity and composition, since in the human body, the pH varies from almost 1 to 9. A neutral 0.9 mass % sodium chloride solution (NaCl, pH 6.31), artificial plasma (NaCl (92.3 mmol), NaHCO3 (26.3 mmol), K2HPO4 (0.9 mmol), KCl (2.7 mmol), NaH2PO4 (0.22 mM), CaCl2 (2.5 mM), MgSO4 • 7H2O (0.82 mm), Na2SO4 (1.48 mm), D-glucose C6H12O6 (1 g / l), pH 7.36) and standard buffer solution for reproducing at a given level of an acidic medium prepared from the corresponding mixture of the Merk company (potassium tetraoxalate KH3C4O8x2H2O, 0.05 M, pH 1.68) were used [13–15].

Samples of each type in the form of a 32.6 g wire were placed in polypropylene flat-bottomed flasks filled with 100 ml of the selected solution and kept for 30 days at 37 °C, making samples after 6, 13, 21 and 30 days, respectively.

For the experiments, Ti-Nb-Ta-Zr alloy wires of six compositions were used in 2 states: after delivery (after drawing, sample 1), after polishing (sample 2). After a selected period of time, samples were taken from the solutions for analysis. The analysis was carried out on a sequential atomic emission spectrometer with induction plasma with the aim of using the ICP-AES method (inductively coupled plasma atomic emission spectrometry) for direct simultaneous determination of titanium, niobium, zirconium and tantalum in solutions.

Electro-chemical corrosion indicators were investigated by the method of cyclic voltammetry (CVA) in a standard electrochemical cell using a universal potentiostat IPC-Pro. The potential sweep rate was 10 mV/s. Electrolyte was saline 0.9% NaCl at temperature 20 °C. Determination of corrosion parameters (stationary potential Еcorr, breakdown potential Еbd and repassivation potential Еr) was carried out. The test samples were in the form of a wire with a diameter of 0.028 cm as the working electrodes. A glass graphite ring counter electrode was used as an auxiliary, and a saturated silver chloride silver electrode served as a reference electrode. The surface of the samples before conducting the experiments was treated with ethyl alcohol and washed with distilled water. Samples only after grinding the surface were investigated due to the need for surface homogeneity for analysis.

Scanning of CVA was started with a potential of -1.40 V and was carried out until an amperage of no more than 5 mA/cm² was achieved, based on the recommendations of the standard. Scanning in the opposite direction led to the value of the repassivation potential. The current density was measured in mA/cm².

3. Results and discussion
The surface morphology of the Ti-20Nb-10Ta-5Zr alloy wire is shown in Figure 1a. High roughness and heterogeneity are noted. It was of interest to study the structure of the surface in areas different from each other and at the same time regularly repeating. The composition of the wire surface in areas
differing in the SEM image is shown in Figure 1 b-c. It is noticeable that it differed in the analyzed areas - areas with high carbon content were presumed to remain after drawing (carbon-containing lubricant was used) and hardened during numerous anneals. In other areas, a high oxygen content was observed, which is quite natural - titanium and tantalum actively adsorb this element, forming oxides, and their formation is characteristic of almost any new surface.

The surface morphology of the Ti-20Nb-10Ta-5Zr alloy wire after grinding is shown in Figure 2a, and the surface composition of the wire is shown in Figure 2 b. It can be seen that after grinding the surface, its uniformity increased. The content of tantalum and niobium was reduced to zero on the surface, while titanium and zirconium remained in the amount of 5–10 atomic percent, and were most likely observed in oxides. The high carbon content on the surface is due to mechanical contamination of the surface.

Similar patterns were obtained for other compositions. It can be concluded that wires of any composition behave identically.

During the immersion tests, the release of metals in the used neutral solutions was absent or was at a level below the detection limit of the device (0.01 mg/l), which allows to call the alloys highly corrosion-resistant. A slight dissolution, slowing down with time due to surface repassivation, was noted in an acidic solution, which is presumably connected with the complexation of titanium and tetraoxalate. There were no significant differences in the behavior of the alloys.

It was shown that the potential of surface repassivation is within 1400 V for all the samples studied, and there is no hysteresis dependence, which is an indicator of the high corrosion resistance of materials (Fig. 3). The values of the breakdown potential of the passive film speak in favor of the same conclusion. For all compositions it was from 500 V and higher, and it can be clearly noted that an increase in the content of both niobium and tantalum in the alloy shifts this characteristic to an even more electrically charged direction.
Figure 1. Morphology (a) and layered composition of light (b, on "a" denoted as "1") and dark (c, on "a" denoted as "2") surface areas of alloy in the initial state
Figure 2. Morphology (a) and composition (b) of the alloy surface after grinding.
Figure 3. Cyclic voltammograms of TiNi (1) and Ti-Nb-Ta-Zr (2) alloys in 0.9% NaCl solution at a temperature of 20 °C

4. Conclusions
Ti-Nb-Ta-Zr of several compositions were prepared in the form of thin wire and investigated for its corrosion resistance. Electro-chemical parameters and alloy dissolution in physiological modeling media were studied. It has been shown that the alloys are quite corrosion-resistant: no dissolution and high Ebd and Ere potential.

Acknowledgments
The work was supported by the Ministry of Education and Science of Russia (grant identifier RFMEFI60417X0196).

References
[1] Petrini L, Migliavacca F 2011 Biomedical Applications of Shape Memory Alloys Journal of Metallurgy 2011 1-15
[2] Duerig T W, Melton K N, Wayman C M, Stockel D 1990 Engineering aspects of shape-memory alloys (Oxford: Butterworth Heinemann Ltd) pp 181 – 194
[3] Shabalovskaya S 1996 On the nature of the biocompatibility and medical applications of NiTi shape memory and superelastic alloys Bio Med Mater Eng 6 267 – 289
[4] Marjan Bahrami Nasab, Mohd Roshdi Hassan 2010 Metallic Biomaterials of Knee and Hip - A Review Trends in Biomaterials and Artificial Organs 24(1) 69 - 82
[5] Surdell D, Shaibani A, Bendok B, Eskandari M K 2007 Fracture of a Nitinol Carotid Artery Stent That Caused Restenosis J Vasc Interv Radiol 18(10) 1297–1299
[6] Bose A, Hartmann M, Henkes H A 2007 Novel, Self-Expanding Nitinol Stent in Medically Refractory Intracranial Atherosclerotic Stenosis: Wingspan Study Stroke 38 1531–1537
[7] Stoeckel D, Pelton A, Duerig T 2004 Self-expanding nitinol stents: material and design considerations Eur Radiol 14 292-301
[8] Xiaoying Lu, Xiang Bao, Yan Huang, Yinghua Qu, Huiqin Lu, Zuhong Lu 2009 Mechanisms of cytotoxicity of nickel ions based on gene expression profiles Biomater 30 141–148
[9] Uo M, Watari F, Yokoyama A, Matsuno H, Kawasaki T 1999 Dissolution of nickel and tissue response observed by X-ray scanning analytical microscopy Biomater 20 747–755
[10] Wataha J, O’Dell N, Singh B, Ghazi M, Whitford G, Lockwood P 2001 Relating nickel-induced
tissue inflammation to Ni release in vivo. J. Biomed. Mater. Res. 58 537–544
[11] Balazic M, Kopac J 2007 Improvements of medical implants based on modern materials and new technologies J. Achiev. Mater. Manuf. Eng 25(2) 31-34
[12] Kim J H, Shin J H, Shin D H, Moon M W, Park K, Kim T H et al. 2011 Comparison of diamondlike carbon-coated nitinol stents with or without polyethylene glycol grafting and uncoated nitinol stents in a canine iliac artery mode Br J Radiol 84 210-215
[13] Nasakina E O, Baikin A S, Sevost’yavon M A, Kolmakov A G, Zabolotnyi V T, Solntsev K A 2014 Properties of nanostructured titanium nickelide and composite based on it Theor Found Chem Eng+ 48(4) 477–486
[14] Nasakina E O, Sevostyanov M A, Golberg M A, Dyomin K Yu, Baikin A S, Goncharenko B A, et al. 2015 LongTerm Corrosion Tests of Nanostructural Nitinol of (55.91 wt % Ni, 44.03 wt % Ti) Composition under Static Conditions: Ion release Inorg. Mater. Appl. Res. 6(1) 59–66
[15] Nasakina E O, Sevostyanov M A, Golberg M A, Dyomin K Yu, Baikin A S, Goncharenko B A, et al. 2015 LongTerm Corrosion Tests of Nanostructural Nitinol of (55.91 wt % Ni, 44.03 wt % Ti) Composition under Static Conditions: Composition and Structure before and after Corrosion Inorg. Mater. Appl. Res. 6(1) 53–58
[16] Nasakina E O, Sevost’yavon M A, Mikhailova A B, Gol’dberg M A, Demin K Yu, Kolmakov A G, et al. 2015 Preparation of a nanostructured shape memory composite material for biomedical applications Inorg. Mater. 51(4) 400-404
[17] Nasakina E O, Baikin A S, Sergienko K V, Sevost’yavon M A, Kolmakov A G, Goncharenko B A, et al. 2015 Biocompatibility of nanostructured nitinol with titanium or tantalum surface composite layers formed by magnetron sputtering Doklady Chemistry 461(1) 86–88
[18] Nasakina E O, Baikin A S, Konushkin S V, Sergienko K V, Kaplan M A, Fedyuk I M, et al. 2018 Receiving of layered composite materials with shape memory effect of medical appointment IOP Conf Ser: Mater Sci Eng 411 012051
[19] Nasakina E O, Baikin A S, Sergienko K V, Leonov A V, Kaplan M A, Seryogin A V, et al. 2017 Formation and Investigation of Composite Material Silver–Nitinol for Medical Purposes Inorg. Mater. Appl. Res. 8(1) 112–117
[20] Nasakina E O, Sevostyanov M A, Mikhailova A B, Baikin A S, Sergienko K V, Leonov A V et al. 2016 Formation of alpha and beta tantalum at the variation of magnetron sputtering conditions IOP Conf Ser: Mater Sci Eng 110 012042
[21] Tomić S, Rudolf R, Brunčko M, Anžel I, Savić V, Čolić M 2012 Response of monocyte-derived dendritic cells to rapidly solidified nickel-titanium ribbons with shape memory properties Eur. Cell. Mater. 23 58–81
[22] Chun-Che Shih, Shing-Jong Lin, Yuh-Lien Chen, Yea-Yang Su, Shiau-Ting Lai, Gaston J. Wu, Ching-Fai Kwok, Kwok-Hung Chung. 2000 The cytotoxicity of corrosion products of nitinol stent wire on cultured smooth muscle cells J. Biomed. Mater. Res. 52 395–403