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CORROSION RESISTANCE OF METAL COMPOSITE MATERIALS WITH SHAPE MEMORY EFFECT OF MEDICAL APPOINTMENT

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Abstract

Corrosion resistance of composite materials based on TiNi with Ta and Ti surface layers in solutions with pH from 1.68 to 9.18 for the long period in static conditions is investigated. The concentration of metals in solution is defined by the AES with ICP. Structure and composition of samples were defined by SEM, AES. Corrosion of all samples in the alkaline environment, artificial plasma and saliva, and also composites and TiNi samples after the polishing in solutions with acidity 3.56-6.31 are not revealed for 2 years of the researches.

Key words: composite materials, tantalum, nitinol, biomedical materials, nanomaterials, corrosion resistance, shape memory effect, superelasticity.

Introduction.

The most known medical material with the shape memory effect is nitinol endowed with mechanical characteristics similar to behavior of living tissues that helps it to adapt to physiological loadings providing necessary service conditions [1]. Implants made of it of plastically deformable in the cooled condition to extremely compact type promoting easier and less traumatic delivery to the necessary site of an organism without serious surgical intervention and then they independently take the functional form in set operational conditions without additional effect [1]. But in addition to positive mechanical characteristics this alloy possesses the high content of a toxic element [2] and disputable level of biocompatibility [3–6]. In works of different authors absolutely various duration and quantities of nickel ions

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release from a nitinol to the environment are given [3-4, 6], breakdown potential of a protective oxide film vary from low for a medical application to high [3, 7].

Formation of composite materials on the basis of classical ones allow to increase its operational characteristics and eliminate shortcomings [8-14]. This work is devoted to corrosion resistance research of metal layered composites on the basis of a nitinol with tantalum or titanium surface layers in the environments modeling physiological in long-term period in static conditions.

Materials and methods

An object for investigations was wires with diameter 280 μm made of nanostructural nitinol (55.91 wt % Ni–44.03 wt % Ti) and composites based on it with tantalum or titanium surface layers, obtained by the magnetron sputtering method [15–17].

The wires in the initial state were sequentially polished by abrasive paper from 180 to 1000 grit and processed finally by GOI (State Optical Institute) paste to a mirror surface with the purpose to surface quality improve. The decrease in the diameter was to 10 μm in comparison with the original. For end stabilization of the B2 phase and shaping, wires in the initial state or after polishing were annealed at 450°C for 15 min in air. The wire diameter was invariable.

Composites were produced in argon at residual and working pressures of 4×10^{-4} and 0.4 Pa, respectively. The magnetron, with a reagent-grade target, was operated at a sputtering distance on the order of 150 mm, at direct current of 860 mA and voltage of 400 V. The sputtering time was 80 min on the main surface with rotation and 30 min on end faces, and the substrate rotation rate was 9 rpm.

The surface morphology and the layer-by-layer composition were investigated on a TESCAN VEGA II SBU scanning electron microscope equipped with an INCA Energy energy dispersive spectrometer system and on a JAMP 9500F JEOL Auger spectrometer in combination with ion etching at argon bombardment under an angle of 30°.

The material was tested for corrosion resistance under static conditions by dipping into solutions with various acidities because pH in the human body changes from 1 to 9. Neutral 0.9 wt % sodium chloride solution, artificial plasma and saliva and four standard buffer solutions to reproduce acidic and alkaline media at the given level, and prepared from corresponding standard trimetric substances (fixanals) made by Merk, were used and listed in Table 1. Wire samples with a weight by 32.6 mg (separately from each other) were placed into flasks with 100 mL of the selected solution and aged totally in a dark place for up to 730 days.

Six types of samples were studied: 1 - TiNi in the initial state (as-received), 2 - TiNi after annealing, 3 - TiNi after polishing, 4 - TiNi after polishing and annealing, 5 - TiNi-4 with Ta surface layer (Ta-TiNi), 6 - TiNi -4 with Ti surface layer (Ti-TiNi). Analysis of solutions with samples was carried out by a sequential atomic emission spectrometry for using atomic emission spectrometry (AES) with inductively coupled plasma (ICP) every 15 days.

Table 1.

The composition and acidity of modeling solutions used for immersion test

pH	Composition
1.68	Potassium tetraoxalate $\text{KH}_3\text{C}_4\text{O}_8 \times 2\text{H}_2\text{O}$, 0.05 M
3.56	Acid potassium tartrate $\text{C}_4\text{H}_5\text{O}_6\text{K}$, 0.025 M
4.01	Acid potassium phthalate $\text{C}_8\text{H}_5\text{O}_4\text{K}$, 0.05 M
6.31	Sodium chloride NaCl, 0.9 wt. %
9.18	Acid sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7 \times 10\text{H}_2\text{O}$, 0.05 M
7.36	Artificial plasma: NaCl (92.3 mM), NaHCO_3 (26.3 mM), K_2HPO_4 (0.9 mM), KCl (2.7 mM), NaH_2PO_4 (0.22 mM), CaCl_2 (2.5 mM), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.82 mM), Na_2SO_4 (1.48 mM), D-glucose $\text{C}_6\text{H}_{12}\text{O}_6$ (5.55 mM) [8, 24–25]
7.55	Artificial saliva NaCl (13.34 mM), NaHCO_3 (7.4 mM), K_2HPO_4 (4.4 mM), KCl (10 mM), NaH_2PO_4 (1.2 mM), CaCl_2 (1.4 mM), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (0.7 mM), Na_2SO_4 (0.13 mM), Na_2S (0.021 mM), carbamide (1 g/l) [8, 24–25]

Results and discussion.

As in previous research [15-16] in this work the untreated surface of 1-TiNi is heterogeneous and covered by spots, dark areas alternate with bright ones, and the high roughness and defects because of drawing during production are clearly expressed. The compositions of bright and dark spots are different: a high content of titanium oxide is revealed in bright ones; and carbon, in dark ones. Both layers attain 4.5 μm in thickness and are not placed over each other. Such a thick surface layer, as was believed, was a result of the long intermediate thermal treatment during the wire production [15]. After annealing, the surface externally is similar to the initial one, except for small increase in a share of light oxide-containing sites.

After polishing practically all defects and the roughness are smoothed, spots are absent, and only traces of treatment are visible. Surface microdefects are grooves with a depth and width of less than 1 μm . The composition of the polished surface is homogeneous: the entire wire is covered by an oxide layer less than 20 nm in thickness. The minus is the nickel presence in the surface layer, though in an insignificant amount. The subsequent annealing promotes formation of an oxide-nitride layer up to 80-150 nanometers in depth, to 50–60 nanometers free from nickel that could affect corrosion resistance of material positively. The researched composite materials had layered structure "a surface layer from the deposited substance (thickness ~ 0.9 microns) – the transitional layer containing elements both of the surface layer and of a basis (thickness ~ 0.2 microns) – a basis".

In figures 1-2 release of metal ions in model media depending on holding time, material treatment, nature and temperature of the environment is shown. There are no results about all samples in the alkaline environment, artificial plasma and saliva, and also about TiNi-3, TiNi-4, Ta-TiNi and Ti-TiNi samples in solutions with acidity 3.56-6.31 since in these cases dissolution of elements was zero or below a limit of detection for all the time of a research.

In the remained cases elements concentration in solutions increases (fig. 1) over time, but leaching of elements in medium considerably slows down. It can be related to sequential processes of the destruction and renewal of the protective oxide film (de- and repassivation) on defect areas [15-16]. And when comparing results on ions release from identical types of samples in this work and in [16] in this case a smaller release of metals is observed that is explained by more perfect surface of as-received TiNi-1.

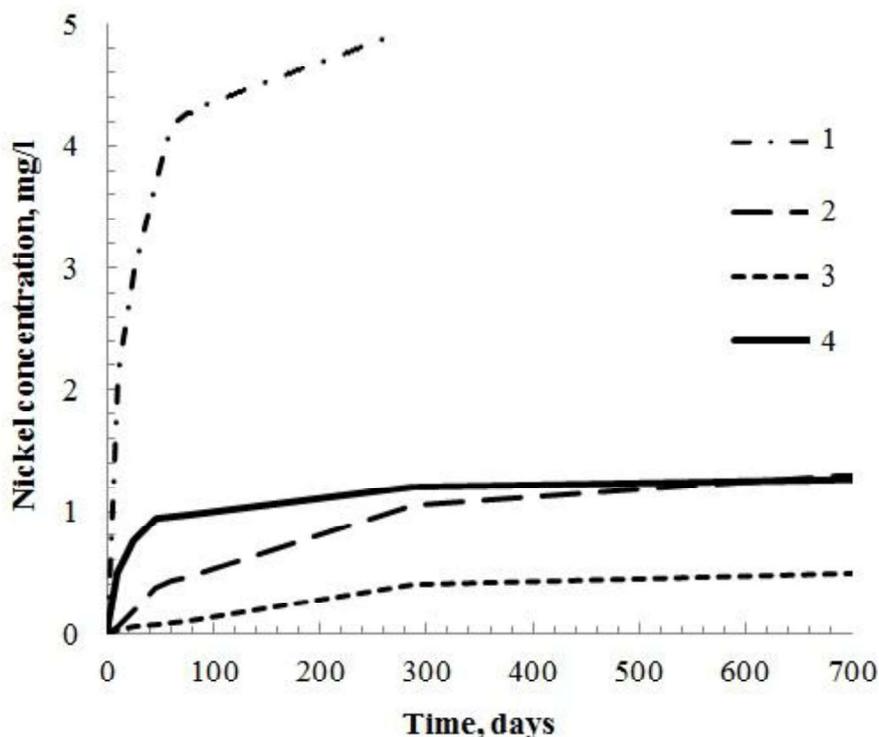


Fig. 1. Nickel concentration in investigated solutions with various acidities with nitinol sample without treatment as a function of sampling time and character of the environment. The marked curves correspond to solution pH: 1 – 1.68, 2 – 3.56, 3 – 4.01, 4 - 6.31

Medium temperature growth insignificantly increases concentration of elements in solution (varies depending on immersion time and metal nature), but at the same time the gradual inhibition of material dissolution is also observed, and at different temperature it occurs almost at the same time (fig. 2). It allows to assume that after initial increase in corrosion due to temperature increase in the following, with the surface repassivation, the degree of the material dissolution practically does not depend on temperature. From the study of nitinol corrosion, passive layer was stable at temperature of human body and higher sensitivity to temperature changes was identified for 316 L to compare with NiTi [18-19].

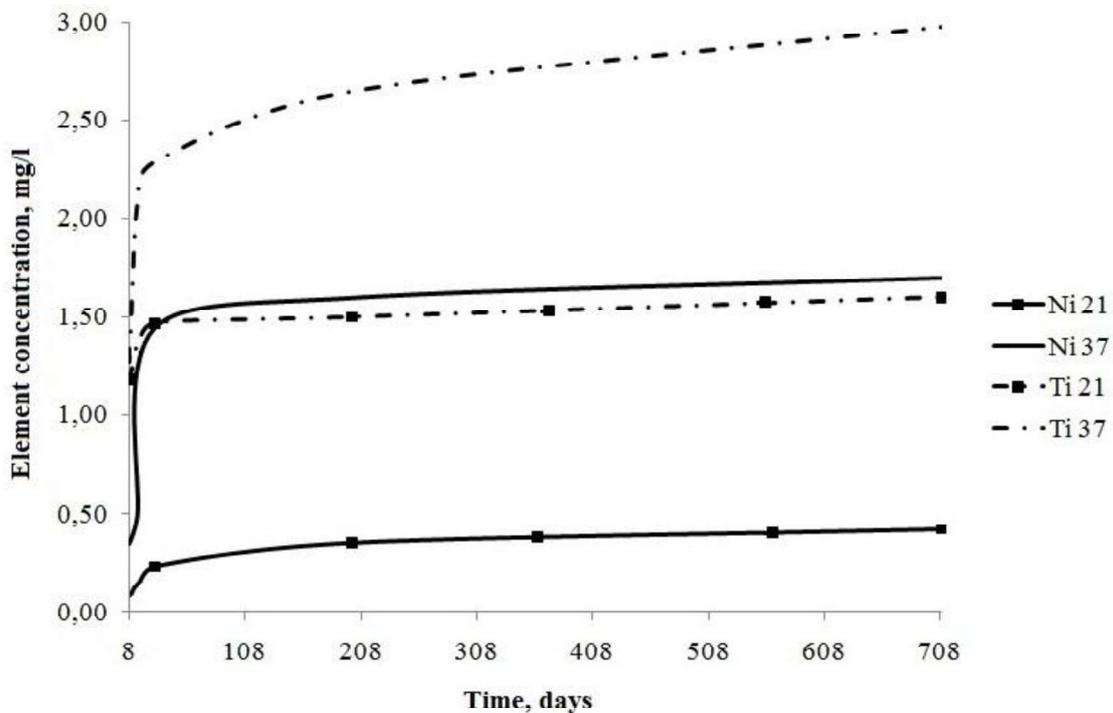
In case of composite material with a tantalum surface layer Ta concentration was also considered (fig. 2 c-d). Insignificant dissolution of material is also observed only in the most acidic environment (most likely on possible defective sites of a surface with an incomplete surface layer that requires separate studying), concentration of tantalum is much less than of titanium which, respectively, is less, than nickel.

Depending on material treatment ions release decreases in the following order: TiNi-2 > TiNi-1 > TiNi-4 > TiNi-3 > Ti-TiNi (if to look on nickel concentration) > Ta-TiNi. According to the literature, the thermal treatment

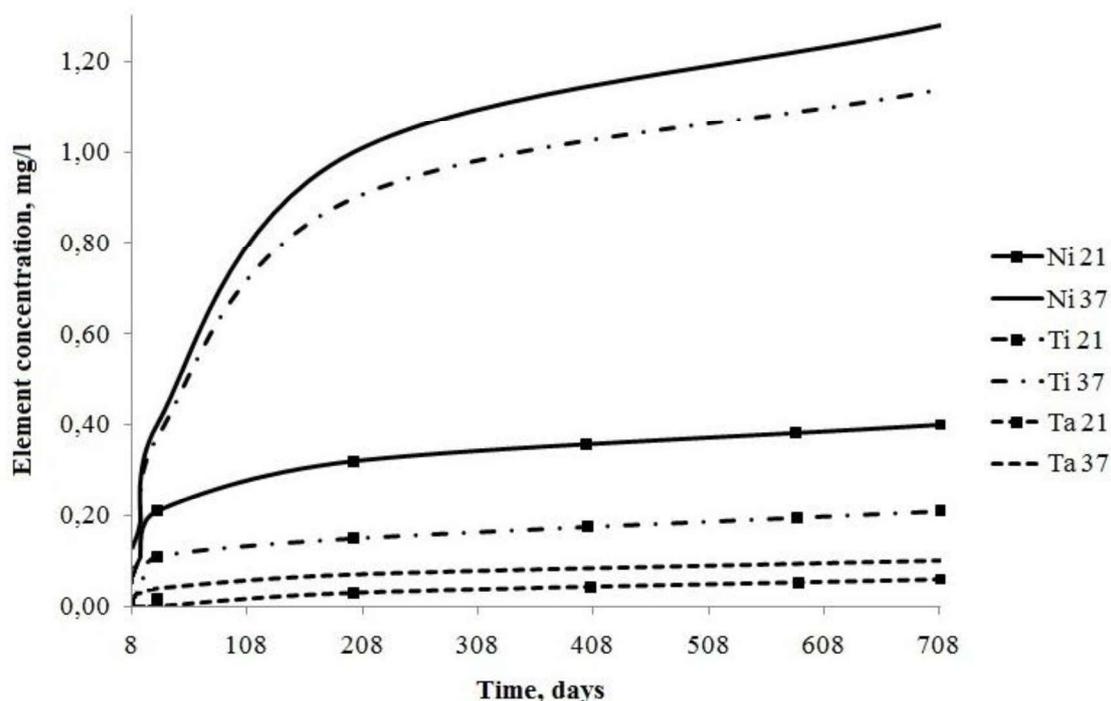
at a temperature from 400 to 1000°C, which is required for stabilization of the mechanical properties, always results in a significant worsening of the corrosion resistance and the surface treatment increases the corrosion resistance [16]. And in case of TiNi-4 and TiNi-3 samples on an initial stage of researches regularity has the return nature. It is possible to assume that in the beginning thicker oxide surface layer of a sample after polishing and annealing acts as the better barrier against diffusion of nickel ions in solution, however a surface loosening as a result of tempering and recrystallization doesn't allow to slow down leaching of elements as effectively as in case of more uniform passive film which is initially received when polishing [15-16].

Because of chemical interaction of Ti with acid media composite with its surface layer obviously less corrosion resistant than with Ta, but they are both more resistant than nitinol without a protective layer.

Results depending on the environment (fig. 1) meet expectations: the greatest release of metals is observed in the most acidic environment, sharply falls with pH increase (acidity lowering), but again (slightly) increases in neutral physical solution, the concentrated source of ions of chlorine, which are related to corrosion activator ions, have a depassivation and pitting corrosion effect, have a metal affinity greater than oxygen, and displace the latter from its compounds with metals [16].



a



B

Fig. 2. Dependence of concentration of the elements dissolved from TiNi-Ti (a) and TiNi-Ta (b) composites in buffer solution with acidity 1.68 on immersion time of sampling and temperature of solution: the marked curves correspond to temperature of 21 ° C, curves without tags – 37 ° C

Conclusions.

Layered composite materials with tantalum or titanium surface layers on a basis of a nanostructural nitinol and this alloy in various state are received and investigated. Its high corrosion resistance is noted.

Corrosion of all samples in the alkaline environment, artificial plasma and saliva and also composites and samples after polishing in solutions with acidity 3.56-6.31 for 2 years of a research isn't revealed.

The greatest concentration of metals is observed in the most acid solution, smaller in physical solution. Concentration of metals increases in solution over time, but the considerable slowdown of an metal ions release in solutions is observed over time.

The annealing following polishing increases corrosion resistance of material on an initial stage of researches, but at long tests regularity has the return nature.

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