Corrosion resistance of nonnickel shape memory alloy

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Abstract. Corrosion resistance of a Ti - (20-30) Nb - 5Zr shape memory alloy were studied. The structure and composition of the materials were determined using SEM 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 were observed.

1. Introduction
Ni-free Ti-based alloys are currently being actively studied for its shape memory effect and superelasticity [1-6].

These alloys are considered potential candidates to replace nitinol, which is widely used in medicine, since the carcinogenic properties of nickel limit the subsequent medical use of this alloy [7-22]. The solution of this problem could be the creation of biocompatible and corrosion resistant surface layers [23]. However, in this case the question arises of the mutual adhesion of the components, especially in the case of variable dynamic loads. While obtaining the alloy only from non-toxic components does not imply this problem. It is only necessary to develop such an alloy, whose characteristics will be comparable with the mechanical properties of nitinol. Potentially mixtures based on the Ti-Nb-Zr system are useful in orthopedics and endovascular surgery.

The development of any material usually pursues the goal of obtaining a new facility with certain properties that are advantageous in terms of its intended use. In the modern world, the fields of science and technology, in connection with their rapid development, are increasingly intertwined, forming interdisciplinary directions, sometimes extremely difficult to separate from each other. Physical-chemical characteristics make it possible to evaluate the resistance of materials under the influence of an aggressive environment (water, oil, salt, alkali, acid, gas, fuel) during operation, including water and moisture absorption, chemical and heat resistance. In the case of metallic materials, this group can also combine chemical properties (oxidizability, solubility and corrosion resistance) and physical (color, specific gravity, density, fusibility, electrical conductivity, magnetic properties, thermal conductivity, and expandability when heated). As a result, a large-scale complex of operational properties is formed, the parameters of which will determine whether the alloy being developed is suitable for receiving minimally invasive medical implants (at the stage prior to biological research).
This work is devoted to a long-term study of the dissolution in static conditions of Ti–(20–30)Nb–5Zr shape memory alloys in the form of a thin wire and its electro-chemical parameters in modelling physiological media.

2. Materials and methods

The alloys of the Ti-Nb-Zr systems of the following compositions were studied: Ti-20Nb-5Zr, Ti-23Zr-5Zr, Ti-25Nb-5Zr, Ti-28Nb-5Zr, Ti-30Nb-5Zr (at.%). The alloys were smelted by the method of vacuum electric arc melting from pure charge materials. The ingots were annealed in vacuum at a temperature of 1000 °C for 12 hours and cooled with the furnace [6]. Then it was subsequently converted into bars and wire by rolling, forging and drawing. 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. In order to stabilize the structure and properties of the material, the wires were annealed at a temperature of 600 °C.

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 immersion in solutions of various acidity and composition. 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.

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, 30 and 60 days, respectively.

For the experiments, Ti-Nb-Zr alloy wires of 5 compositions were used in 3 states: after drawing (sample 1), after polishing (sample 2) and after annealing (sample 3). 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 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 Ecorr, breakdown potential Ebd and repassivation potential Er) 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 a 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
During immersion tests, there was no metal yield from the solutions used, or was below the detection limit of the device (0.01 mg / l), which allows us 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 titanium and tetraoxalate complex formation. There were no significant differences in the behavior of the alloys depending on the composition.

The results of electrochemical studies are shown in Figures 1-3.

![Cyclic voltammograms of Ti-25Nb-5Zr alloys in a 0.9% NaCl solution at a temperature of 20 °C.](image)

**Figure 1.** Cyclic voltammograms of Ti-25Nb-5Zr alloys in a 0.9% NaCl solution at a temperature of 20 °C.
Figure 2. Cyclic voltammograms of Ti-20Nb-5Zr alloys in a 0.9% NaCl solution at a temperature of 20 °C.

Figure 3. Cyclic voltammograms of Ti-30Nb-5Zr alloys in a 0.9% NaCl solution at a temperature of 20 °C.
It was shown that the surface repassivation potential for all studied samples is within 1400 V, which is an indicator of the high corrosion resistance of materials. The same conclusion is supported by the values of the breakdown potential of the passive film, for all alloys, components from 500 V and higher, and it can be clearly noted that an increase in the content of niobium in the alloy shifts this characteristic to an even longer electro-long side.

4. Conclusions

Ti–(20–30)Nb–5Zr 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 were observed.

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