IMET RAS

Applications of nanostructural shape memory alloy for medical devices

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Introduction

NiTi alloys possessing a shape memory effect and mechanical characteristics similar to the behavior of living tissues have been already used for years as the material for production of medical devices, including implants, for example stents (Figure 1), without the need for additional devices except catheter-carrier. However, nitinol contains nickel (including on its surface) which is toxic for organism. Different authors give completely different durations and magnitudes of the nickel ion release from microstructural nitinol into the medium, as well as level of biocompatibility and electro-chemical corrosion characteristics. As is well-known, formation of nanostructures is able to afford to give to materials special, controlled characteristics. On the other hand, the high density of intergranular surface defects could lead to a poor corrosion performance.

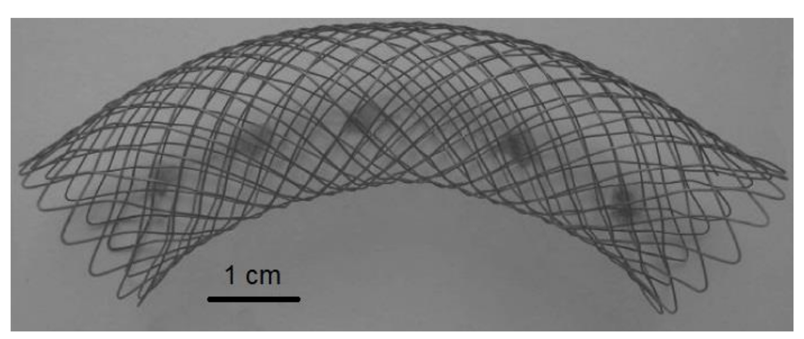

Figure 4. Stent applied to restore esophageal and intestinal patency

Aim

The purpose of this study is to investigate the composition, structure and properties of polycrystalline nitinol with nanograins.

Materials and Methods

Nanostructural NiTi (55,91 weight % Ni – 44,03 weight % Ti) wires for production of non-invasive implants (stents) was tested for corrosion resistance under static conditions by dipping into solutions with various acidities (pH from 1.68 to 9.18, Table 1) during two years, for static mechanical properties and biocompatibility.

The structure was determined with the use of the transmission electron microscope (TEM), X-ray diffractometer, scanning electron microscope (SEM) and on a Auger spectrometer.

Table 1. pH and composition of the solutions used for immersion tests

№	pH	Composition
1	1.68	Potassium tetraoxalate $KH_3C_4O_8x2H_2O$, 0.05 M
2	3.56	Acid potassium tartrate $C_4H_5O_6K$, 0.025 M
3	4.01	Acid potassium phthalate $C_8H_5O_4K$, 0.05 M
4	6.31	Sodium chloride NaCl, 0.9 wt.%
5	9.18	Acid sodium tetraborate $Na_2B_4O_7x10H_2O$, 0.05 M
6	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), $MgSO_4 \cdot 7H_2O$ (0.82 mM), Na_2SO_4 (1.48 mM), D-glucose $C_6H_{12}O_6$ (5.55 mM)

Sampling from solutions for analysis was after a selected period (10, 25, 45, 60, 75, 236 or 287, 704 or 754 days). Analysis was carried out using atomic emission spectrometry (AES) with inductively coupled plasma (ICP).

The biocompatibility of the nanostructured nitinol was measured in vitro using standard test systems: the cultures of myofibroblasts from human peripheral vessels and human bone marrow mesenchymal stromal cells (MSC) were used as standard cell models.

Results

The bright field TEM image in figure 2 shows that nitinol grains resemble nanofibers with a cross-section size of 30 to 70 nm and the length of several microns. Thus, grains are extended along the wire axis. the material volume is represented by the base of the B2 phase of TiNi and inclusions of Ti2Ni intermetallides.

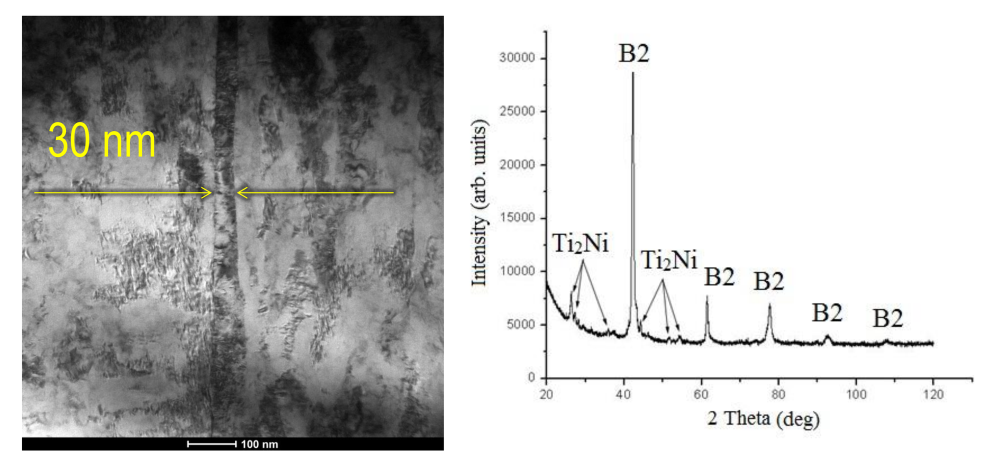

Figure 2. Bright-field TEM image and X-ray diffraction patterns

The wire surface before treatment is heterogeneous, after annealing the surface externally is similar to the initial one, whereas after polishing (Figure 3) practically all defects and the roughness are smoothed, and only traces of treatment are visible. The composition of the polished surface is homogeneous: the entire wire is covered by an oxide layer less than 20 nm in thickness.

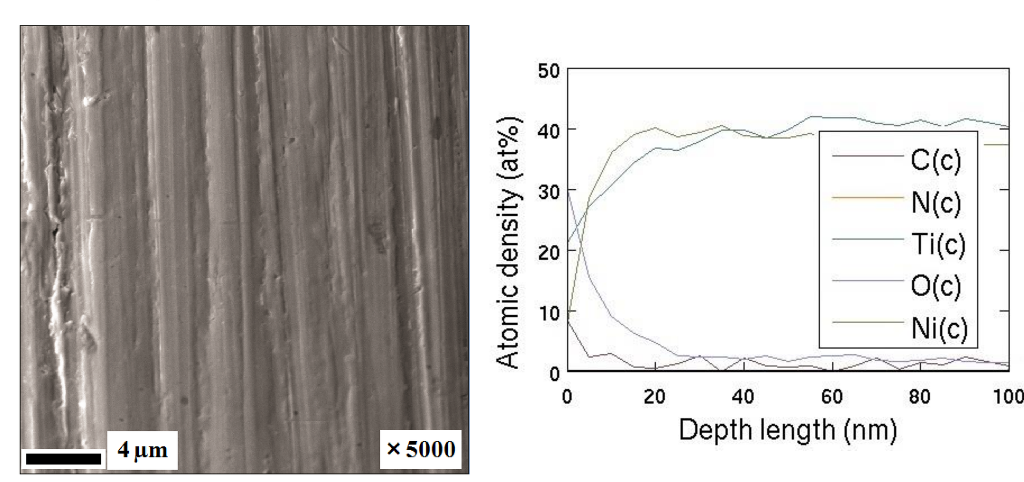

Figure 3. Surface morphology and composition of the NiTi polished sample

Results of mechanical stretching tests (Table 2) shown positive influence of annealing on strength properties of alloy in both structural states, and strength properties of a nanostructural nitinol exceeded strength properties of microstructural by 1,3 — 1,5 times. Nitinol wire polishing after drawing promotes increase in static properties of a nanostructural alloy for 18%. Relative elongation of all nanostructural samples were of 51-53% via 9-20% of microstructural.

Table 2. Effect of annealing on nitinol mechanical properties

№	Sample	σ0.2, MPa	σu, MPa	Ψ, %
1	Microstructural nitinol before treatment	397	1223	9
2	Nanostructural nitinol before treatment	507	1485	51
3	Microstructural nitinol, annealing of 450 ° C, 15 min.	464	1435	13
4	Nanostructural nitinol, annealing of 450 ° C, 15 min.	742	1885	52

Insignificant corrosion is observed in acidic and neutral media, and the nickel concentration is less than the average magnitudes cited in the literature; however, the titanium content is revealed in solutions. There is no results about all samples in the alkaline environment and artificial plasma, and also about polished samples in solutions with acidity 3.56-6.31 since in these cases release of elements was zero or below a limit of detection for the overall time of the investigation.

Comparison of the treatment effect on the corrosion resistance of samples (Figure 4) makes it possible to conclude that the samples undergo the most corrosion after annealing, and the mechanical treatment, as was expected, strongly increases the corrosion resistance of nitinol.

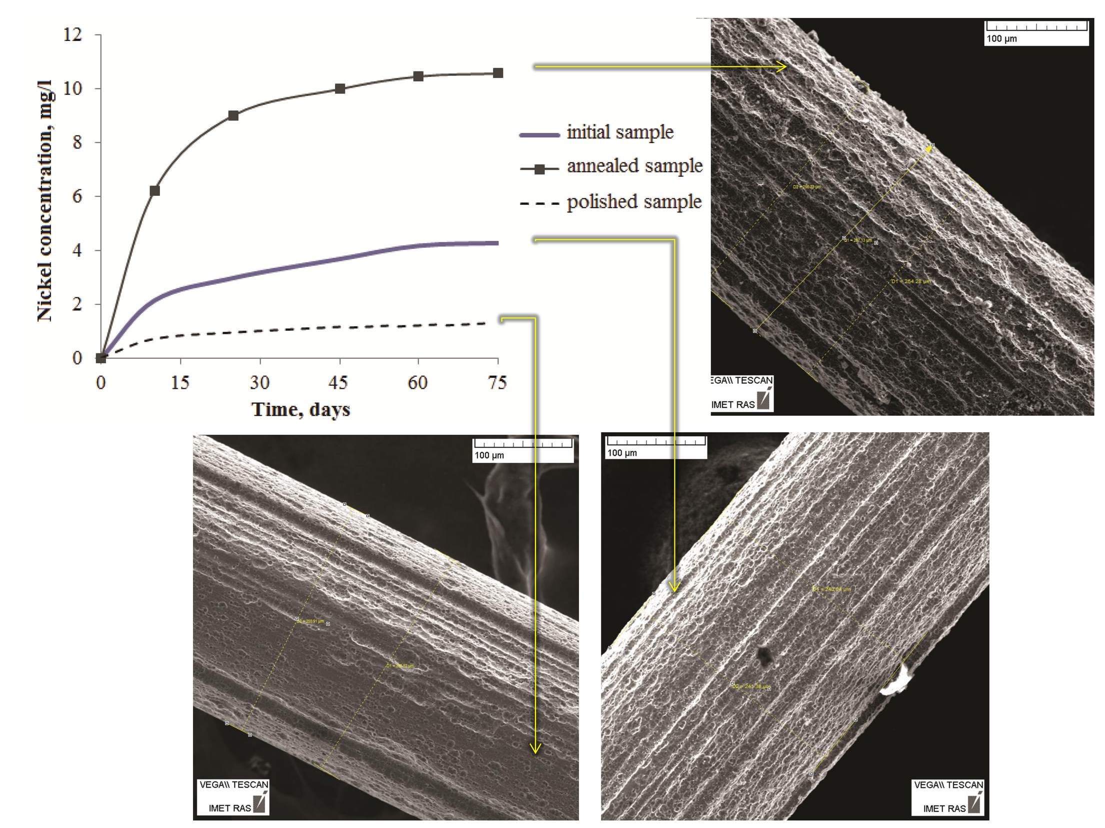

Figure 4. Nickel concentration in solution with pH 1.68 as a function of sample treatment and surface morphology after 2-year immersion

We observe the significant retardation of the nickel ion release (and insignificant concentration as a whole) and the absence of titanium ion release form nanostructural nitinol samples in weakly acidic and neutral solutions after mechanical polishing. Traces of pitting corrosion on the surface of polished samples are visible only after two years of holding in the most acidic medium (Figure 4); wires held in the remaining media look intact equally (Figure 5). The greatest depth of the surface oxide layer, approximately 25 nm, is observed for polished wires after holding in neutral solutions (Table 3). This leads to a conclusion of the occurrence of a strong and homogeneous protective surface layer of titanium oxide, which serves as a barrier to the release of nickel into the medium, and the high corrosion resistance of investigated nanostructural nitinol.

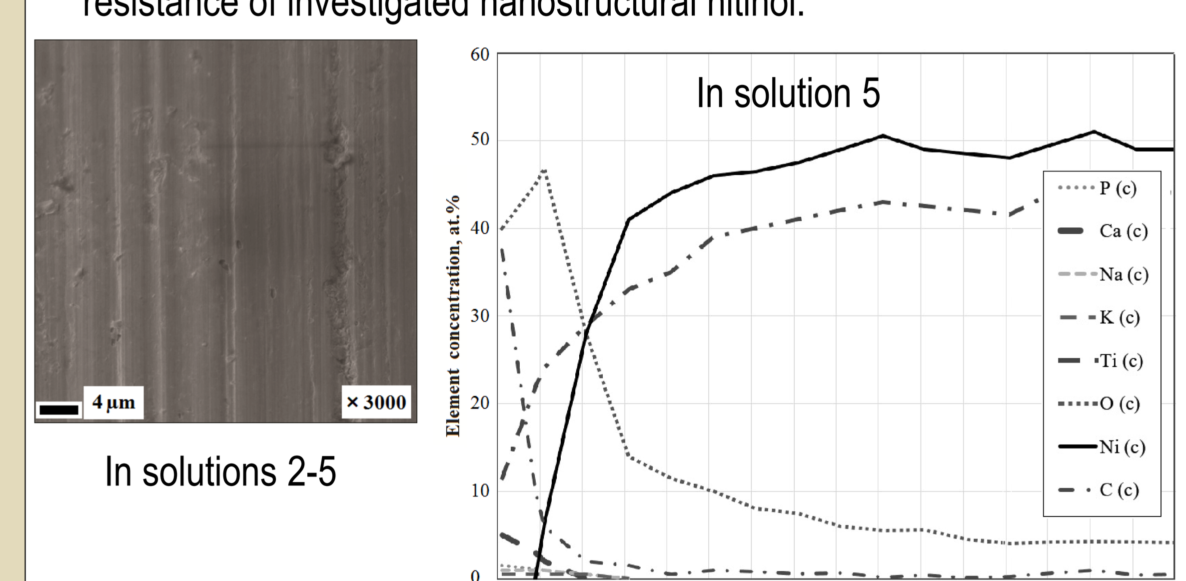

Figure 5. Surface morphology and composition of the NiTi polished sample after 2-year immersion

Table 3. Diameters of each type of NiTi wire sample before and after immersion for 2 years in solutions with various pH values

Solution pH	1.68	3.56	4.01	6.31/7.36	9.18
Oxide layer thickness / nm	8–13	13–17	15–20	23–28	≈ 10
Nickel surface concentration / at.%	8	5	3	0	3

Results (Cont.)

In the case of myofibroblasts and MSC, the percentages of vital cells for NiTi, was 91 ± 3 and 95 ± 1, respectively. The calculated mitotic index value for the cells growing on the NiTi surface was 3.1% for the myofibroblast culture and 1.8% for the MSC culture. Thus, the material samples used in the study had not a short-term toxic effect on the cells that overgrew its surfaces de novo.

Conclusion and Acknowledgements

The nickel release is less in comparison with data for microstructural nitinol in a solution of any acidity. A significant retardation of the nickel ion release and the absence of titanium ion release in the weakly acidic and neutral solutions with polished samples are observed. A simultaneous 7–11% increase in strength and plasticity in comparison with microstructural nitinol was attained. Toxicity of samples hasn't been revealed.

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