Receiving of layered composite materials with shape memory effect of medical appointment

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Abstract. Tantalum and titanium surface layers were created on nanostructural TiNi substrates when the conditions of magnetron sputtering are varied. The state of the TiNi surface after various treatments has been studied. Structure and composition of samples were defined by SEM, AES. With increase in time and output of sputtering and decrease in deposition distance surface layer thickness not linearly increases. The transitional layer provide high adhesion of a surface layer to a substrate.

1. Introduction

Materials with shape memory effect (SME) are the best candidates for the creation of medical implants that are plastically deformed in a cooled state to an extremely compact form (facilitating easier and less traumatic delivery to the necessary site of the organism without cavitary surgery) and independently assuming functional form in the specified operational conditions without additional impact [1-12]. 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 stresses, providing the necessary operating conditions. But in addition to positive mechanical characteristics, this alloy is endowed with a number of shortcomings: the difficulty of processing in the manufacture of products, high content of a toxic element, a disputable level of biocompatibility.

In the modern world, an effective way to improve operational characteristics and eliminate the drawbacks of classical materials is the formation of composite materials on their basis [13-14].

This work is devoted to the comparison of the surface state of nitnol depending on various treatments and of metal layered composites based on it with surface layers of tantalum or titanium of medical appointment.

2. 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 [14].

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 4x10^{-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. Preparatory ion etching of the substrate (cleaning, activating, and polishing the surface by bombarding it with argon ions) was carried out with the discharge parameters U_e = 900 V, I_e = 80 mA.

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°.

3. Results and discussion

The initial TiNi surface 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 (figure 1a). 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.

After annealing, the surface externally is similar to the initial one, except for small increase in a share of light oxide-containing sites (figure 1b).
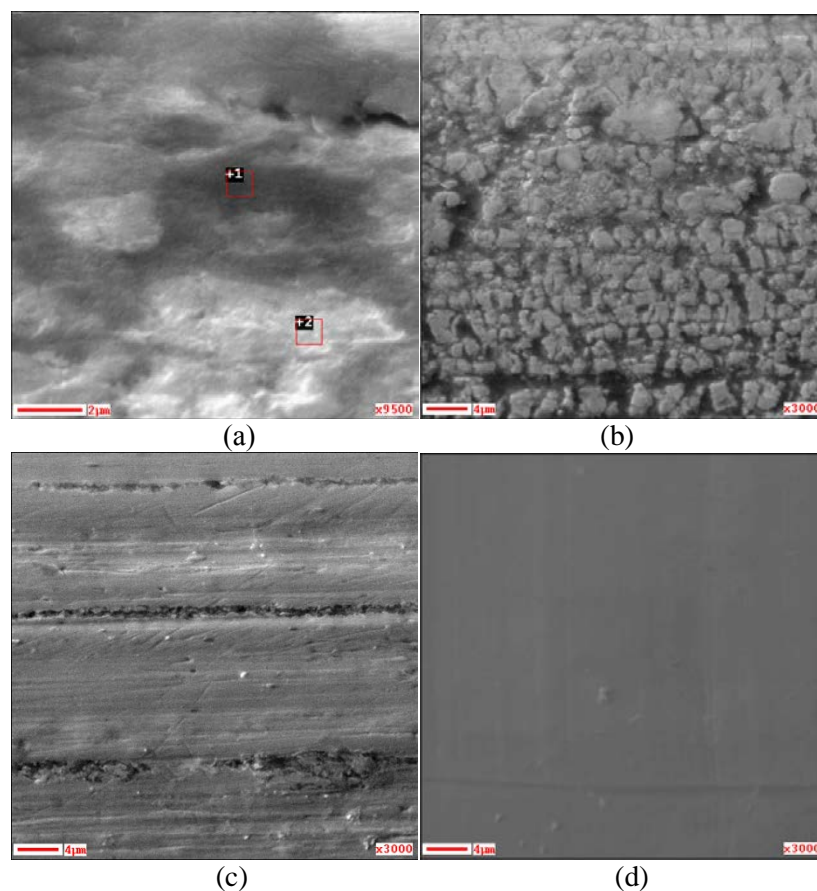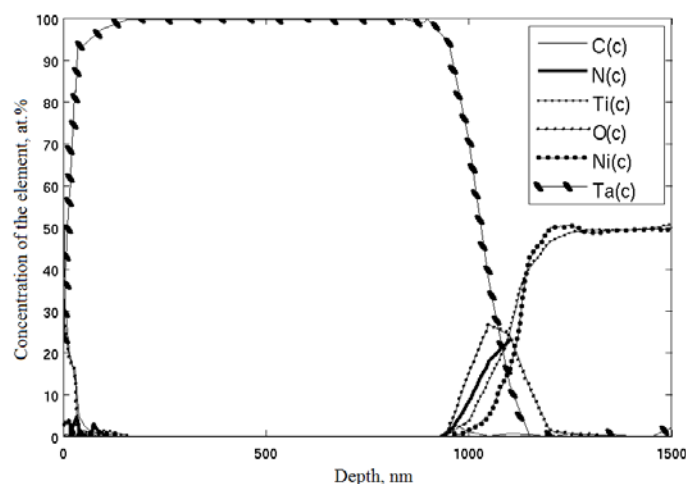

(a)   (b)

(c)   (d)

Figure 1. Morphology of the surface of nitinol: a) in the initial state, b) after annealing, c) after grinding, d) after grinding and annealing.

After polishing practically all defects and the roughness are smoothed, spots are absent, and only traces of treatment are visible (figure 1c). 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 presence of nickel in the surface layer, though in an insignificant amount.
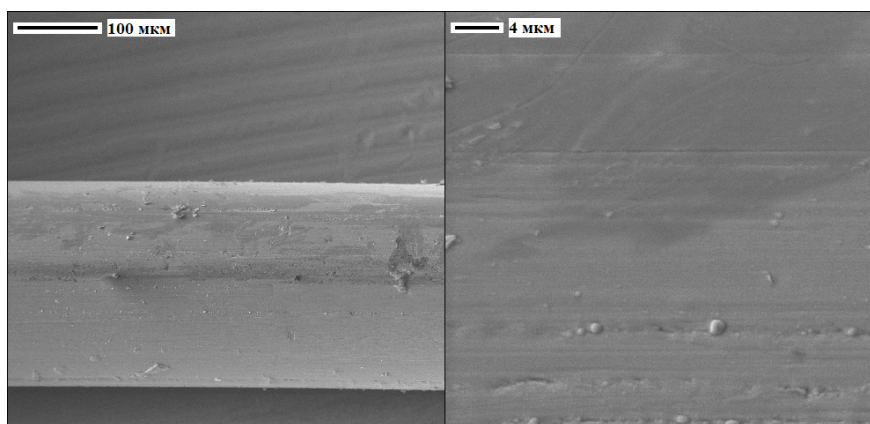
The subsequent annealing promotes formation of an oxide-nitride layer up to 80-150 nanometers in depth, to 50–60 nanometers free from nickel that could affect corrosion resistance of material positively. Surface defects were not observed at all, the entire roughness was smoothed, an extremely high surface uniformity was observed (figure 1d).

The received 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" (figure 2a), the morphology of the surface corresponds to the morphology of the surface of the substrate after grinding and annealing (figure 2b).

With increasing time and power of sputtering and a decrease in the sputtering distance, the thickness of the surface layer increases nonlinearly. The regions of saturation of the surface and transition layers are marked, after which the thickness practically does not change when the conditions change. The transition layer provides high adhesion of the surface layer to the substrate.

(a)

(b)

Figure 2. The layered composition (a) and morphology (b) of the surface of composites with a tantalum surface layer.

4. Conclusion
Layered composite materials with surface layers of tantalum and titanium and a base of nanostructured titanium nickelide, as well as a base material in a different state, were obtained and investigated.

Acknowledgments

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