The effect of the titanium surface layer thickness on the characteristics of a layered composite material

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Abstract. Nano- and micro-dimensional surface layers of titanium on flat and wire NiTi substrates were obtained. The structure and composition of the samples was determined using SEM, AES, Auger spectroscopy and X-ray diffraction. With increasing deposition time, the thickness of the surface layer increases nonlinearly. The transition layer provides high adhesion of the surface layer to the substrate.

1. Introduction

Nitinol (NiTi) widely recognized in many areas of human activity, in particular – medicine, due to its unique mechanical properties (superelasticity, compliance with the delay law, shape memory effect (SME)) [1–2]. However, there is some likelihood of a negative effect of nitinol on the body, as well as corrosive destruction of the material in aggressive biological media.

In this regard, intensive research is being conducted to find ways to improve its corrosion resistance and biocompatibility. To improve the “natural” conversion protective oxide layer of nitinol, chemical passivation, anodizing, oxidation in boiling water, autoclave or low pressure, electropolishing, etc. are used to form a uniform surface layer of titanium oxide, with a minimum nickel content, up to several hundred nm. However, after these types of treatment, the cases of a decrease in corrosion resistance under cyclic thermal and mechanical effects are noted.

Ceramic, metal and polymer coatings generally have different mechanical properties than nitinol, so they can improve the corrosion resistance of nitinol under static conditions, but in dynamic conditions they will more likely accelerate the destruction of the material due to additional surface stresses. It is possible to create thin metal surface layers that would adapt to the behavior of a more massive substrate. The methods of physical vapor deposition make it possible to quickly and efficiently obtain thin films and surface layers of diverse nature in a relatively short time on virtually any substrate. The use of the magnetron sputtering method to create surface layers makes it possible to avoid substrate overheating [3].

The purpose of this work was to create a layered composite biomedical material based on a shape memory alloy NiTi and a surface layer of highly corrosion-resistant and biocompatible titanium with a high degree of adhesion between the components, avoiding the generation of heat capable of spontaneously changing the phase composition and mechanical properties of nitinol, varying the thickness of the surface layer.
2. Materials and methods

A layered composite material "nitinol substrate – a titanium surface layer" was obtained on the Torr International complex using the method of magnetron sputtering \([3\text{--}14]\) in argon gas atmosphere at residual and working pressures of \(~4\times10^{-4}\text{ Pa}\) and \(~0.4\text{ Pa}\), respectively.

For cleaning, activating and polishing the surface of the substrate, argon ions were bombarded with discharge parameters \(U_e = 900\text{ V}, \ i_e = 80\text{ mA}\) – preliminary ion etching. The temperature on the surface of the substrate in any mode did not exceed \(150\text{ °C}\). A magnetron with a target of chemically pure titanium worked at a sputtering distance of about \(20\text{ mm}\) at a constant current of \(860\text{ mA}\) at a voltage of \(400\text{ V}\) for various sputtering times (5–120 min) while rotating the substrate at a speed of 9 rpm.

As substrates used plates and wire with a diameter of \(280\text{ μm}\) of nanostructured nitinol with composition of \(55.91\text{ wt.}\%\ \text{Ni} - 44.03\text{ wt.}\%\ \text{Ti}\). The wires in the initial state were subjected to successive grinding of the surface with emery paper from 180 to 1000 grit with the final processing of GOI paste. Reducing the diameter was up to 10 microns compared to the original. The depth of the surface defects after treatment was less than 1 micron.

To determine the phase composition, an X-ray diffractometer "Ultima IV" from the company "Rigaku" was used. Surface morphology and research layered elemental composition was investigated by the scanning electron microscope (SEM) TESCAN VEGA II SBU, equipped with an attachment for energy dispersive analysis INCA Energy, atomic emission spectrometer glow discharge GDS 850A with high frequency alternating current source and Auger spectrometer JAMP-9500F company JEOL in combination with ion etching during argon bombardment at an angle of 30°. The mark of the depth at which the atomic contents of the elements reached the plateau was taken as the thickness of the surface layer using Auger electron spectroscopy. Fractographic studies were also performed on a TESCAN VEGA II SBU microscope (SEM).

3. Results and discussion

Externally, the surface layer repeats the substrate morphology (figure 1). On wire samples, traces of surface grinding are clearly pronounced - dendritic "smears". In this case, even with a small sputtering time (5 min), homogeneous films are formed that do not differ from those obtained with a longer time. According to previous studies at the beginning the layer formation has islet character, and then there is a more uniform distribution of deposited titanium on the surface, while there is a constant mixing of the sputtered atoms (which acquire additional energy when spraying from the target) with the surface atoms (substrates or previously deposited), which causes the formation of a transition layer \([5]\). However, it can be concluded that with a layer thickness of about \(100\text{ nm}\) in this work, the islands are already smoothed.

Radiographs of samples show that the phase composition of the substrate does not change depending on the duration of the deposition layer. This means that the thermal impact of the deposited particles is not enough to change the phase composition of the sensitive material. Regardless of the layer thickness, its phase composition also remains unchanged and is represented by beta-titanium, which does not correspond to the phase composition of the cast sputtered target. Thus, it can be assumed that it is the process of magnetron sputtering that contributes to the formation of this crystalline structure, which agrees well with literature data \([4\text{--}14]\).

The study of samples on the gap showed that the components of the composite does not exfoliate from each other even in the zone of destruction. Preliminary-ion etching promotes better adhesion, contributing to the formation of a uniform transition layer between the substrate and the deposited surface layer.

With an increase in sputtering time, the thickness of both the surface (consisting only of the sputtering substance) and the transition (containing elements of both the substrate and the sputtering substance) layers increases, but according to a non-linear decreasing law. A gradual saturation of the layers is observed, and the thickness of the transition layer practically ceases to increase after a mark of \(150\text{--}200\text{ nm}\).
Figure 1. SEM images of the samples surfaces, obtained at sputtering time: (a) – 5 min, (b) – 10 min, (c) – 20 min, (d) – 30 min.

4. Conclusions
Nano- and micro-dimensional surface layers of titanium on flat and wire NiTi substrates were obtained. Externally, the surface layer repeats the substrate morphology. With a layer thickness of about 100 nm and bigger the initial islands growth are already smoothed. The phase composition of the substrate does not change depending on the duration of the deposition layer. Regardless of the layer thickness, its phase composition is represented by beta-titanium.

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