Structure of tantalum coatings on NiTi substrate deposited by magnetron sputtering

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Abstract. The paper provides the results of studies of the structural-phase state of tantalum coatings prepared by magnetron deposition. The coatings were deposited on substrates made of titanium nickelide with a shape memory. The NiTi temperature during coating deposition did not exceed 100 °C. The structural-phase state of Ta was determined by X-ray diffraction at different stages of coating formation. It has been shown that at the initial stage of deposition, two-phase coatings (α- and β-Ta) are formed. The synthesis of the coating from Ta leads to the growth of interplanar distance of the B2 austenite phase in the crystallographic direction (100). The growth of interplanar spacing is caused by formation of microstresses during interaction with incident tantalum ions. The lattice parameters of the B19 'phase, responsible for appearance of the shape memory effect, do not change during deposition of the tantalum coating.

1. Introduction
Biomechanical hysteresis behavior of body tissues defines the special requirements for a similar hysteresis behavior for materials used for production of implants. Mainly, the creation of implants harmoniously functioning with the body tissues will stabilize the body functioning and create the conditions for the long-term functioning of implants in a given mode. One of such materials with physical-mechanical properties close to body tissues and exhibiting hysteresis behavior is titanium nickelide (NiTi) alloy. However, being in contact with a biological fluid, which is an aggressive medium, corrosive processes can occur on the surface of NiTi implants. In addition, nickel, present in NiTi in a structurally free state, creates the probability of a negative, carcinogenic effect of the alloy on the body.

At the same time, the medical performance of implants, stents and catheters from NiTi can be significantly improved by applying the functional anticorrosive coatings to their surfaces. For example, oxide coatings and tantalum-containing coatings (Ta) on metal implants improve their anticorrosive properties and increase chemical inertness and biocompatibility [1, 2]. The most effective method of NiTi coating application on the surface is magnetron deposition.

The goal of this work is to study the structural-phase state of tantalum coatings during magnetron formation on titanium nickelide.

2. Materials and method of research
Technical alloy NiTi with the ratio of elements: Ti - 53.46 wt. %, Ni - 46.54 wt. % was chosen as the material for research. The samples for research were cut from a massive rolled alloy plate across the
direction of rolling [3]. The samples were cut out by the method of electric-spark cutting using a brass wire. This cutting method minimizes the size of the deformed near-surface layer in the sample. The deformation layer was removed by mechanical and electrolytic polishing of the surface.

Magnetron deposition of Ta was performed on the ion-plasma unit VUP-5M at the Institute of Nuclear Physics of the Republic of Kazakhstan. Argon (Ar) served as the plasma-forming gas; the residual pressure in the working chamber was 3·10^{-5} Pa. The modes of Ta deposition (cathode current, voltage and deposition time) are indicated in Table 1. The samples had room temperature before coating deposition. The coating thickness was measured by the Rutherford backscattering method at the accelerator UKP-2.1.

X-ray structural analysis was performed on the diffractometer D8 ADVANCE ECO (Bruker, Germany) using radiation of a CuKα copper tube. The software Bruker AXS DIFFRAC.EVA v.4.2 equipped with the ICDD PDF-2 international database was used to identify the phases and to study the crystal structure. The conditions for shooting of the X-ray diffraction patterns were as follows: 40 kV, 25 mA, 2θ=20-90°, step 0.03°, standing time at a point - 1 sec. Under these shooting conditions, the depth of X-rays penetration into the material is maximum 10 µm, which makes it possible to determine the thickness of the deformed near-surface layer.

Table 1. Modes of tantalum coating deposition on the titanium nickelide samples

| Deposition mode | Deposition time, min | Coating thickness, nm |
|-----------------|----------------------|-----------------------|
| 112 W (U=400 V, I=280 mA) | 10 | 160 |
| | 20 | 300 |
| | 40 | 500 |

3. Experimental results and discussion

According to the results of the qualitative X-ray structural analysis (Figure 1 a), it was established that the matrix phase of the NiTi alloy in initial state is a compound represented by the B2 superstructure - austenite. In addition to the austenite phase (B2), the volume of the material contains a martensite phase responsible for the hysteresis behavior - B19' and the particles of secondary phases of the Ti2Ni type in a concentration of 17% of the material volume. The content of the B19' phase in the material is not more than 4%. The volume of the studied material contains metastable phase formations of Ni4Ti2OX and Ni4Ti3 with a content up to 0.2%. Also, the studied samples contain up to 0.3% structurally free nickel.

At the initial stage of coating formation, a peak with intensity of 540 imp./sec appears after 10 minutes of deposition (Figure 1 b) with the angle value of 2θ=33.659, corresponding to β-Ta with a tetragonal lattice oriented in the (002) direction. The interplanar distance d is 2.66 Å. In the range of 2θ angles from 34.871 to 40.033 an amorphous tantalum halo with a reflection oriented in the (110) direction is formed. According to the card (COD9008552), this reflex belongs to the cubic α tantalum. Another reflection at the angle of 2θ=70.5 also belongs to α-Ta, which is more ordered in the (112) direction, d=1.337 Å.

As noted in several papers, for example [4-10], formation of a tantalum coating in two different crystalline states is possible. It was also noted that β-Ta formed at the first stages of coatings synthesis is hard, brittle and thermally unstable. The thermal effect transforms β-Ta into a stable alpha-phase. It should be noted that at this stage NiTi still constitutes the main phase of the sample. The main reflex (B2) of the titanium nickelide (110) phase broadens slightly, which indicates a disorientation as a result of stresses formation in the lattice.
Further growth of the coating, deposition time of 20 minutes, leads to formation and significant growth of amorphous Ta halo (Figure 1c) and an increase in intensity of the peak characteristic of β-Ta in the (002) direction. At this stage of coating formation the β-Ta phase is the main one, however, the alpha-phase reflexes (112) are still distinguishable due to averaging of the results. In addition to Ta, the X-ray diffraction pattern of the samples with a 300 nm thick coating contains a peak of the B2 phase oriented in the (110) direction. The interplanar distance of the B2 (100) phase, relative to the value obtained at the previous stage of coating formation, remains unchanged.

When the film thickness reaches 500 nm, the deposition time is 40 minutes, the coating structure becomes almost completely amorphous (Figure 1d). The reflexes of NiTi are barely distinguishable on the X-ray diffraction pattern, while the reflections of the β-Ta phase, which is the main one, are clearly visible. Considering the increase in intensity of β-Ta, which is thermally unstable, it can be stated that the NiTi surface is not heated during deposition.

Table 2 shows the results of precision measurements of the lattice parameters of the NiTi - B2 matrix phase and the B19' phase in the NiTi samples with no coatings and with a Ta coating by the magnetron method. It can be seen that, as a result of tantalum coatings deposition, the interplanar distance of the B2 lattice in the crystallographic direction (100), the angle 2θ=29 degrees, slightly increases relative to the value in the samples with no coatings. At the same time, the interplanar distances of the B2 phase formations oriented in other directions have not changed. Also, the interplanar distances of the B19' phase formations, which are responsible for the shape memory effect appearance, have not changed either.
Table 2. Lattice parameters of B2 and B19' phases in the titanium nickelide samples

| 2θ  | 29 | 42 | 61 | 77 | 39 | 41 | 43 | 44 |
|-----|----|----|----|----|----|----|----|----|
| d, Å (NiTi) | 2.999 | 2.127 | 1.504 | 1.228 | 2.289 | 2.181 | 2.06 | 2.015 |
| d, Å (NiTi+Ta) | 3.022 | 2.127 | 1.503 | 1.227 | 2.287 | 2.181 | 2.065 | 2.018 |

The change in the interplanar distance of the B2 phase, at the initial stage of coatings formation, is probably caused by formation of microstresses during interaction with incident Ta ions. The result of such interaction can be densification of the substrate structure or formation of a solid solution of tantalum implantation, since it is known that tantalum and other elements of group 5 are able to form solid solutions with both titanium and nickel.

4. Conclusion
Thus, it has been shown that the tantalum coating formed under the magnetron deposition modes $U = 400$ V, $I = 280$ mA is two-phase. Synthesis of the Ta coating leads to increase of the interplanar distance of the B2 austenite phase in the crystallographic direction (100), which is defined by formation of microstresses on the titanium nickelide surface during interaction with incident Ta ions. The lattice parameters of the B19' phase, which is responsible for the shape memory effect appearance, do not change during deposition of the tantalum coating. It can be stated that the Ta coating does not significantly change the structural-phase state of alloy with a shape memory effect and can be used as a protective barrier for the medical products made of titanium nickelide.

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