Formation tantalum coating on NiTi surface by magnetron sputtering technique

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Abstract. The materials of research the structure and morphology of the tantalum coating on the surface of the NiTi alloy in this work presents. Tantalum was deposited by the DC - magnetron sputtering method. The influence of the energy supplied to the magnetron on the formation of the Ta-coating is shown.Changes in the structure of the coating at different stages of its formation are shown.It was found that with a significant decrease in the energy supplied to the magnetron, tantalum is deposited more uniformly. Besides the gradient of mechanical stresses in the coating is reduced.

1. Introduction
Titanium nickelide is used in medicine as an implant material. One of the requirements for such materials is maximum resistance to biologically active media [1-3].Nickel content in NiTi alloy is often the cause of implant rejection. Hence the question arises about the possibility of limiting the transition of nickel to environment. In this regard, it becomes urgent to study the methods of modifying the surface of nitinol, including the application of anticorrosive coatings. This paper discusses the results of studying the structure of a tantalum coating at different stages of formation. The coating was applied on a VUP-5M DC magnetron installation according to a previously developed technique [4-6]. Investigation of the structure of the sprayed film showed that under the selected mode, weak adhesion of the coating to the surface is formed. The reason is the large number of large structural defects in the coating material and the presence of a thin oxide layer on the substrate surface. As a solution to the problem of low adhesion, it is proposed to reduce the energy supplied to the magnetron at the initial stage of coating formation.

2. Experimental methods and material
Substrate - technical alloy NiTi with the ratio of elements: Ti - 53.46 wt. %, Ni - 46.54 wt. %. The samples were cut out by the method of electric spark cutting from a massive forged plate of Ni-Ti alloy across the rolling direction. The size of the samples for research is 15 × 2 × 0.6 mm³.

The material is a eutectic mixture with six main components. The matrix phase is a NiTi compound in the austenitic high-temperature state. The austenite phase is represented by the B2 superstructure and has a body-centered cubic lattice of the CsCl type. The B19 'martensitic phase is represented by a NiTi compound with a monoclinic lattice. The phase content in the material is not more than 4%.
The Ti2Ni secondary phase has an fcc structure in the Fd-3m symmetry space group, ordered along the main direction (227). This is the main implementation phase for the eutectic composition in the Ni-Ti system. This phase has the form of rounded particles with a diameter of 0.5 - 20 microns, located separately and in clusters (Figure 1a, b). Ti₂Ni particles make up 17% of the material volume.

The synthesis of corrosion-resistant coatings on NiTi alloy samples was carried out by magnetron sputtering on a VUP-5M direct current setup. The synthesis parameters for the tantalum (Ta) coating are as follows: plasma-forming gas - argon (Ar), residual pressure in the working chamber - 3 • 10⁻⁵ Pa. A more detailed description of the methodology for synthesizing coatings using magnetron sputtering technology is described in [7-9].

It is known that the effect of flows of charged atoms can form a complex gradient structure in the surface layer of NiTi and change the phase composition of the alloy. To determine the possibilities of reducing the effect of the gradient, the power of the current supplied to the tantalum target was selected from 14 to 112 W. Three Ta plating modes were selected: 1) - 112 W (U = 400 V, I = 280 mA - standard mode); 2) - 64 W (U = 400 V, I = 160 mA - ½ of the standard mode); 3) - 14 W (U = 350 V, I = 40 mA - ¼ from standard mode).

The phase composition was monitored on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using radiation from a CuKα copper tube. To identify the phases and study the crystal structure, the BrukerAXSDIFFRAC.EVAv.4.2 software equipped with an international PDF-2 database was used. The control of the elemental composition was carried out by the method of energy dispersive analysis (EMF) using an EMF - attachment Bruker on a scanning electron microscope HITACHI TM3030. The control of the coating thickness was carried out by the method of Rutherford backscattering of protons (accelerator UKP-2-1, INP, Kazakhstan). Surface morphology was studied by optical, scanning electron, and atomic force microscopy.

3. Experimental results and discussion

An optical image of the surface of a NiTi substrate on figure 1a shows. The structure like a uniform matrix with embedded Ti₂Ni-type particles looks. The position of such particles on figure 1b shows. In the recesses of the matrix particles with a size of up to 5 microns are located. There are traces of surface mechanical machining. Hence several types of surface irregularities must be taken into account when applying the coating. These are abrasion marks, particles and areas of the deformed matrix around them. All this to the emergence of stress concentrators can contribute.

First of all Ta at a standard power of magnetron (112 Wt) was deposited. The coating has a complex heterogeneity of the structure. The formation of β-Ta with a strongly deformed lattice phase analysis showed (a card PDF COD9008552, crystallographic direction (002), d=2,66 Å). There is a small amount of α-Ta (α card PDF COD1534932, (110), d=1,337 Å). Its crystal lattice is also deformed. A large percentage of defects into a isolated amorphous phase are separated (Figure 1c'). The heterogeneity of the coating structure the internal stress gradient enhances.
A sector with localized delamination of Ta coating on the 1c figure shows. During the formation of the coating spontaneously delamination was occurred. But in general, the coating evenly was lay. There is Ta coating the relief of the substrate replicate. There is an increase in the contrast of large defects and irregularities of the substrate surface.

Taking into account the inhomogeneity of the substrate surface and the highly defective structure of Ta, the presence of stress concentrators at the substrate / coating interface can be assumed. The destruction of the Ta coating is provoked by the presence of stress concentrators.

The inhomogeneity of the substrate surface is due to the presence of technological particles. Therefore, it is impossible to influence it. But it is possible to reduce the number of defects at the boundary of materials and in the coating itself.

In magnetron deposition, the coating by the impingement of ionized atoms onto the surface is formed. A decrease in ion energy the coating formation mechanism will change. For this, the energy supplied to the magnetron was reduced. Coatings with magnetron energies of 64 and 14 W were synthesized. Reducing the energy to 64 W to a change in the phase composition did not lead. At 14 W, the amount of amorphous phase to a minimum decreased. The main phase $\alpha$-Ta.

![Figure 2. SEM image of NiTi alloy surface after Ta deposition: a - at 112 W, b - at 64 W, c - at 14 W](image)

In Figure 2a the surface of the coating at 112 W formed is shown. Areas with disturbance of uniformity of coverage are circled. These defects have the shape of rounded notch. At 64 W, the defect size is reduced. But their number by an order of magnitude is increasing. Defects over the entire surface are located (Figure 2b).

![Figure 3. AFM image of the surface of a Ta film 50 nm thick: a - × 35000, b - × 140,000](image)

The surface formed at 14 W Figure 2c shows. A significant decrease in the size of defects is observed. The number of defects is 2 times less than with the standard application method. Spontaneous detachment of tantalum does not occur.
Next, the surface of the coating was examined at various stages of formation. The coating was formed at a magnetron power of 14 W. The surface of a Ta film with a thickness of $\leq 50$ nm (first stage), 180 nm (second stage), and 700 nm (third stage) is considered. With a further increase in thickness, the surface morphology does not change.

At the first stage, the Ta-coating looks like a discontinuous amorphous film (Figure 3). As the thickness increases, signs of a crystalline structure appear.

The magnetron synthesis of coatings is characterized by the growth of crystallites in the direction perpendicular to the surface. This leads to the formation of a columnar structure. Figure 4 shows the surface of a Ta-coating with a thickness of 180 nm (second stage). The columnar structure is clearly visible. Crystallites at the second stage of film formation are sparse (Figure 4b). Therefore, they can be easily distinguished.

![Figure 4. AFM image of the surface of a Ta film 50 nm thick: a - 10×10μm, b - 2×2μm](image)

At the third stage, with a thickness of more than 700 nm, the film acquires a more continuous character (Figure 5). This is due to the formation of new crystallites between the crystallites of the first stage and above them. This leads to the growth of the amorphous component.

In Figures 4 and 5, the red line outlines the areas with discontinuity of the film. With an increase in the thickness of the coating on flat areas, these holes disappear. Holes remain longer in the vicinity of process particles and large defects on the substrate surface.

![Figure 5. AFM image of the surface of a Ta film 700 nm thick, 10×10 μm](image)

From the above, it follows that with the minimum energy supplied to the magnetron, Ta sits more evenly. A more uniform film can objectively better reduce the release of Ni to the environment.

4. Conclusion
Various modes of magnetron deposition of Ta on NiTi alloy surface are considered. The possibility of phase composition regulating of Ta-coating during magnetron deposition is shown. Reducing of the magnetron energy allows to get more uniform coating.

Acknowledgements
The work was carried out within framework of the grant funding project of Ministry of Education and Science of the Republic of Kazakhstan No. AP08052572.

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