X-Ray Diffraction Studies of the Molybdenum Thin Films Magnetron-Sputtered on the TiNi Alloy Surface[1]

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Abstract – The structural-phase conditions of the subsurface layers of NiTi with the molybdenum coatings with the thickness of 200÷500 nm, are sputtered by the magnetron sputtering technique has been investigated by the method of X-ray diffraction analysis. The material of coating is corresponds to single-component chemical composition, single-phase condition and one is found in the crystal state with the *BCC*-structure typical for molybdenum. The special features of thin atomic crystal structure of the material of coating and the substrate, which are adjacent to it has been investigated. It is established that the crystal *BCC*-structure of molybdenum in the coating has the oriented microdeformations of the different signs: compression in the plane of surface and tension along the normal to the surface. In the region of under the coating the crystal *BCC*-structure of the TiNi has the increased lattice parameter.

1. Introduction

Investigation of the influence of the surface modification of materials and/or presence on it of the coatings, which are characterized by chemical composition, by thickness and by the method of their forming, and also the study of the properties of coatings is actual at present.

It is necessary to use of materials in medicine to keep mechanical properties of material, to protect material and its environment from the harmful interreaction. TiNi is one of the claimed materials for medicine at present. TiNi is known for its physico-mechanical and physico-chemistry properties, such as the shape memory effect and super-elasticity. It is necessary when the TiNi or TiNi-based alloys are used for the medical purposes to keep its function properties (superelasticity) or shape memory effect, at the same time, to improve its corrosion resistance. There are numerous papers [1, 2] in which shown that the realization of this objective is possible without a change of the chemical composition in the volume of alloy, leads to a change in the temperature intervals of martensite transformation and, as a result, the transformation temperatures are remove. In this case, the modification of surface properties of material is effective, it leads to a change of chemical composition, atomic crystal structure of the basic phases of alloy and microstructure in the thin subsurface layer of material after ion implantation or electron beams treatment [1].

Among the tasks, connected with the surface modification of the TiNi and TiNi-based alloys, special position occupies the problem of developing protective layers on surface of the TiNi in the form of the thin films, which, simultaneously, would prevent the ion yield of metals into the biomedium, they did not lead to the decrease of the effects of super-elasticity or memory of form, and they would possess the high parameters of adhesion, corrosion resistance, biocompatibility.

Most attractive for the solution of this complex problem is the magnetron sputtering technique of coatings and its combined with the ion implantation and/or electron beams treatments to achieve the formation of uniform coatings with the necessary chemical composition and a thickness [1, 2].

The purpose of this work is the study of structural-phase conditions of the subsurface layers of TiNi with molybdenum coatings are sputtered by the magnetron sputtering technique.

2. Experiment

The investigated $Ti_{49.5}Ni_{50.5}$ alloy was prepared from iodides titanium and nickel of grade NO using six-fold arc remelting. Samples 1×15×15 mm in size were spark cut from the ingot. Before the measurements, the samples were annealed at 1073 K for 1 h in vacuum higher 10^{-3} Pa and then furnace cooled. The surface layer mechanically and electrolytically polished.

The obtained samples were divided into two groups. To one of the sides of samples from the first group were s sputtered the coatings from chemically pure Mo with a thickness of 200 nm, and coatings from the same element on the surfaces of samples from the second group had in ~2 time great thickness.

Magnetron sputtering was carried out on the VU-1BC (RETC at ISPMS SB RAS) in vacuum 10^{-4} Pa.

The thickness of coatings was controlled according to the data about the chemical composition in the surface layer, by the obtained method of Auger-electronic spectroscopy (AES).

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Investigation of the structure parameters have been studied by the methods of X-ray diffraction analysis on the DRON-7 diffractometer using a symmetrical and asymmetric schemes of Bregg–Brentano (Co–K_α radiation with the wavelength $\lambda_{\alpha 1} = 0.178892$ nm).

The lattice parameters a_{Mo} and a_{B2} determined by precision method with the construction of the extrapolation graph of dependence on the angular function Nelson–Ryles [$\Phi(\Theta)$].

For development and evaluating the elastic-stressed condition were removed the diffractograms using a asymmetric scheme with the direction of primary beam (angle α) from 3 to 12° and were built the graph of the dependences $a_{hkl}(\sin^2\Psi)$, where $\Psi = \Theta_{hkl} - \alpha$ is the angle between the normals to the reflecting plane (*hkl*) and to the surface of pattern [2]. The amount of the deformation of the crystal *BCC*-structure of the material of coating along the selected direction was calculated using this formula:

$$\varepsilon_\psi = \frac{a_\psi - a_0}{a_0},$$

where a_0 is the lattice parameter of Mo according to the data [6]. The value of microstresses was calculated according to the formula

$$\sigma_\psi = \frac{a_\psi - a_0}{a_0}\frac{E}{\upsilon},$$

where E is the Young's modulus and v is the Poisson's ratio.

The separation of the contributions from the microdistortions of lattice and sizes of the coherent-scattering region to the physical broadening of diffraction lines for coatings was carried out by the approximation method [2, 5]. Graphing was conducted in the coordinates

$$\left[(\delta(2\Theta) - \frac{\delta^2(2\Theta)_{ins}}{\delta(2\Theta)}\frac{\cos\Theta}{\lambda}\right]^{1.5} \text{ from } \left(\frac{\sin\Theta}{\lambda}\right)^{1.5},$$

where $\delta(\Theta)$ is the measured half-width of the diffraction line and $\delta(\Theta)_{ins}$ is the instrumental half-width of the diffraction line. The degree of extrapolation function was selected as being equal to 1.5, because of experimental diffraction profiles had the intermediate form between the Lorenz and Gauss functions.

3. Experimental results and discussion

According to data of OES for all groups of patterns the coating consists only of Mo without any admixtures, and its thickness in the first group of patterns was 200 nm, and in the second group of patterns was 500 nm.

The analysis of the diffractograms of patterns with the Mo coatings showed that the subsurface layer of material contains two phases. One of them consists, apparently, of Mo which is found in the crystal condition with the *BCC*-structure and the second phase is the B2-phase of TiNi. Figure 1 shows the typical X-ray diffraction patterns with the Mo coatings which were obtained using a symmetrical (*a*) and asymmetric schemes (*b*).

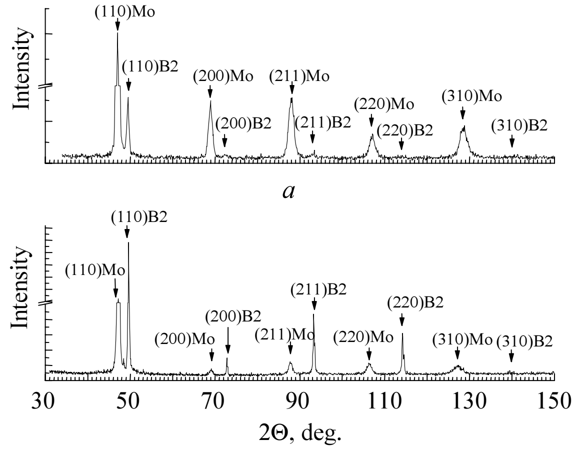

Fig. 1. The typical X-ray diffraction patterns with the Mo coatings of 500 nm thickness which were obtained using a symmetrical (*a*) and asymmetric schemes (*b*)

It should be noted that on the diffractograms, obtained in the asymmetric surveys, with the small glancing angle, the decrease of the intensity diffraction lines of B2-phase and, respectively, the growth of the intensity diffraction lines of Mo was observed. This result is correlation with result obtained according to AES. The chemical composition and structural-phase condition of coating correspond to the single-component *BCC*-structure of molybdenum, distributed on the pattern surface in the form of uniform thin layer. In addition, the width of diffraction lines the profiles of the *BCC*-phase of molybdenum considerably exceeds the width of diffraction lines B2-phase, and on the diffractograms was not discovered the presence of diffraction lines from the second phases.

Figure 1 illustrates the typical extrapolation dependences of the lattice parameters of Mo and B2-phases in the test samples, obtained using a symmetrical scheme.

Line *1* in Fig. 2 is the extrapolation dependence of the a_{B2} parameter for the diffraction lines of B2-phase of TiNi.

The value of the lattice parameter of B2-phase, obtained from these dependences, composes $a_{B2} = 3.0143 \cdot 10^{-10}$ m and in all patterns with the coating considerably exceeds this value in the virgin sample without the coating ($a_{B2} = 3.013 \cdot 10^{-10}$ m).

A noticeable difference of the values of the lattice parameter of B2, measured in the direction of normal to the surface of model, in the surface layer with the coating and without it, means that the crystal structure of B2 of matrix phase is characterized by the increased lattice parameter in the region near-boundary with the coating.

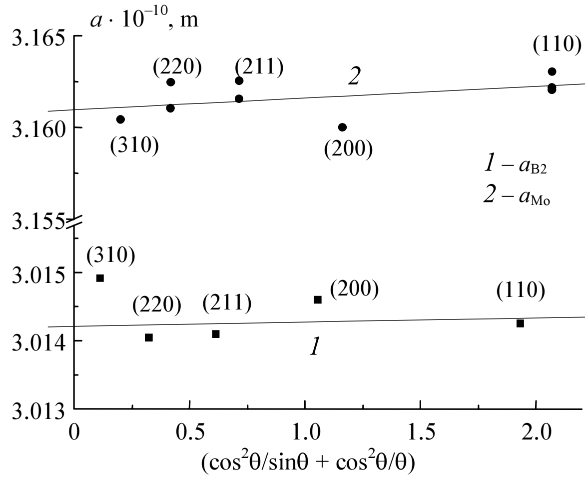

Fig. 2. The extrapolation dependences the Mo and B2-phase of TiNi lattice parameters on $\Phi(\Theta)$, calculated in the samples with the molybdenum coatings of 500 nm thickness

This conclusion is confirmed by the fact that on the X-ray diffraction patterns, the value of the measured in the direction of normal to the surface lattice parameter of B2-phase increased.

Line *2* in Fig. 2 is the extrapolation dependence of the a_{Mo} parameter for the diffraction lines of *BCC*-phase of Mo.

The analysis of these dependences, are built for the samples with the molybdenum coatings of different thickness, showed that the lattice parameter of *BCC*-structure is correspond to $a = 3.1606 \cdot 10^{-10}$ m, it is on the 0.45% more than tabular value [6].

It was shown in [2] that in the special case of cubic structure the definition of microdeformations and connected with them microstresses of the first kind, can be produced on the asymmetric schemes with the $d_{hkl}(\sin^2\Psi)$ plots or $a_{Mo}(\sin^2\psi)$ plots. The latter makes it possible to use for the analysis of internal stresses and calculation of the microdistortions of lattice the diffractogram, obtained over a wide range of angles from ~20 to ~165°, with a constant angle α. It should be noted that for all models with the different glancing angles α, the linear dependence $a_{Mo}(\sin^2\Psi_{hkl})$ has incline. It indicates that in the molybdenum coatings happen the microdeformations and connected with them microstresses of the first kind.

According to obtained data, the molybdenum coating is in the state of compression in the plane of surface and tension along the normal to the surface for all samples.

The values of microdeformations and microstresses in the molybdenum coating are given in the Table.

The Table shows, that the average value of microdeformations and microstresses of the 1st kind connected with them in the molybdenum coatings, does not depend on the thickness of the coating.

One of the reasons for the distortion of the crystal *BCC*-structure of molybdenum in the coating can be a difference in the coefficients of thermal expansion material of coating and TiNi. According to literature data, the linear coefficient of the thermal expansion of B2-phase of TiNi composes value $\alpha \approx 13 \cdot 10^{-6}\ \mathrm{K}^{-1}$ and for molybdenum $\alpha \approx 5.6 \cdot 10^{-6}\ \mathrm{K}^{-1}$ (values are given at the temperature $T \approx 300$ K) [7]. Because of this, during cooling of sample after sputtering, the base layer (TiNi) is compressed more rapidly and compresses molybdenum film in the direction of tangent to the surface. As a result, coating is extended perpendicular to surface, which is evinced by an increase of the lattice parameter in this direction.

Table. Values of microdeformations and microstresses of the 1st and 2nd kind for the samples with the Mo coatings

Mo	E, GPa [7]	ν [7]	ε^{I}, %	σ^{I}, GPa	ε^{II}, %	σ^{II}, GPa
200 nm	300	0.31	±0.51	±4.94	0.35	3.8
500 nm	300	0.31	±0.52	±5.03	0.43	4.2

From the analysis of the approximating graph of the dependence $\left[(\delta(2\Theta) - \frac{\delta^2(2\Theta)_{ins}}{\delta(2\Theta)}\frac{\cos\Theta}{\lambda}\right]^{1.5}$ on $(\sin\Theta/\lambda)^{1.5}$, it was revealed that the broadening of the diffraction lines of the *BCC*-structure of the coating (with a both thickness of 200 and 500 nm) is caused by the presence of the microdeformation, connected with the stresses of the 2nd kind.

Coherent-scattering region (CSR) exceed about 100 nm (determined according to reflexes $(110)_{Mo}$ and $(220)_{Mo}$ and is not introduced the contribution to the physical broadening of diffraction lines. The Table shows that the value of microdeformations and microstresses of the 2nd kind in the molybdenum coatings and weakly increase with an increase of its thickness.

4. Conclusion

The structural-phase conditions of the subsurface layers of NiTi with the molybdenum coatings with the thickness of 200÷500 nm, are sputtered by the magnetron sputtering technique has been investigated by the method of X-ray diffraction analysis. The special features of thin atomic crystal structure of the material of coating and have the substrate, which are adjacent to it has been investigated.

Thus, it is possible to formulate the following conclusions.

1. The material of coating is corresponds to single-component chemical composition, single-phase condition and one is found in the crystal state with the *BCC*-structure typical for molybdenum.
2. In the region of under the coating the crystal *BCC*-structure of the TiNi has the increased lattice parameter.
3. It is established that the crystal *BCC*-structure of molybdenum in the coating has the oriented microdeformations of the different signs: compression

in the plane of surface and tension along the normal to the surface.

4. It is revealed that the coherent-scattering region (CSR) exceed about 100 nm and is not introduced the contribution to the physical broadening of diffraction lines. It is caused by the presence of the microdeformation, connected with the stresses of the 2nd kind.

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