Adhesion Strength of Magnetron Sputtered Molybdenum and Tantalum Thin-Films on TiNi Substrate[1]

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Abstract – Estimation methods of hardness, adhesion strength, morphology of surface, and also chemical analysis of Mo and Ta thin-films covered on TiNi substrate by magnetron sputtering with different thickness are considered. It is shown that magnetron sputtering of thin-films on TiNi substrate resulted in increase of microhardness of near-surface area of material with thickness ≈ 1 µm. Mechanical and adhesion strength of coatings depends on chemical composition of film and substrate, as well as on thickness of film. Specimens with Ta thin-film coating demonstrated two main mechanisms of destruction of the coating, namely particle exfoliation of coating and after that full exfoliation. By the way, specimens with Mo thin-film coating demonstrated much more adhesion strength for "film-TiNi substrate" system, but specimens in question demonstrated only particle exfoliation of coating under equal force of load.

1. Introduction

Researches of nanostructural coverings acquire great value now in connection with their increasing use in applied problems. In a number of works [1, 2] it is shown, that in cases when it is necessary to keep functional properties of a material and to protect a material from an aggressive environment, it is rather effective to use nano- and submicrocrystalline coverings of various chemical compounds. There are certain predetermined requirements for such coverings. For example, if used in medicine they are supposed to possess high corrosion firmness, tolerance and biocompatibility to biotissues [3–5]. Therefore, the problem of creation of barrier layers or coverings on a surface TiNi is of great importance. Since the relief on a TiNi surface can essentially vary as a result of structural martensite transformations, at formation of coverings for such material it is necessary to give special attention to adhesion strength of a covering and ways of its increase.

The purpose of the given work is to study the laws of formation of the alloyed layers on a TiNi surface, possessing high adhesion strength and providing the increase of physicomechanical, physicochemical characteristics.

2. Materials and research methods

Samples for research are made of $Ti_{49.5}Ni_{50.5}$ alloy. The blanket was cleaned by mechanical polishing and, further cleaned electrolytically in a solution of acids of 75% CH_3COOH – 25% $HClO_4$ in a current 10–12 s at pressure 30–35 V.

Magnetron sputtering was done on the plant by magnetron dispersions Leibold Z-80 (Germany), targets from chemically pure Mo and Ta of 70 mm diameter were used, distance from a target to the sample was 70 mm, substrate temperature was constantly maintained at 200 °C, dusting speed was equal to 10 micron/h, pressure Ar at dusting $P = 0.3$ Pa, magnetron current $J = 2.5$ A, pressure $U = 270$ V, pressure on substrate U =0 V.

The study of morphology of a surface and definition of its structural elements was done by methods of computer optical microscopy on Axiovert 200 MAT microscope.

The study of chemical compounds of the surface, as well as the control of a thickness of the covering was done by the method of Auger analysis (AA).

One of the most important characteristics of coverings is durability of their coupling with a substrate. For quantitative definition of size of adhesion, we use methods of direct separation of a film from a substrate or methods of a shift in relation to the substrate [3, 5, 6].

Estimation of adhesion strength of thin-film coverings was done by scratch-testing methods in CSEM Micro Scratch Tester measuring equipment. The analysis of the structure of the material around and in scratches was done with use of both optical metallography and raster electronic microscopy on LEO EVO 50 microscope.

The principle of scratch-testing method lies in the creation of a sample of a longitudinal scratch at uniform movement of a diamond cone (Rockwell indenter) and at constantly increasing normal loading on a surface (Fig. 1). In the given work a scratch was put on a surface of investigated systems (covering-substrate) by Rockwall indenter with constant speed $V = 9.63$ mm/mines. Force of loading effecting on indenter, increased linearly from 0 to 6 H. As a result of constantly effecting made effort at cave-in indenter the material under it collapsed.

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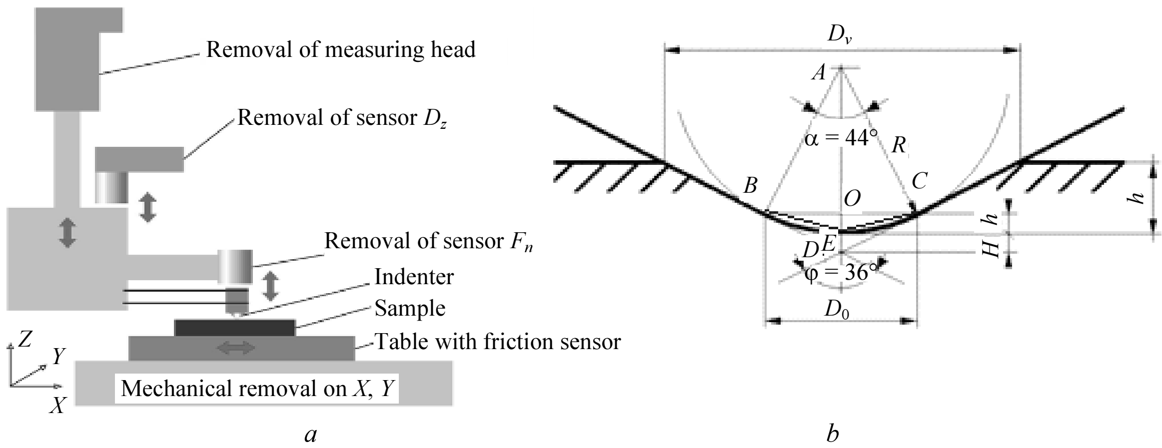

Fig. 1. Schematic image: *a* – installations Micro Scratch Tester; *b* – Rockwell indenter [7]

Rockwell indenter represents a diamond cone of a certain form and dimensions, converting in the top to a spherical segment (Fig. 1, *b*). As a result of indenter actions the scratch with the characteristic form, depending on the indenter form will be formed.

Using the given technique we started with the assumption, that coupling with a substrate provides a coat layer directly adjoining to a substrate. Due to this fact, the following forces and durabilities of coupling were defined at movement of the indenter through a covering [5, 8].

Durability of coupling of a film with a substrate was calculated using the following formula [5]:

$$P_{adh} = \frac{F_{adh}}{D\,\upsilon}, \quad (1)$$

$$F_{adh} = F_N - F_f, \quad (2)$$

where F_{adh} is the force of coupling; D is the width of a scratch; υ is the speed of indenter movement on the sample; F_N is the normal loading force on indenter at carrying out of indentation; F_f is the force of a friction arising at indenter movement on a surface of the sample.

In order to take the form of indenter parameters into consideration D should satisfy the following conditions:

$$D = \begin{cases} D_0, \, h \le h^*, \\ D_V, \, h \ge h^*, \end{cases} \quad (3)$$

where D_0 is if the form of the indenter in the form of a sector segment; D_V is if the form of the indenter in the form of the truncated cone; h is the depth of immersing indenter; h^* is the depth of transition from one formula of calculation D to another.

Experimental data were processed with use of standard software package of the device before we obtained the dependences of change of normal force, depth of penetration of indenter in a material, forces of friction and force of coupling, factor of friction and acoustic issue from distance along a scratch formed at indenter moving. An example of dependences obtained in the experiment for the sample made of TiNi with a covering made of Ta of 200 nm in thickness is presented in Fig. 2.

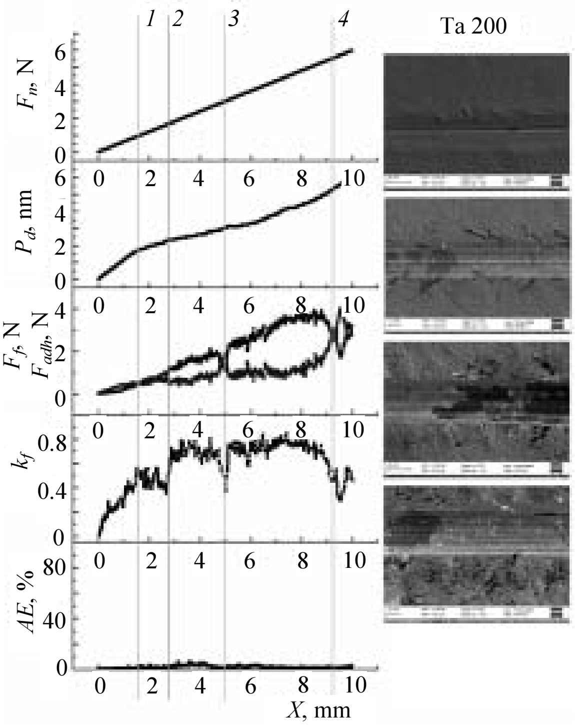

Fig. 2. Dependences of change of the following parameters F_n, P_d, F_f, F_{adh}, k_{tr}, AE during the indenter movement on the TiNi sample with a covering from tantalum of 200 nm thickness

3. Results and discussion

The analysis of structure of blankets by AA method has shown, that the thickness of each covering of the first group makes up (200 ± 30) nm, the second – (500 ± 30) nm, and below these layers a lengthy intermediate layer settles down containing ≈ 20 at % of oxygen and ≈ 10 at % Carbon (Fig. 3). It is established, that thin films from Mo and Ta have homogeneous (in thickness and in area of a covering) chemical compound corresponding to the chemical compound of cathodes.

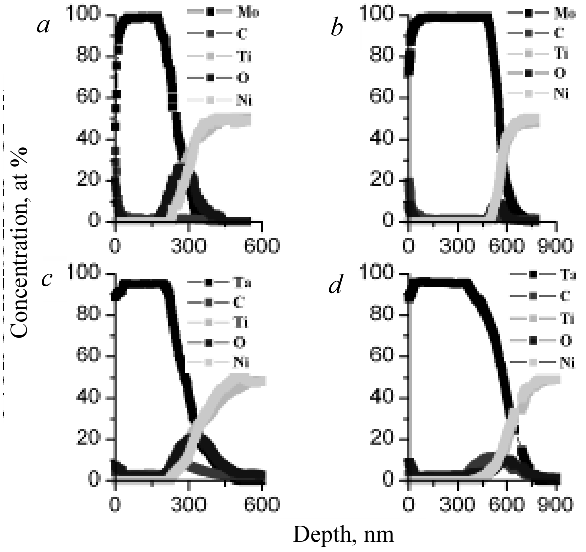

Fig. 3. Distribution of chemical elements in surface layers of TiNi alloy with coverings from Mo with the thickness of 200 (*a*) and 500 nm (*b*), coverings from that of the thickness of 200 (*c*) and 500 nm (*d*)

In Figure 4 metallographic pictures of surfaces of TiNi samples are illustrated – initial electrolytic polished surface and the surface after the drawing of coverings from Mo and Ta with change of their thickness (200 and 500 nm).

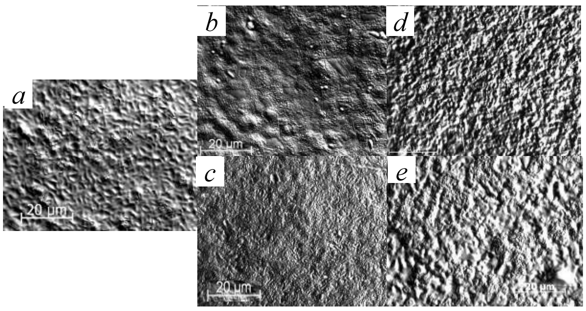

Fig. 4. Metallographic pictures of a surface initial polished TiNi (*a*), coverings from Mo with the thickness of 200 (*b*) and 500 nm (*c*), coverings from Ta with the thickness of 200 (*d*) and 500 nm (*e*) on a substrate from TiNi

It can be seen, that the surfaces of the samples with coverings of 200 nm in thickness have more smooth relief, than initial one or a surface with coverings of 500 nm in thickness. Detailed metallographic analysis has shown that morphology typical for the initial surface of the material of the substrate, remains after drawing of coverings of both types, irrespective of their thickness. Surfaces of the samples compared in Fig. 4 have identical phase contrast and differ only in roughness caused by technological parameters of the method used in work of drawing of the covering. In other words, data of metallographic analysis indirectly show, that both kinds of coverings have homogeneous microstructure, identical thickness, which does not depend on the grade of a chemical element or on the size (on depth) of the put layer.

Electronmicroscopical images of areas of the beginning of destruction of films from Ta of 200 and 500 nm in thickness at scratching a diamond pyramid (Rockwell indenter) are presented in Figs. 5, *a* and *b*, correspondingly. The analysis of these images shows, that samples with coverings from Ta have shown two basic mechanisms of destruction of a covering, namely – partial exfoliation of the coverings with its full exfoliation afterwards.

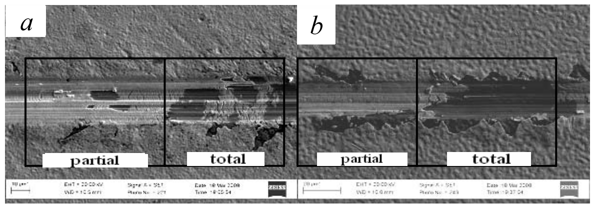

Fig. 5. Metallographic pictures of destruction at scratch-testing of coverings from Ta with the thickness of 200 (*a*) and 500 nm (*b*) on a substrate from TiNi

On the contrary, samples with a covering from Mo, and thickness of 200 and 500 nm, have shown only partial exfoliation of the covering that is well shown in Fig. 6 where we can see only origin of cracks in a scratch.

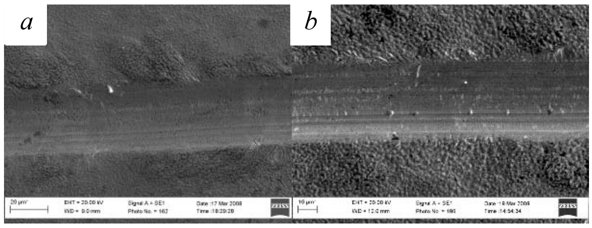

Fig. 6. Metallographic pictures of destruction at scratch-testing of coverings from Mo with the thickness of 200 (*a*) and 500 nm (*b*) on a substrate from TiNi

In Figure 7 the curves characterizing change of forces of coupling F_{adh} with a substrate from TiNi, calculated under formula (2) for films from Mo (Fig. 7, *a*) and Ta (Fig. 7, *b*) depending on length of a scratch are represented. From comparison of these dependences it follows, that on the sites of identical extent, F_{adh} for coverings from Mo is higher than for coverings from Ta. On the contrary, coverings from Mo possess a higher adhesion strength, than coverings from Ta.

In Table 1 values of critical force of loading, forces of coupling, strength of coupling, etc. system "covering-substrate" at which the formation of cracks or peeling of the covering occur are shown. From comparison of data about sizes of forces of coupling (Fig. 7) follows, that the first separations of a covering from Ta of 200 nm thickness have occurred on the distance of 2.72 mm at critical force of loading

1.657 H, and at the covering from Ta with the thickness of 500 nm – on distance of 1.12 mm at critical force of loading 0.655 N. Critical strength of coupling for a covering from Ta of 200 and 500 nm thickness has made up to 240 and 310 MPa, correspondingly.

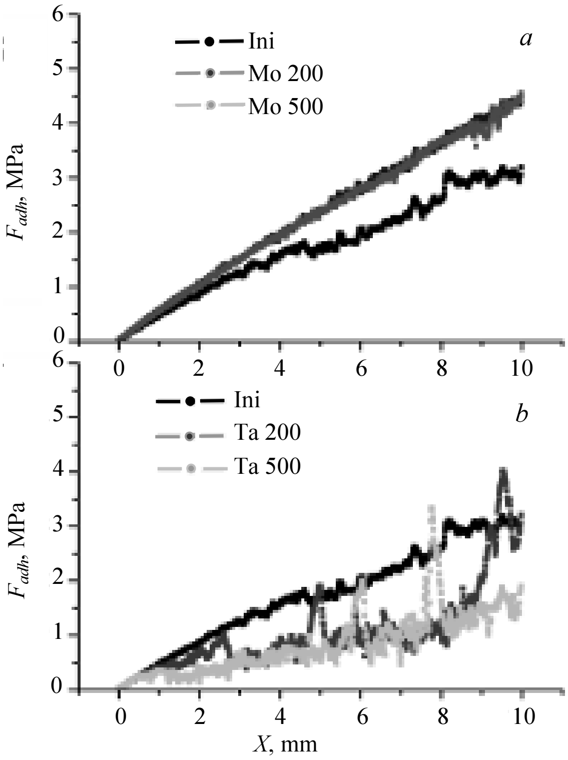

Fig. 7. Change of force of coupling of thin-film coverings from Mo (*a*) and Ta (*b*) with a substrate from TiNi depending on the length of a scratch

Table 1. Values of critical sizes of coupling of system "covering-substrate"

Material	Ta 200 nm	Ta 500 nm
Distance from the beginning of scratch up to the end of break *L*, mm	2.72	1.12
Critical force of loading F_N, N	1.657	0.655
Penetration depth *Pd*, μm	2.7	0,4
Critical force of adhesion F_{adh}, N	0.79	0.35
Constant of friction k_f	0.47	0.55
Critical adhesion strength P_{adh}, MPa	240	310

As for the coverings from Mo, the sizes of critical force and critical strength of coupling were impossible to estimate, as along all scratch separations of a covering from Mo were not observed, by the position of which, we define values of parameters of adhesion in a point of a primary separation of the covering from the substrate, and then count their critical values. Smaller durability of coupling of a covering from Ta with a substrate can also be connected with increase of level of micropressure owing to structure crushing [2, 5, 8].

4. Conclusions

1. It is established, that coverings from Mo and Ta have homogeneous in the thickness and the area of covering chemical compound corresponding to the chemical compound of cathodes; and below these layers there is an intermediate layer containing ≈ 20 at % O and ≈ 10 at % C.

2. The technique of an estimation of the adhesive strength, based on association of methods of scratch-testing that take into account the indenters geometry, optical and raster electronic microscopy is adapted.

3. Samples with a covering from Ta (thickness of 200, 500 nm) have shown two basic mechanisms of destruction of a covering (partial and full exfoliation) whereas samples with a covering from Mo, thickness of both is 200 and 500 nm, have shown only partial exfoliation of the coverings in the form of cracks in a scratch. Samples with a covering from Mo, on the contrary, have shown high adhesive durability and separations were not observed throughout all scratch covering.

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