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Investigation of Mechanical Properties of Oxide Films on the Base Nb, Ta and Zr

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Abstract. The mechanical properties of anodic oxide films of Nb, Ta and Zr were studied by the nanoindentation method. Anomalously high elastic recovery after deformation was observed for oxides with thickness of 20 nm. An analogue of this behavior can be elastic membrane fixed on soft base that does not prevent the membrane from bending. Increase of the oxide thickness to 300 nm reduced the effect associated with the high elasticity of oxide and easy deformation of the soft metal substrate, and was accompanied by an increase in the plastic component of deformation, which is similar to the behavior of ceramic materials with low elastic and significant residual plastic deformation.

Introduction

Currently, the most interesting materials for produce of medical implants are Nb, Ta and Zr, which significantly surpass Ti in terms of resistance to corrosion processes. High chemical stability of these metals is ensured by oxide films that are arbitrarily formed on their surface [1] and have high continuity, adhesive and mechanical strength [2]. The protective properties of such films can be enhanced by anodic oxidation, which provides a forced increase in their thickness when exposed to high external electric fields in gas or liquid environment [3]. However, the effective use of oxides based on Nb, Ta and Zr requires a thorough study of their physical properties, which will allow them to be used to create medical implants that can maintain their parameters during prolonged contact with living tissues without harming the latter.

The difficulty in studying of mechanical properties of thin oxide films with a thickness of 10–100 nm has long been determined by the lack of methods that allow such studies to be carried out, in particular, to measure the elastic modulus and hardness of oxides. The emergence of nanoindenters in combination with methods for analyzing such experimental results has opened up new opportunities in the study of both micro- and nanoobjects [4]. In modern devices, the indenter movement is measured with an accuracy of up to 0.1 nm, which allows testing at loads less than 10 μN and imprint depths of several nanometers [5].

Materials and Methos

The test samples were made of metal (Nb, Ta and Zr) plates with a thickness of 500 μm. To remove impurities and relieve mechanical stress, the metal plates were annealed in a vacuum ($P = 1\cdot10^{-4}$ Pa) for 0.5–1.0 hour at $T = 2000$ ºC. The annealing temperatures did not exceed the recrystallization temperature and the temperature of polymorphic transformations of the annealed metals.

To form of amorphous oxide film on the metals surface, the anodic oxidation technique was used [6]. The sample (anode) and tantalum foil (cathode) were placed in a cell with electrolyte (0.01 % aqueous solution of orthophosphoric acid). Anodic oxidation was carried out in two successive modes: galvanostatic and voltstatic. In the galvanostatic mode, a constant current density $j = 1$ A/m^2

was maintained with voltage changing in the range from 0 to 200 V. The magnitude of the anodizing voltage U_a determined the oxide film thickness [7]

In the voltstatic mode, a constant voltage was maintained on the sample, the current at this time decreased due to increase in the oxide stoichiometry and increase in its electrical resistance. When the current decreased by 10 - 15 times, the process stopped.

Hardness tests were carried out on Nano Indenter II nanohardness meter from MTS System (USA) with a Berkovich diamond indenter in the form of triangular pyramid. A capacitive sensor was used to measure the indentation depth, loading was carried out up to value of 15 mN, the loading rate was from 0.0001 to 20 mN/s. Before taking measurements, the device and the sample were thermally stabilized. The values of hardness H and elastic modulus E of the samples surface layer were determined using the Oliver-Pharr method [4]. In order to avoid the influence of substrate, the indentation depth during coating testing did not exceed 10 % of the coating thickness.

Experimental Results

At first the elastic modulus and hardness were studied for oxide films obtained by anodic oxidation of niobium and tantalum. After vacuum annealing at T = 2000 °C, the metal substrates had a coarse-grained structure in the form of monoblock grains ranging in size from 200 to 2000 µm. X-ray structural studies showed the presence of texture with orientation [110] in the plates of both metals. The formation of oxides was carried out to thicknesses of 20, 100 and 300 nm, the width of oxide-metal transition zone did not exceed 3 nm [8].

The results of amorphous niobium oxide films testing for thicknesses of 20, 100 and 300 nm at low loads on the indenter (up to 0.5 mN) are shown in Fig. 1.

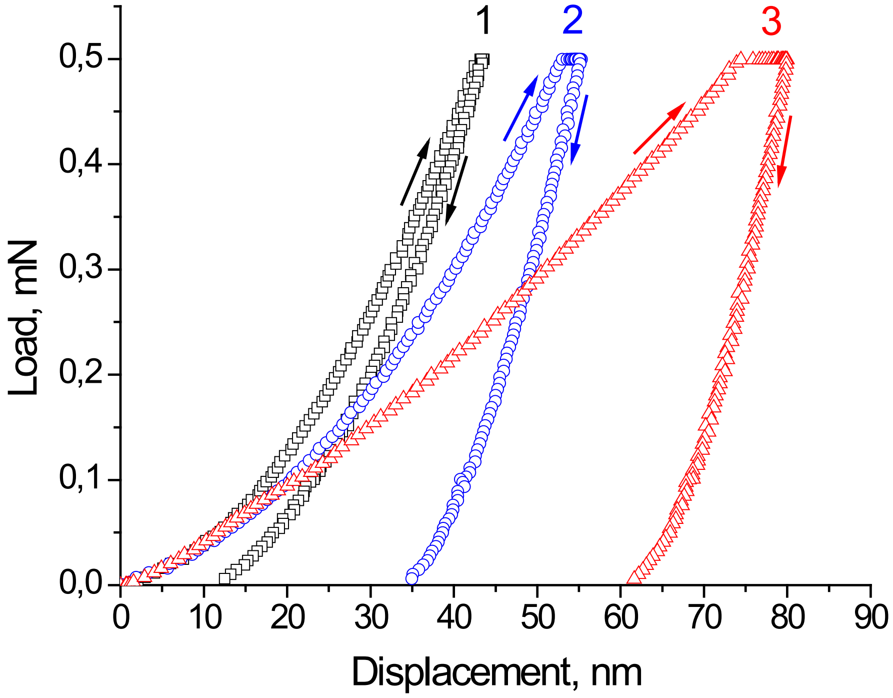

Fig. 1. Loading curves for Nb_2O_5/Nb systems with oxide films of thickness: 1 – 20 nm, 2 – 100 nm, 3 – 300 nm

For oxide with layer thickness of 20 nm, an abnormally high elastic recovery after deformation was observed. Curve (Fig. 1, curve 1) practically returned to the starting point when the load was removed, which is not typical for ceramic materials, which usually demonstrate a fairly high residual deformation. This result for thin amorphous oxide film can be explained by its higher strength, hardness and elasticity, compared to metal substrate. An elastic membrane fixed on soft base that does not prevent the membrane deflecting and can be an analogue of such behavior. At increase of oxide thickness the effect of soft niobium substrate decreased. The elastic modulus for thick oxides decreased, and contribution of the plastic component to oxide deformation increased.

The thin oxide demonstrated the ability to elastic deformation to fairly high values. The observed value of deflection without failure was almost twice the thickness of oxide film.

Despite the almost complete absence of plastic deformation under the selected loads, the loading diagram for the sample with a thin Nb_2O_5 layer had a nonlinear character, which was associated with the rounding of the Berkovich indenter tip (r ~ 150 nm), that is, with the transition from the indentation of spherical body at the initial moment of deformation to the indentation of triangular pyramid at subsequent stages. An increase in the oxide thickness to 100 nm and, especially, to 300 nm reduced the effect associated with the high elasticity of the oxide and the slight deformation of the soft metal substrate, and was accompanied by increase in the plastic component of the deformation (Fig. 1, curves 2 and 3), that is similar to the behavior of ceramic materials, which usually demonstrate low elastic and significant residual plastic deformation.

With load increasing to values of 10 mN, step was observed on all three dependences, which characterized the free movement of the indenter without increasing the applied load (Fig. 2). Its beginning approximately corresponded to the initial thickness of the oxides, especially for samples with a thick oxide coating, when the effect of oxide bending into the metal substrate was significantly reduced. The appearance of step on the dependence was associated with the destruction of oxide layer by indenter and its advancement into metal substrate with gradual strengthening of material at the point of contact with the indenter.

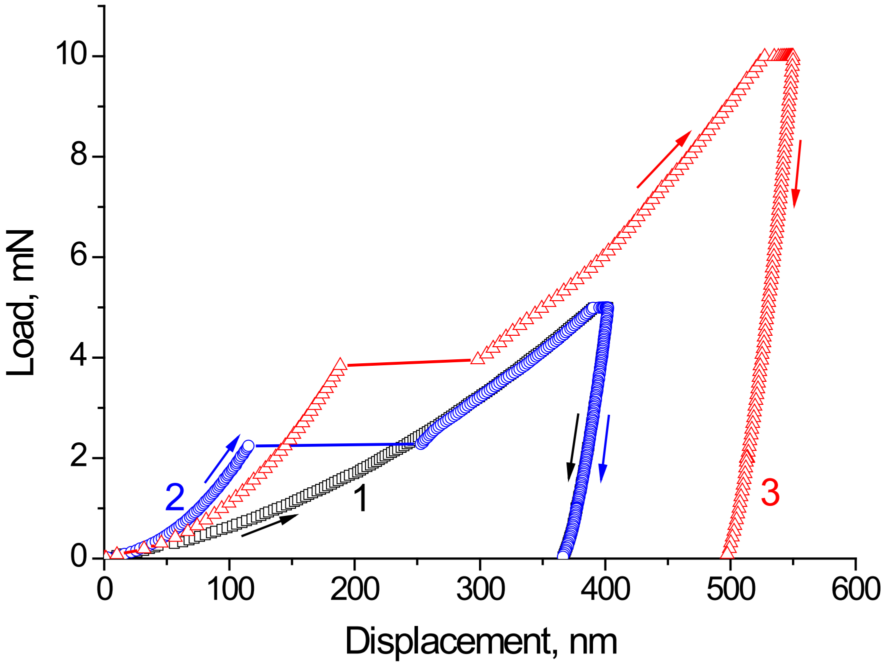

Fig. 2. Loading curves for Nb_2O_5/Nb systems with oxide films of thickness: 1 - 20 nm, 2 – 100 nm, 3 – 300 nm

The subsequent deformation and further behavior of the samples during unloading are typical for metals and largely determined the properties of the surface metal substrates where oxides were formed. At the end of unloading, a bend in the dependence was observed, associated with the rapid expulsion of the indenter from sample. This effect was practically absent for the sample with thin oxide layer (Fig. 2, curve 1), and appeared and intensified at increase of surface oxide thickness

(Fig. 2, curve 2). Such behavior of the metal-oxide system is explained by partial peeling of thick oxide films from the metal substrate during samples deformation.

When testing similar systems based on tantalum Ta_2O_5/Ta with the same oxide layers thicknesses, the results were qualitatively similar and differed only quantitatively. Table 1 shows the results of determining of the elastic modulus E and hardness H for oxide films of Nb_2O_5 and Ta_2O_5. The data are presented for oxides of different thicknesses in comparison with the data obtained for Nb and Ta covered with a natural oxide film ~1 nm thick, formed upon contact of these metals with atmospheric oxygen.

As can be seen from the Table 1, the elastic modulus of the oxide and metal are close both in the case of Nb and Ta. The hardness of thin anodic oxide films differs little from the hardness of the metal. Differences in hardness appear only with a significant increase of the oxide thickness. In addition, for thick oxides, compared with thin ones, both in measurements at different points of the surface and in measurements associated with different depths of indenter penetration, a large spread in hardness is observed, which indicates their heterogeneity. When moving into the depth of the oxide, its hardness increased, while the surface demonstrated properties characteristic of a looser layer.

Table 1. Elastic modulus E and hardness H of niobium and tantalum oxide films in bilayer metal-oxide systems

Substrate metal	Oxide		*E*, [GPa]	*H*, [GPa]
	Type	Thickness, [nm]		
Nb	Natural	~ 1	110 ± 6	2.13 ± 0.16
	Anodic	20	106 ± 7	2.12 ± 0.20
		100	105 ± 9	2,21 ± 0.31
		300	100 ± 10	3.96 ± 0.90
Ta	Natural	~ 1	190 ± 4	2.43 ± 0.10
	Anodic	20	193 ± 7	2.60 ± 0.06
		100	175 ± 6	2.75 ± 0.07
		300	194 ± 5	8.43 ± 0.22

After vacuum annealing (T = 250 °C, τ = 1 hour) of the Nb_2O_5/Nb system with oxide layer thickness of 100 nm, the loading curve changed significantly (Fig. 3).

It is necessary to take into account the fact that oxygen diffused into the metal substrate during annealing. As a result, the chemical composition of oxide film and substrate in the interphase boundary changed, and the transition zone expanded. The step formed on the dependence (Fig. 3, curve 2) narrowed significantly upon destruction of the oxide film, and the dependence front after the step became steeper, which indicates an increase in the hardness of niobium upon dissolution of oxygen from the oxide.

Before applying the oxide coating, the zirconium plate was also annealed in vacuum. The oxidation modes were the same as for niobium and tantalum, and the thickness of the grown oxide was 200 nm. The elastic modulus was measured both on the part of the sample not coated with oxide and on the oxidized surface (Fig. 4). The elasticity of the metal substrate was 100 GPa, and did not change as the indenter advanced deeper into the material. The elasticity of the bilayer ZrO_2/Zr system was approximately 1.5 times greater than the elasticity of the base metal and was 158 GPa near the surface. Then the elastic modulus decreased, and at a penetration depth of indenter into the sample of about 200 nm, a puncture of the surface anodic oxide film occurred. At this point, the elastic modulus of the ZrO_2/Zr system became the same as for zirconium.

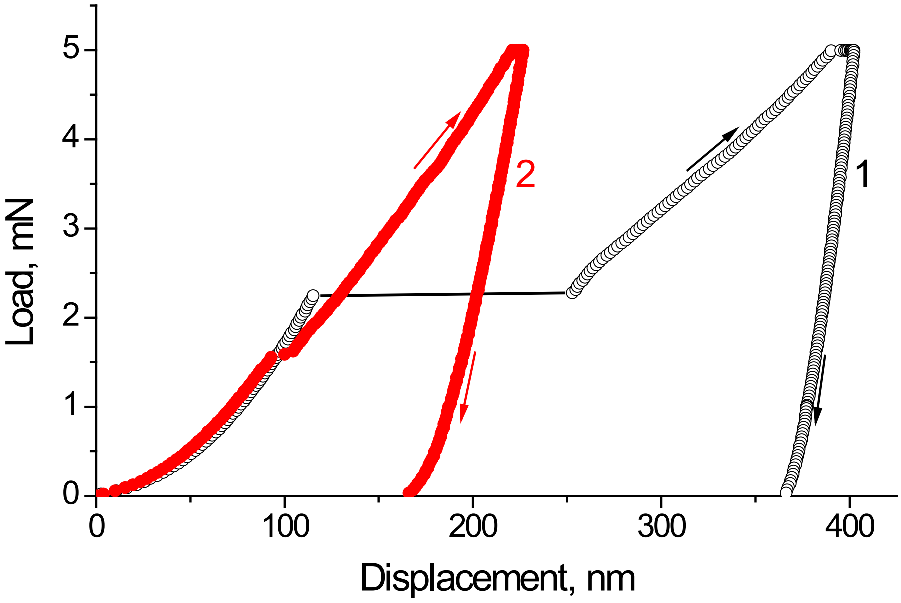

Fig. 3. Loading curves for Nb_2O_5/Nb systems with oxide thickness of 100 nm in the initial state (1) and after vacuum annealing (2)

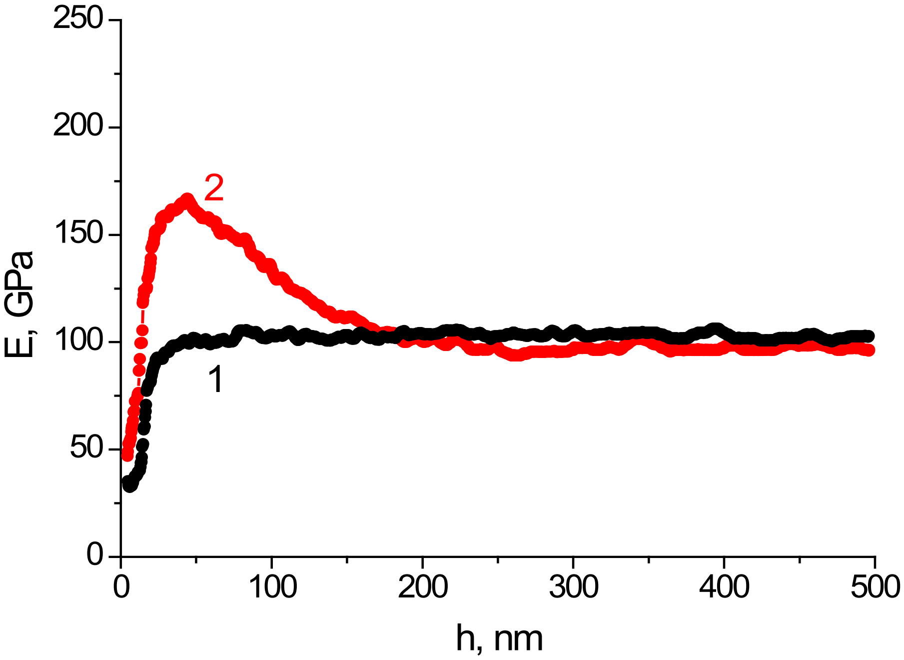

Fig. 4. Dependence of elastic modulus on the depth of indenter movement for zirconium (1) and ZrO_2/Zr system (2)

After vacuum pulsed photon annealing, which activates crystallization processes in the oxide phase, the mechanical characteristics of ZrO_2/Zr system changed (Fig. 5). While the characteristics of the zirconium substrate remained the same ($E \approx 100$ GPa), the elasticity of the bilayer system reached this level only at indenter movement depth of 500 nm, which is 2.5 times greater than the oxide thickness and determines the zone of oxygen dissolution from the oxide to the metal. It should be noted that the violation of oxide stoichiometry during annealing had virtually no effect on its elasticity, while the elasticity of the base metal increased significantly with formation of solid solution of oxygen in zirconium. This method allows to estimate the diffusion profile of impurity distribution in the metal surface layers.

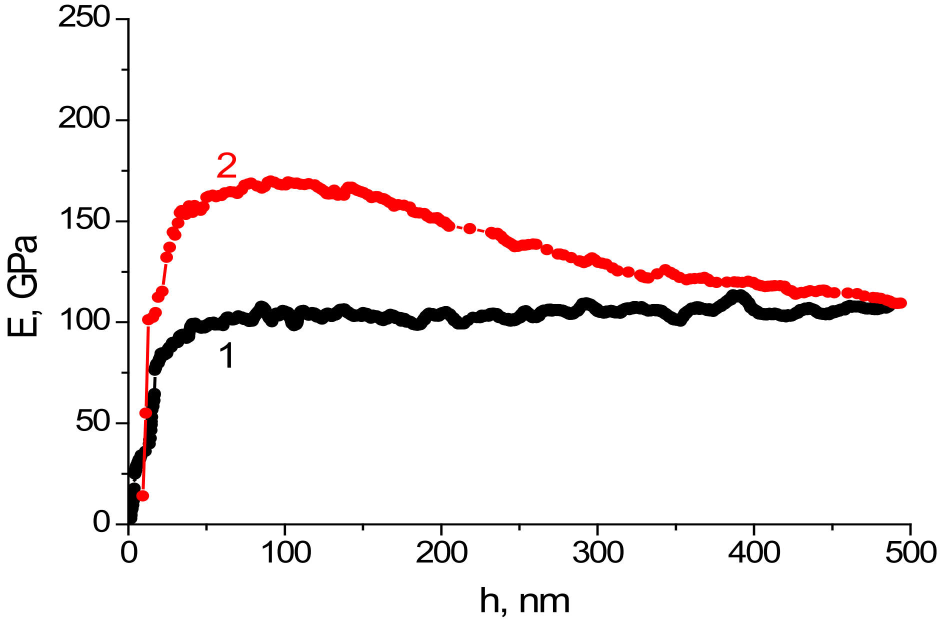

Fig. 5. Dependence of elastic modulus on the indenter movement depth for zirconium (1) and the ZrO_2/Zr system (2) after pulsed photon annealing

Table 2 shows the summary results of mechanical tests of zirconium and the metal-oxide system based on it.

Table 2. Elastic modulus E and contact depth h for zirconium and ZrO_2/Zr system

Sample		Contact depth *h*, [nm]	Elastic modulus *E*, [GPa]
ZrO_2/Zr initial	metal	20 – 80	101.516 ± 7.670
	oxide	20 – 80	149.625 ± 5.723
ZrO_2/Zr pulsed photon annealing ($\tau = 0.2$ s)	metal	40 – 100	101.253 ± 7.843
	oxide	40 – 100	158.258 ± 12.093

The obtained results show that the study of the mechanical properties of thin oxide films using a nanoindenter allows obtaining information about the elasticity and hardness of such objects, as well as monitoring the transformation of mechanical properties as a result of external influences.

Conclusion

The nanoindentation method was used to obtain the values of the elastic modulus E and hardness H of anodic oxide films of valve metals in the thickness range of 20-300 nm, which are E = 105 GPa and H = 2.2 GPa for niobium anodic oxide film, E = 193 GPa and H = 2.7 GPa for tantalum anodic oxide film, and E = 160 GPa and H = 2.5 GPa for zirconium anodic oxide film.

Amorphous oxide coatings up to 50 nm thick are capable of withstanding abnormally high elastic deformation without damaging the integrity of the oxide. This ability is lost with an increase in the thickness of the oxide film.

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