Functional Materials 14, No.3 (2007)

Elasticity module and hardness of niobium and tantalum anode oxide films

S.N.Dub, V.V.Starikov

National Technical University "Kharkiv Polytechnical Institute",
21 Frunze Street, Kharkiv, 61002, Ukraine

Received February 1, 2007

The elasticity modulus and hardness of oxide films obtained by anodic oxidation of niobium and tantalum have been studied. Relation of these characteristics with surface oxide thickness has been considered. It is established that the amorphous oxide coatings of small thickness show an anomalous high elasticity and are capable to withstand considerable deformations without the oxide film failure. This property is lost when the oxide film thickness increases. For the first time the elasticity module and hardness values for anodic niobium and tantalum oxide films of various thickness have been obtained.

Исследованы модуль упругости и твердость оксидных пленок, полученных методом анодного окисления ниобия и тантала. Рассмотрена связь этих характеристик с толщиной поверхностного оксида. Установлено, что аморфные оксидные покрытия малой толщины имеют аномально высокую упругость и способны выдерживать значительные деформации без нарушения целостности оксида. Эта способность теряется при увеличении толщины оксидной пленки. Впервые получены значения модуля упругости и твердости для анодных оксидных пленок ниобия и тантала различной толщины.

The interest in research of thin oxide films on the niobium and tantalum surface is defined by their wide application in many branches. So, in electronics, those are used as dielectric layers, because high breakdown voltage and high dielectric permeability [1]; in mechanical engineering, as protective coatings with high stability against chemical and electrochemical corrosion [2]; in medicine, as surface stimulators with electret properties improving integration of implant in biological tissues [3]. Such wide application fields are defined by unique properties of oxide films. Besides of electric and chemical characteristics, the mechanical properties of oxides are also of importance because they define the oxide durability under various external influences or at deformations of objects with oxidized surfaces.

The research of mechanical properties of thin (10–100 nm) oxide films was hampered for long time due to absence of techniques allowing to carry out such researches, for example, to measure the elasticity module and oxide hardness [4]. The standard techniques of similar tests can be used only for objects of much larger thickness. The development of nanoindenters combined with analytical processing procedures of such experimental results has opened new opportunities in research both micro- and nanoobjects [5]. So, in modern devices, the indenter displacement is measured to within 0.1 nm, thus allowing to carry out the test under loading less than 10 μN and print depths about several nanometers [6].

The purpose of this work was to study the elasticity module and hardness of oxide films obtained by anodic oxidation of 500 μm thick niobium and tantalum foils. Prior to forming the oxide coatings, the metal foils were annealed in vacuum ($2\cdot10^{-4}$ Pa) at 2300 K for 30 min. After annealing, the metal substrates had monoblock grain structure with grain size of 200 to 2000 μm. The texture with (110) orientation was found in

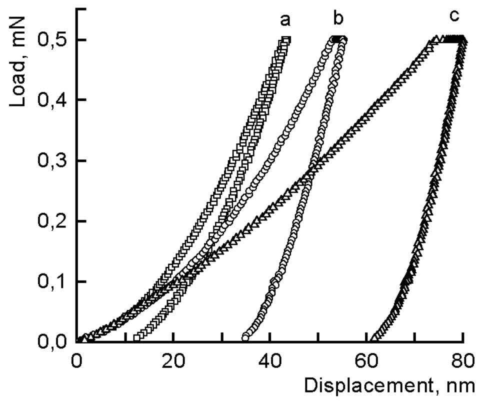

Fig. 1. Load-displacement curves under 0.5 mN load for niobium oxide films of thickness (nm): 20 (a), 100 (b), 300 (c).

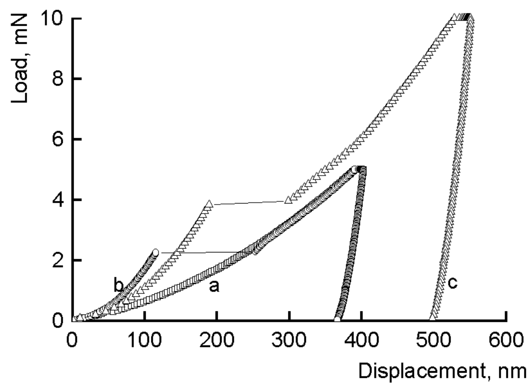

Fig. 2. Load-displacement curves under 10 mN load for niobium oxide films of thickness (nm): 20 (a), 100 (b), 300 (c).

foils of both metals using X-ray diffraction. Oxidation of niobium and tantalum was carried out consequently in galvanostatic and voltagestatic modes in 0.1 % aqueous phosphoric acid [2]. In the first mode, the constancy of oxide growth rate was controlled by maintenance of constant current density of 1 A/m^2 at increasing voltage in the electrochemical cell. The oxide geometric thickness was calculated using the final voltage applied to the electrochemical cell. At the second stage of oxide film growth, the reached voltage did not change while the current dropped exponentially because of electric resistance increase at restoration of oxide film stoichiometry and increase its electric thickness up to the geometric one. The oxide forming was carried out to thickness 20, 100 and 300 nm. The obtained Me_2O_5 films had amorphous structure and the width of the oxide-metal transition zone did not exceed 3 nm [7].

The hardness of samples was measured using Nano Indenter II of MTS System (USA) with Berkovich diamond indenter shaped as a trihedral pyramid. A capacitor gauge was used to measure the print depth, the load was applied up to 15 mN, the loading rate was 0.0001 to 20 mN/s. Before measurement, the temperature of device and sample was equalized.

The test results for amorphous niobium oxide (Nb_2O_5) films of 20, 100 and 300 nm thickness at low indenter loading (up to 0.5 mN) are presented in Fig. 1. For 20 nm thick oxide, the high elastic restoration after deformation was observed, that is not typical of ceramic materials (Fig. 1). Such a result for thin amorphous oxide film can be explained by its higher durability, hardness and elasticity as compared to the metal substrate. An elastic membrane fixed on a soft basis that does not hinder the membrane flexure can be taken as an analogue for such behavior. When the oxide thickness was grown, the influence of soft niobium substrate was reduced. The elasticity module of thick oxide films was decreased and contribution of plastic component to the oxide deformation was increased. Thin oxide films have shown the elastic straining up to rather high values. The observable values of oxide flexure without failure exceeded almost twice its thickness.

The plastic straining of a sample with thin Nb_2O_5 layer was not observed but its loading curve at the chosen loadings was nonlinear, that was associated with the Berkovich indenter rounded shape, that is, with transition from indentation of spherical body (r ~ 150 nm) during the initial deformation to indentation of trihedral pyramid at the following stages.

The increase of oxide thickness to 100 nm and especially up to 300 nm reduced the effect connected with the oxide high elasticity and easy straining of soft metal substrate and was accompanied by increase of plastic strain (Fig. 1.b, c) approaching to the test results for ceramic materials.

When the load was increased to values of 0.5 to 4 mN, a plateau that characterized the indenter free displacement without load increase was observed in all three dependences (Fig. 2). Its onset corresponded approximately to initial oxide thickness, especially for samples with thick oxide coating when the effect of oxide flexure into the metal substrate decreased essentially. Appearance of the plateau on the dependences is connected with failure of oxide layer by indenter and advancement of indenter into the metal substrate with gradual hardening of metal in the contact with indenter.

The following straining and the further behavior of samples under unloading were characteristic for metals and defined mainly by properties of metal substrates on which the oxides have been formed. At the end of unloading, a bend was observed in the dependence connected with fast indenter pushing out of the sample. This effect practically was absent in the samples with thin oxide layer (Fig. 2a) but appeared and amplified at increase of surface oxide thickness (Fig. 2b). Such behavior of metal-oxide bilayers was accounted to separation of thick oxide films from metal substrate at the sample straining.

Testing of similar systems on the base of tantalum $Ta–Ta_2O_5$ with the same thickness of oxide layers has shown results qualitatively similar to the above ones and differing only quantitatively. The results of elasticity module *E* and hardness *H* determination for oxide films Nb_2O_5 and Ta_2O_5 are presented in the Table for different thickness of surface oxide in comparison with the data obtained for Nb and Ta coated with 1 nm thick natural oxide films formed under contact of these metals with air oxygen. It is seen that elasticity modules of oxide and metal were closes both for niobium and tantalum bilayers. The hardness of thin anodic oxide films is close to the metal hardness, too. The difference in hardness are observed only at essential increase of the oxide thickness. Besides, for thick oxide in comparison with thin one, a dispersion of hardness values over the sample surface is observed that testifies to thick oxide heterogeneity. The hardness increases in the oxide bulk, while the surface shows properties that were characteristic for more loose layer.

Thus, the research of mechanical properties of thin oxide films by means of Nano Indenter allows to obtain reliable data on the elasticity and hardness of such objects and also to monitor the transformation of mechanical properties under external influences. Amorphous oxide coatings of small thickness are capable to withstand abnormal high elastic deformations without oxide failure. This ability is lost at increase of oxide film thickness. The plateau formation in the loading curve is connected with the puncture of surface oxide by indenter. The step onset and extent depend on integrated properties of metal-oxide bilayers. The values of elasticity module and hardness for anodic niobium and tantalum oxide films of various thickness have been obtained for the first time.

Table. Elasticity modulus *E* and hardness *H* of niobium and tantalum oxide films in metal-oxide bilayers

Metal of substrate	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

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Модуль пружності та твердість ніобієвих і танталових анодних оксидних плівок

С.М.Дуб, В.В.Старіков

Досліджено модуль пружності та твердості оксидних плівок, одержаних методом анодного окиснення ніобію і танталу. Розглянуто зв'язок цих характеристик з товщиною поверхневого оксиду. Встановлено, що аморфні оксидні покриття малої товщини мають аномально високу пружність і здатні витримувати значні деформації без руйнування плівки оксиду. Ця здатність втрачається при зростанні товщини оксидної плівки. Вперше отримано значення модуля пружності та твердості для анодних оксидних плівок ніобію і танталу різної товщини.