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Formation of nanostructures on the basis of porous anodic niobium oxide

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Self-organization of nanoscale structures under an electrochemical treatment is most pronounced during the formation of porous anodic metal (aluminum, titanium, niobium, and tantalum) oxides. A theoretical approach is proposed to describe the processes of the self-organization that allows one to determine the conditions for the formation of porous niobium oxides with amorphous or crystalline structure. The studies have shown the influence of the electrolyte nature on the formation of oxide layers. The use of an activator (fluoride) provides the conditions for the formation of oxides with different surface morphology at the initial stage of anodizing. By varying the mode of niobium anodizing, one can investigate the nature of pore nucleation at the initial stage of their growth, as well as track the in-time evolution of their geometrical dimensions, depending on the formation conditions, and synthesize porous AOFs on niobium with an amorphous or crystalline structure.

Keywords: electrochemical dissolution, anodic behavior, niobium, porous niobium oxide, electrolyte synthesis.

Самоорганизация наноразмерных структур при электрохимической обработке наиболее ярко проявляется в ходе формирования пористых анодных оксидов металлов (алюминия, титана, ниобия, тантала). Предложен теоретический подход к описанию протекающих процессов самоорганизации, позволяющий определять условия образования пористых оксидов ниобия аморфной или кристаллической структур. Проведенные исследования показали влияние природы электролита на формирование оксидных слоев. Использование активатора (фторида) позволяет на начальной стадии анодирования обеспечивать условия для формирования оксида с различной морфологией поверхности. Варьируя режимом анодирования на ниобии можно исследовать характер зарождения пор на начальной стадии их роста, а также проследить эволюцию во времени их геометрических размеров в зависимости от условий их формирования и синтезировать пористые АОП на ниобии аморфной или кристаллической структур.

Формування наноструктур на основі пористого анода з оксиду ніобію. *І.М.Рищенко, Л.В.Ляшок, В.П.Гомозов, С.А.Водолажченко, С.Г.Дерібо.*

Самоорганізація нанорозмірних структур при електрохімічній обробці найбільш яскраво проявляється у ході формування пористих анодних оксидів металів (алюмінію, титану, ніобію, танталу). Запропоновано теоретичний підхід до опису процесів самоорганізації, що дозволяє визначати умови утворення пористих оксидів ніобію аморфної або кристалічної структури. Проведені дослідження показали вплив природи електроліту на формування оксидних шарів. Використання активатора (фториду) дозволяє на початковій стадії анодування забезпечувати умови для формування оксиду з різною морфологією поверхні. Варіюючи режимом анодування на ніобії можна досліджувати характер зародження пор на початковій стадії їх зростання, а також простежити еволюцію за часом їх геометричних розмірів в залежності від умов їх формування і синтезувати пористі АОП на ніобії аморфної або кристалічної структур.

1. Introduction

Nanoporous niobium oxide formed using the electrochemical method can have an amorphous or crystalline structure and can be used to create composite materials with controlled nanostructured surface morphology [1, 2]. An anodic oxide film (AOF) on niobium has unique properties (nanometer-sized pores, high chemical and thermal stability, catalytic activity, etc.), which make it promising from a practical point of view. This material can effectively be used to create a wide range of devices, such as gas sensors [3], solar batteries [4], catalysts [5], thin-film lithium batteries [6], etc. Therefore, the development of the technology of electrochemical formation of porous AOF on niobium and analysis of its properties has substantial scientific and practical significance.

From both technological and economical points of view, one of the most promising methods of oxide nanomaterials formation is anodic oxidation of valve metals in electrolytes that are poor oxide solvents [4]. It was shown in [5] that AOFs formed on niobium in fluoride-containing electrolytes have a self-organized nanoporous structure. Despite available scientific information on the formation of porous niobium oxides (PNO) [5, 7, 9], most of the works do not sufficiently reflect the dependence of the anodic oxide characteristics on the conditions of its formation. The relevance of finding the answer to this question has determined the target of the present research.

Studies [7–9] are dedicated to analysis of PNO formation. These studies state that, depending on the electrolysis conditions, an amorphous or crystalline oxide with different surface morphology can be formed on niobium. Analysis of [4, 6, 7] shows that the PNO is formed in fluoride-containing electrolytes, which are weak solvents of oxide film. The anionic composition of the electrolyte significantly affects the dynamics of processes in the energetically inhomogeneous passivating layer. According to the sorption ability, a fluoride-ion exhibits an activating effect.

Depassivation of the sample begins at the sites with the highest activity, and then spreads out to less active sites. The interaction of fluoride with the AOF surface leads to the formation of a water-soluble complex $[NbF_7]^{2-}$ [9], which causes local oxide dissolution, contributing to the nucleation of pores and formation of the porous AOF structure.

The amorphous anodic oxide is characterized by a closely packed cell; the cells are directed perpendicular to the metal surface and parallel to each other. The hemispherical shape of the bottom of the growing cell is preserved [8]. Despite the fact that the rate of chemical dissolution of the oxide is approximately two orders of magnitude lower than the rate of electrochemical dissolution, and the duration of anodization is rather long due to chemical dissolution, the pore walls can lose mechanical strength and crumble. Consequently, the less aggressive the electrolyte, the greater is the limiting thickness of the porous layer [9].

Under certain anodizing conditions, the AOF crystalline structure is formed in the shape of microcones on niobium [9]; this fact can be used in various devices. It is considered that a non-porous oxide barrier layer forms first, and then it transforms into a crystalline oxide under the action of an electrolyte and a strong field. Over time in the process of oxidation of the metal, the microcones grow together into a continuous layer of the crystalline oxide. There is no consistency in the scientific literature regarding the mechanism of nucleation and formation of the crystalline structure of the porous AOF on niobium. In [5] it is stated that the formation of the crystalline phase occurs under the action of internal stresses as the thickness of the oxide increases. In [7], it is assumed that the formation of the niobium oxide microcones may be associated with the inhomogeneous chemical dissolution of the anodic film upon anodization. Thus, there is no unified approach explaining the mechanisms and factors influencing the formation of pore arrays and structures during anodic oxidation; this fact significantly retards their practical implementation in the field of ordered nanostructures. Therefore, the purpose of this work is to develop theoretical foundations on the formation process of porous nanostructured niobium oxides with amorphous or crystalline structure.

2.Experimental

The study of the niobium anodic behavior was carried out using 1 M H_2SO_4 solution with addition of HF solution (0.1 M; 0.25 M; 0.5 M; 1 M). All electrolytes were prepared from reagents of the "chemically pure" brand and "analytical grade" using distilled water. Polarization studies were carried out with a P-45X machine. As a working electrode, a niobium foil with a thickness of 0.1 mm and a purity of 99.99 % was used. The samples were chemically polished for 5–10 s at room temperature (20–25°C) in a solution of the following composition: $H_2SO_4:HNO_3:HF = 5:2:2$. Lead served as a counter-electrode material. The reference electrode was saturated in silver chloride. The magnitudes of the potentials are given relative to the normal hydrogen electrode. The morphology of the obtained coatings was studied using scanning electron microscopy (SEM) using a JSM-7001F microscope.

3. Results and discussion

Initially, the niobium surface structure looked like as defective, containing a natural oxide film and inheriting defects after preparatory operations. In this regard, it was assumed that the distribution of the electric field is non-uniform along the niobium surface when the potential is applied; therefore, the speed of the processes of electrochemical growth and dissolution of the oxide is not the same in different parts of the surface and depends on the degree of imperfection and the composition of a liquid double electric layer. In the defective areas, the dissolution process must proceed rapidly with the formation of pore nuclei at low field strength and nuclei of the crystalline phase under the action of a strong field.

It has been established that when niobium is anodized in 1 M H_2SO_4 solution, a general trend of increased film density with an increase in HF concentration is observed (Fig. 1); this may be due to the interaction of *F* with the Nb_2O_5 film, which leads to activation of the oxide surface. Fig. 1 shows a single anode current maximum which implies irreversibility of the process of the niobium oxide formation. The peak current increases with increasing concentration of fluoride ions in the electrolyte. The sharp rise in the anode current and the transition of the system to the passive state are associated with the formation of oxide monolayer having the highest oxidation state at the boundary with the electrolyte.

The curves show an increase in voltage in the range of potentials from −0.05 to +0.45 V, which corresponds to the formation of a barrier film on niobium. In electrolytes *1* and *2*, the next current increase corresponding to the growth of a porous oxide is much higher than in solutions *3* and *4*. This behavior can be explained by the fact that the dissolution rate of the centers on the active surface in these electrolytes prevails over the rate of AOF formation. Chronoamperograms (Fig. 2) of the niobium electrode show that anodization of niobium in the electrolyte without fluorides (curve *5*) leads to an exponential decrease in current density over time, which is typical for formation of a barrier-type film with high resistance [3, 4]. An increase in HF concentration is accompanied by an increase in the residual current at a constant voltage, indicating the formation of an oxide coating with more developed (porous) surface.

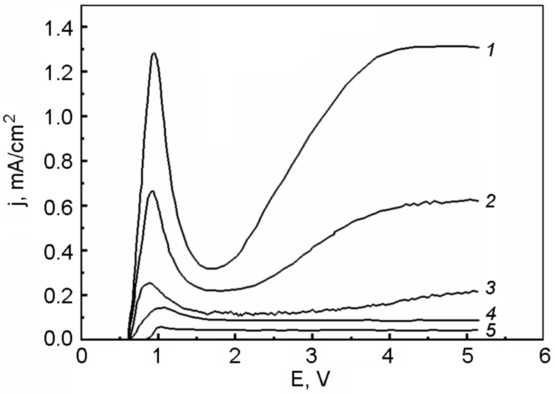

Fig. 1. Niobium potentiodynamic anodic dependences obtained in the solutions: *1* — 1 M H_2SO_4 + 1 M HF; *2* — 1 M H_2SO_4 + 0.5 M HF; *3* — 1 M H_2SO_4 + 0.25 M HF; *4* — 1 M H_2SO_4 + 0.1 M HF; *5* — *1 M* H_2SO_4.

Under certain conditions of anodization, namely, under the action of a strong electric field, the crystalline AOF in the shape of microcones is formed on the surface of niobium (Fig. 2b). This kind of crystallization was first described by Vermily (2). Unlike thermal crystallization, in this case, there is no transformation of an amorphous AOF into a crystalline state — the crystals grow on the surface of the metal under the already existing amorphous film. It is important to note that the crystallization is observed only on AOFs of transition metals, whereas thermal crystallization can occur on oxides of all metals.

There are controversial views on the mechanisms of nucleation and formation of the crystalline structure of the AOF on niobium. We have considered the crystallization at the initial stage of the AOF formation on niobium as a result of the influence of lower oxides, which are formed during the AOF growth in the transition layer at the metal — oxide interface. In compounds with oxygen, niobium exhibits oxidation states from the lowest +2 to the highest +5. The formation of metal ions of

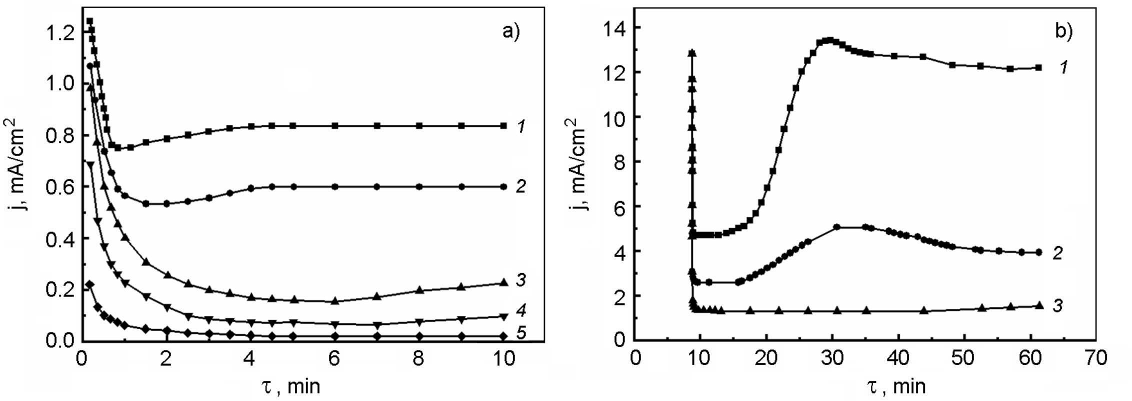

Fig. 2. Chronoamperograms of a niobium electrode in the following modes: a) $U = 20$ V: *1* — 1 M H_2SO_4 + 1 M HF; *2* — 1 M H_2SO_4 + 0.5 M HF; *3* — 1 M H_2SO_4 + 0.25 M HF; *4* — 1 M H_2SO_4 + 0.1 M HF; *5* — *1 M* H_2SO_4. b) $U = 60$ V: *1* — 1 M H_2SO_4 + 1 M HF; *2* — 1 M H_2SO_4 + 0.5 M HF; *3* — 1 M H_2SO_4 + 0.25 M HF.

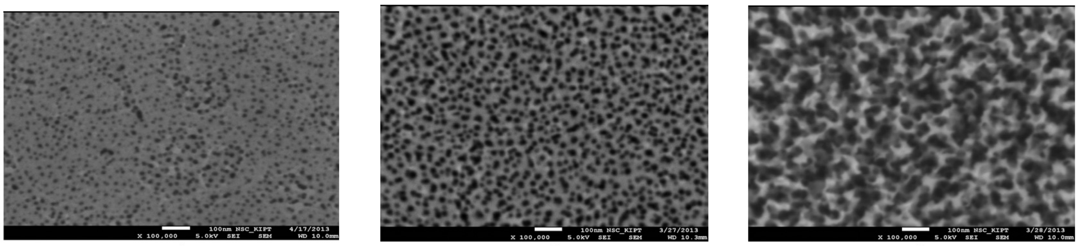
1 *2* *3*

Fig. 3. SEM images of surfaces of niobium anodic oxide synthesized during 1 h: *1* — 1 M H_2SO_4 + 0.25 M HF, 20 V; *2* — 1 M H_2SO_4 + 0,25 M HF, 60 V; *3* — 1 M H_2SO_4 + 0.5 M HF, 60 V.

higher valency occurs due to the oxidation of lower oxides. The process of electrochemical oxidation of the niobium electrode can be represented by the following chain of transformations:

$$Nb > NbO > NbO_2 > Nb_2O_5.$$

Thus, the formation of the niobium oxide occurs by the solid-phase poly-surface mechanism. The formation of the AOF is proceeding in stages, and not throughout the entire surface, but simultaneously in several areas. The probability of such a multilayer process is much greater than for single-stage niobium oxidation to a higher oxide.

In the lower oxides, in contrast to the higher ones, the M–O bond is predominantly ionic, and they exist in a crystalline form in the transition layer. It can be assumed that these oxides are the nuclei of future crystals. During the time period from the start of anodization to an increase in the current flowing through the $Nb–Nb_2O_5$ electrolyte system, the destruction of the barrier-type AOF and the development of crystals take place (Fig. 3). This period of the crystal growth is called incubation. As the anodization voltage increases, the incubation period decreases; this indicates a high rate of the crystalline phase development.

The process of the crystalline oxide coating formation during the anodic oxidation of niobium is described as follows: the initial stage consists of the formation of a barrier type AOF. Under the action of a strong electric field, the nuclei of the crystalline phase destroy the amorphous barrier layer, and gradually the entire surface of the sample is covered with the crystalline oxide.

The SEM results (Fig. 3) confirm the presence of a self-organized porous oxide film synthesized on niobium in solutions containing F^-. It should be noted that the oxide coating structure substantially depends on the HF concentration. At the 0.1 M HF concentration, round pores with a diameter of 6 to 12 nm are formed over the entire surface of the sample. As the HF concentration increases, the electrolyte aggressiveness increases as well; this in turn contributes to an increase in the pore diameter. At the 0.5 M HF concentration, the oxide dissolution process appears to dominate over the process of its formation, which re-

Table. Key geometric characteristics of niobium porous oxide films

HF concentration, M	d_{pore}, nm	Film thickness, nm
0.1	6–12	90
0.25	8–20	160
0.5	15–36	200

sults in the destruction of the AOF structure due to erosion of pores walls (Fig. 3).

As the voltage increases from 20 to 60 V, the surface morphology of the oxide film also changes, as can be seen from a comparison of Fig. 3.1 and 3.2. This may be due to an increase in the dissolution rate of the oxide due to the local heating of the electrolyte in the pores at high voltages. The thickness of the synthesized amorphous niobium porous oxide films is in the range from 90 to 200 nm and also, like morphology, directly depends on the anodizing conditions (Table).

As noted above, with the electrochemical formation of an AOF on niobium, by varying the anodizing mode, it is possible to obtain the crystal structure of the oxide. In contrast to thermal crystallization, in this case, the transformation of the amorphous AOF into crystalline does not occur, and the crystals grow on the metal surface beneath the already existing amorphous film. The evolution of the crystals takes a long time, so this crystallization is observed with voltstatic anodizing. The growing crystals have the shape of irregular polyhedra. The authors of [8] called such formations as niobium microcones. This type of crystalline formation consists of needle-like crystals radially diverging from the beginning of the crystallization nucleus. The irregular shape of the crystals is caused by different rates of growth at different sectors. All the microcones consist of highly branched niobium oxide nanofibers and create a very developed surface that can have diverse functional applications, given that the crystalline niobium oxide is much more stable with increasing temperature than the corresponding amorphous oxide.

4. Conclusions

Thus, a theoretical approach has been proposed to describe the processes of a self-organization of porous niobium oxides; the approach allows determining the conditions for formation of an amorphous or crystalline structure. The studies have shown the influence of the electrolyte origin on the formation of the porous oxide. The use of an activator (fluoride) at the initial stage of the anodization allowed us to provide conditions for the formation of oxide coatings with different surface morphology. By varying the anodization mode, one has a possibility to investigate the nature of pore nucleation in the oxide at the initial stage of its growth, to track the in-time evolution of geometric dimensions depending on the formation conditions, and to synthesize porous AOFs on amorphous or crystalline niobium.

References

1. S.Minagar, C.Berndt, J.Wang et al., *Acta Biomaterialia*, **8**, 2875 (2012).
2. G.Poinern, N.Ali, *Fawcett Mater.*, **4**, 487 (2011).
3. G.Korotcenkov, *Mater. Sci. Engin.*, **139**, 1 (2007).
4. J.Z.Ou, R.A.Rani, M.H.Ham, *Acsnano*. **6**, 4045 (2012).
5. K.Nakajima, T.Fukui, H.Kato et al., *Chem. Mater.*, **22**, 3332 (2010).
6. J.E.Yoo, J.Park, G.Cha et al., *Thin Solid Films*, **531**, 583 (2013).
7. I.Sieber, H.Hildebrand, A.Friedrich, P.Schmuki, *Electrochem. Commun.*, 7, 97 (2005).
8. J.Zhao, X.Wang, R.Xu et al., *Electrochem. Solid-State Lett.*, **10**, 31 (2007).
9. R.L.Karlinsey, *Electrochem. Commun.*, **7**, 1190 (2005).