

Electrochemical Synthesis of Crystalline Niobium Oxide

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Abstract. Features of creation of porous nanostructured oxides of transition materials on an example of niobium are considered. It has been experimentally shown that variation in anodizing modes makes it possible to obtain non-porous and porous amorphous anodic oxide films (AOF) and films of the crystalline type. It is determined that the process of AOF formation on niobium, as well as its structure and properties depend on such parameters as the type of electrolyte, anodizing voltage, activator concentration, the duration of the process. It is confirmed that the presence of an activator in the electrolyte is a necessary and decisive factor in the process of forming a nanostructured anode oxide layer. To obtain a nanostructured surface of niobium oxide, a necessary condition is the introduction of fluoride into the electrolyte, but also an important task is to determine the type of compound with which F⁻ ions are introduced into the electrolyte. It has been experimentally determined that the optimal solution for the rapid growth of porous crystalline oxide is a solution consisting of a background electrolyte in the form of 1M H₂SO₄ with the addition of a fluoride ion activator in the form of 0.5M NaF. The increase in the activator accelerates the formation of the crystal structure on the surface of niobium. It is shown that higher voltage and longer anodizing time leads to an increase in the size of microcones and their number on the surface of niobium. Optimal for the formation of porous crystalline oxide is a voltage of 60 V in the electrolyte 1M H₂SO₄ + 0.5M NaF for 2 hours.

Introduction

The development of new and improvement of existing technologies for formation of anode oxide coatings on valve metals has attracted the attention of researchers for many years. The interest is due primarily to possibility of forming of anodic oxide coatings with a wide range of functional properties. Recently, the electrochemical method of synthesis of nanoporous structures has been intensively studied, as this process is quite simple and cost-effective [1, 2, 3].

To date, intensive research is being conducted to create porous nanostructured oxides of transition materials, among which of particular interest is niobium oxide, which has unique properties (nanometer-sized pores, high chemical and thermal stability, catalytic activity, etc.). This makes it promising from a practical point of view [4].

Variation of anodizing modes makes it possible to obtain non-porous and porous amorphous anodic oxide films (AOF) and films of the crystalline type. Non-porous (barrier oxide films) are formed in electrolytes that do not dissolve the oxide [4]. Electrochemical synthesis of porous niobium oxide is carried out in solutions that are poorly soluble in the oxide, usually electrolytes that contain fluoride ions. The surface structure of such coating consists of highly branched nanofibers of niobium oxides and creates a very developed surface, which can have a variety of functional applications [5, 6, 7]. However, quantitative data on the rate of formation of various oxides types and factors that affect it in the literature are almost absent.

In connection with the above, it is important to study the role of the activator and the anodizing regime in the formation of nanoporous niobium oxide of amorphous or crystalline types.

Self-organization of nanosized porous structures on valve metals is most clearly manifested during electrochemical synthesis, which allows to create anode oxides with unique physicochemical properties [8]. However, unified approaches to explaining the mechanisms of the initial stage of growth of the anode oxide film (AOF) on valve metals, the origin of pores in them and the dependence of the geometric parameters of the nanostructure of anode oxides on the formation conditions have not been created yet.

Under certain anodizing conditions, AOFs with a crystal structure in the form of microcones are formed [9, 10]. This fact leads to the widespread use of such films in various devices and structures, for example, in electric capacitors and electrochromic indicator devices, as well as in thin-film lithium-ion batteries.

Researchers' views on the mechanism of nucleation and formation of the crystal structure of porous niobium AOF are contradictory. Thus, it is noted [11] that formation of the crystalline phase occurs under the action of internal stresses that occur with increasing oxide thickness. In [12], it is assumed that formation of microcones of niobium oxide should be associated with inhomogeneous chemical dissolution of the anode film during anodizing.

However, in our opinion, the crystallization may be affected by lower oxides formed during the growth of AOF in the transition layer at the metal-oxide interface. In compounds with oxygen, niobium exhibits oxidation states from lower +2 to higher +5. The formation of stable valence metal ions occurs in the ionization process not directly, but through intermediate stages of formation of lower valence ions. That is, higher oxides are formed by oxidation of lower oxides. The process of electrochemical oxidation of the niobium electrode can be represented by the following conversion chain: $\text{Nb} \rightarrow \text{NbO} \rightarrow \text{NbO}_2 \rightarrow \text{Nb}_2\text{O}_5$ [13].

Thus, the formation of niobium oxide occurs by a solid-phase multi-surface mechanism. The formation of AOF is gradual, not on the entire surface, but simultaneously in several areas. The probability of carrying out such polylayer process is many times higher than for one-stage oxidation of niobium immediately to higher oxide [14].

Local inhomogeneities on the metal surface, grain boundaries, dislocations, impurity atoms and other structural and chemical defects are centers of increased surface energy. At these centers, the diffusion of oxygen into the metal is facilitated and it is here that the formation of oxides of lower valence is possible. We can assume that these oxides are the nuclei of future field crystals [11].

Higher refractory metal oxides are insulators with a wide forbidden band and therefore have poor electronic conductivity, while lower oxides are semi-metallic phases that exist in the transition layer as a crystalline phase.

Niobium oxide crystals are formed under the action of a strong electric field in the surface layer of metal from embryos under an amorphous film.

Experimental

As a starting material for the synthesis of porous anodic niobium oxide used high-purity niobium foil (thickness 0.1 mm; purity 99.99 %). Before each experiment, niobium was chemically polished to a mirror finish at room temperature (20-25 °C) in a solution of the following composition: H_2SO_4 : HNO_3 : HF = 5:2:2. Then the samples were washed with distilled water and dried in air.

Anodic oxidation of niobium was performed in a fluoroplastic cell in potentiostatic mode using a DC source B5-50. The voltage and current in the system were monitored using digital universal voltmeters B7-35. The working electrode (anode) was a niobium plate, the auxiliary electrode (cathode) was a lead mesh, and graphite was used in fluoride-containing solutions. The time of AOF formation depended on the electrolysis conditions and varied in the range from 1 to 2 hours (Table 1).

Table 1. Conditions of anodic oxidation of niobium

Electrolyte	High-voltage, [V]	Time, [h]
1M H ₂ SO ₄	60	1
1M H ₂ SO ₄ + 0,5M HF	70, 80,90	1, 2
1M H ₂ SO ₄ + 1M HF	60, 70, 80	1, 2
1M H ₂ SO ₄ + 0,25M NaF	60	1, 2
1M H ₂ SO ₄ + 0,5M NaF	60, 70, 80	1, 2
1M H ₂ SO ₄ + 1M NaF	60	1, 2

Polarization measurements were performed using a PI-50-1.1 potentiostat complete with a PR-8 programmer at scan rate of potential in the range of $1 \cdot 10^{-1} \dots 1 \cdot 10^{-3}$ V/s in the potentiodynamic mode.

Nb was used as the anode, the cathode was a lead grid, and the reference electrode was saturated argentine chloride. The magnitudes of the potentials were recalculated relative to the normal hydrogen electrode.

The test samples were niobium plates sized $20 \times 5 \times 0.1$ mm, on the surface of which AOFs were formed by anodizing. The samples were insulated with acid-resistant varnish, the working surface of the electrode was 5 mm^2 .

1M H₂SO₄ was used as the working solution. The measurements were performed at open circuit conditions in a sequential scheme. The experimental data were processed using program EIS Spectrum Analyzer and Origin Lab. This program allows you to model the frequency dependences of different equivalent circuits and compare them with experimentally obtained results, thus, allows you to choose an equivalent circuit that will most accurately describe the frequency behavior of the studied system [15]. Evaluation of the synthesized oxide coatings was performed by analyzing the calculated parameters of the selected equivalent schemes.

The microstructure of the obtained samples was studied using the method of scanning electron microscopy (SEM) using microscopes JSM-7001F and JSM-6390LV. X-ray phase analysis of the films was performed on a DRON-2 diffractometer (CuK- α radiation).

Results and Discussion

By the method of electrochemical oxidation it is possible to form an anode film on niobium, which is an array of nanotubes oriented perpendicular to the substrate, having an amorphous structure or crystalline, having a surface porosity and is electrically conductive. Much attention in the literature is paid to the study of the influence of the conditions of anodic oxidation of niobium on the main characteristics of the obtained porous oxide coatings.

In this work, three types of oxide structures were formed, namely: nonporous, porous and crystalline. The process of formation of AOF on niobium, as well as its structure and properties depend on the following parameters: type of electrolyte; anodizing voltage; activator concentrations; process duration.

As a rule, the formation of AOF on niobium is carried out in acidic electrolytes, despite this, there are works that use alkaline solutions. Regularities of the course of the anodic process on niobium in aqueous solutions of electrolytes are complicated by the presence on its surface of natural oxide layers. Natural oxide on niobium affects the properties of the electric double layer, and hence all the reactions that take place at the oxide/electrolyte interface.

A review of the literature showed that the structure, morphology and kinetics of the formation of a porous oxide film on niobium are influenced by the nature of the background electrolyte and activator [16].

Thus, in this work, sulfuric acid was used as a background electrolyte, as well as an electrically conductive additive. The main attention is paid to the study of the effect of the activator.

The presence of the activator in the electrolyte is necessary and crucial in the process of forming a nanostructured anode oxide layer, as the formation of a porous AOF requires the presence of two competing processes: the formation of the oxide and its dissolution.

It is known that halogen ions contribute to the local deposition of the niobium surface, which is possible at active centers with low adsorption energy [17]. When anodic polarization of niobium in acidic halogen-containing (Cl^- , Br^- , F^-) electrolytes, activation of niobium occurs only in solution with fluoride ions due to the interaction of F^- with Nb_2O_5 film with the formation of water-soluble complex ion $[\text{NbF}_7]^{2-}$:



Fig. 1 shows that the activation of the niobium surface is in the electrolyte with the addition of F^- (Fig. 1, curve 4), as evidenced by the rise of the current at a potential shift of more than 1.5 V. In sulfuric acid electrolyte without impurities, as well as in solutions with the addition of NaCl and NaBr, the nature of the obtained dependences (Fig. 1, curves. 1–3) is similar. The dependences have the form of a classical passivation curve, which indicates the formation of a nonporous oxide film on the niobium surface.

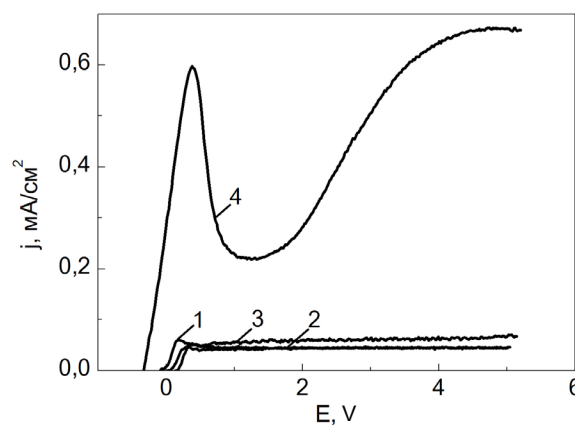


Fig. 1. Potentiodynamic anodic polarization dependences for niobium: 1 – 1M H_2SO_4 ; 2 – 1M H_2SO_4 + 0,25M NaCl; 3 – 1M H_2SO_4 + 0,25M NaBr; 4 – 1M H_2SO_4 + 0,25M NaF.

Thus, the introduction of fluoride into the electrolyte of anodic oxidation of niobium is a necessary condition for obtaining a nanostructured oxide surface. But also an important task is to determine the type of compound with which F^- ions are introduced into the electrolyte.

To develop ideas about the general laws of electrochemical behavior of niobium in the sulfuric acid electrolyte and to explain the effect of the cation, the analysis of anodic polarization dependences was performed (Fig. 2). The obtained curves have a maximum in the range of potentials from +0.05 to +0.45 V, which correspond to the formation of a porous film on niobium, and in electrolyte 1 the current rise corresponding to the growth of porous oxide is much higher than in solution with the addition of HF (Fig. 2, curve 2). This behavior of the system can be

explained by the fact that the rate of dissolution of the active centers of the surface in this electrolyte prevails over the rate of formation of AOF.

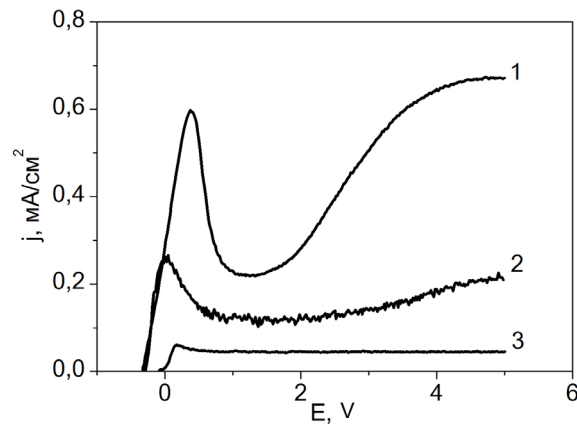


Fig. 2. Potentiodynamic polarization dependences for niobium: 1 – 1M H₂SO₄ + 0,25M NaF; 2 – 1M H₂SO₄ + 0,25M HF; 3 – 1M H₂SO₄.

Lower current is observed in the electrolyte with the addition of HF. This fact can be explained by the fact that HF belongs to the acids of medium force and incompletely dissociates in solution. In turn, NaF dissociates completely, which increases the concentration of fluoride ions, resulting in a change in the electrophysical parameters of the process (current density, temperature in the reaction zone, etc.), which directly affect the kinetics of formation and characteristics of the oxide layer.

For further studies of the electrosynthesis of porous crystalline niobium oxide as an activator was chosen fluoride ion in the composition of HF and NaF. It should be noted that the formation of a crystalline film in the electrolyte with the addition of NaF occurs much faster than with the cation HF and to obtain porous coatings of the crystal structure, it is advisable to use it.

Fig. 3 shows the effect of HF concentration on the process of formation of niobium oxide.

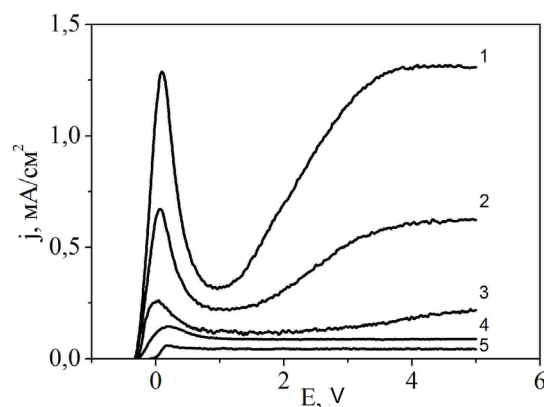


Fig. 3. Potentiodynamic anodic polarization dependences for niobium: 1 – 1M H₂SO₄ + 1M HF; 2 – 1M H₂SO₄ + 0,5M HF; 3 – 1M H₂SO₄ + 0,25M HF; 4 – 1M H₂SO₄ + 0,1M HF; 5 – 1M H₂SO₄.

At a low concentration of HF (Fig. 3, curve 4) the maximum current is quite small and at subsequent anodizing does not depend on the potential. This indicates that the amount of fluoride ions is so small that they can not provide a uniform distribution of pores over the entire surface of the sample and the growth process of the film prevails over its dissolution.

With increasing concentration of HF in the studied range, there is a general tendency to increase the current density, which indicates the formation of a porous structure of the porous structure in this electrolyte.

It should be borne in mind that with increasing concentration of F^- there is an intense dissolution of the oxide film, which leads to deformation of its structure, and at low concentrations there is the formation of a continuous barrier layer.

Thus, the formation of an oxide coating with a uniform distribution of pores is possible only in a certain range of concentrations F^- . This is confirmed by micrographs of the AOF surface, which show (Fig. 4, b) that at a concentration of 0.5M HF the oxide surface has an etched appearance. The morphology of the sample synthesized in a solution of 1M H_2SO_4 + 0.25M HF (Fig. 4, a) is a porous oxide. The pores are open at the top and evenly distributed over the entire surface.

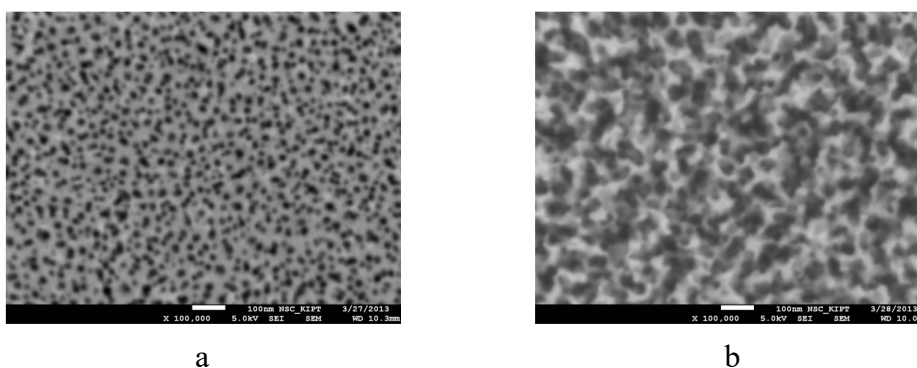


Fig. 4. Photomicrograph of the surface of anodic niobium oxide synthesized for 1 hour at a voltage of 20 V: a – 1M H_2SO_4 + 0,25M HF; b – 1M H_2SO_4 + 0,5M HF.

Therefore, judging by the obtained dependences, we can say that the optimal solution for the formation of porous AOF on niobium is 1M H_2SO_4 + 0.25M HF.

Slightly different molding conditions are required for crystal film growth. It was determined that in the sulfate acid electrolyte with a NaF content of 0.25 mol/dm³ the nature of the chronoamperogram (Fig. 5, curve 3) is similar to that obtained by adding HF (0.1...0.5) mol/dm³, however, further increasing the concentration of NaF leads to the formation and growth of the crystalline phase. As can be seen from Fig. 5 on curves 1 and 2 there is an incubation period, which is characterized by a constant current during which the formation of crystallization centers. For the formation of a crystalline film on niobium in a solution of NaF requires a much lower concentration of fluoride ion than in the HF activator.

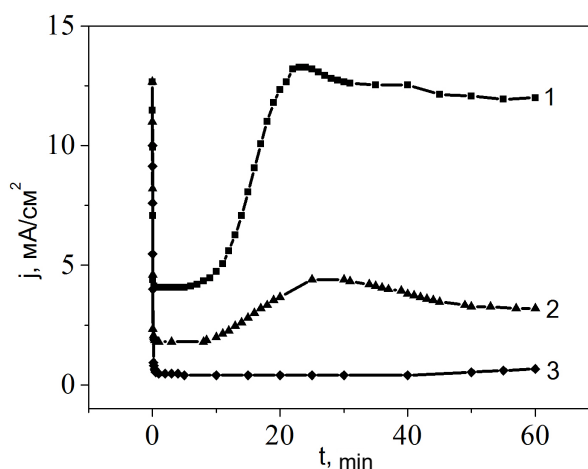


Fig. 5. Chronoamperograms of the niobium electrode at a voltage of 60 V: 1 – 1M H_2SO_4 + 2M HF; 2 – 1M H_2SO_4 + 1M HF; 3 – 1M H_2SO_4 + 0,5M HF.

It takes much longer to form an oxide film of the crystalline type in a solution containing 1M $\text{H}_2\text{SO}_4 + 0.5\text{M HF}$. This is evidenced by micrographs of the surface of the AOF, synthesized for 2 and 5 hours (Fig. 6).

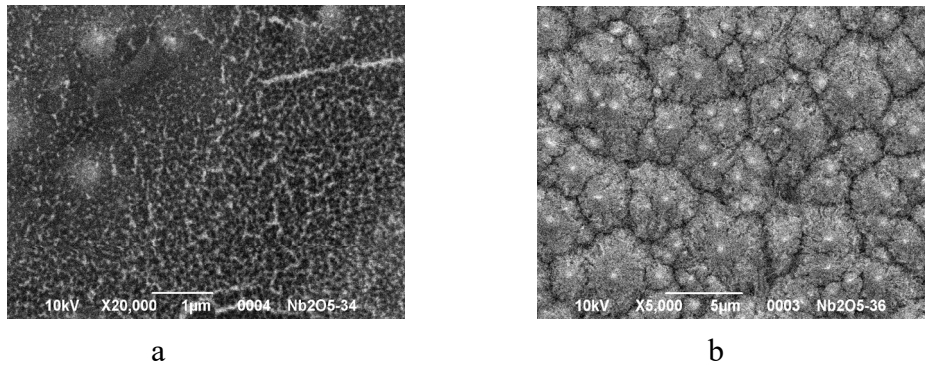


Fig. 6. SEM-micrographs of surface of porous niobium oxide: a – 1M $\text{H}_2\text{SO}_4 + 0,5\text{M HF}$, $U = 60 \text{ V}$, $t = 2 \text{ h}$; b – 1M $\text{H}_2\text{SO}_4 + 0,5\text{M HF}$, $U = 60 \text{ V}$, $t = 5 \text{ h}$.

The method of X-ray diffraction analysis confirmed that the niobium AOF synthesized within 1 hour are X-ray amorphous (Fig. 7).

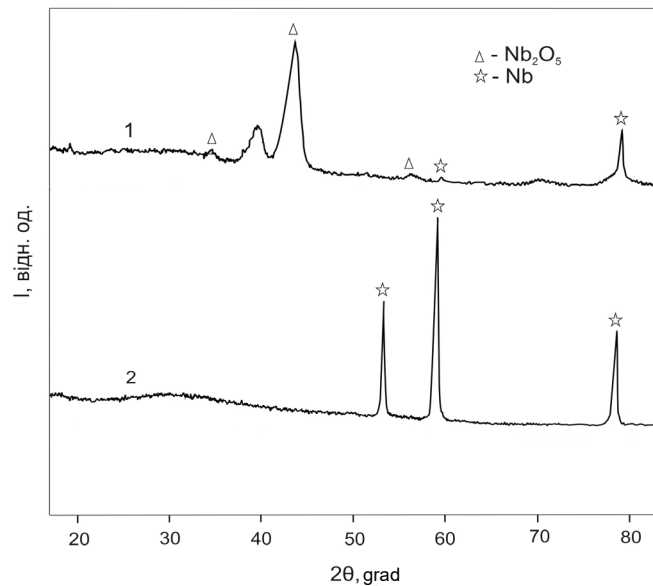


Fig. 7. Radiographs of AOF of niobium synthesized in a solution of 1M $\text{H}_2\text{SO}_4 + 0.5\text{M HF}$ at 60 V: 1 – 5 hours; 2 – 1 hour

At long anodizing in the same electrolyte (fig. 7) crystalline oxide is formed. On the obtained radiograph there are peaks corresponding to crystalline Nb_2O_5 .

It should be noted that the formation of AOF of the crystalline type is possible in a certain range of concentrations of the NaF cation. After all, increasing the NaF concentration to 1 mol/dm³ contributes to the destruction of the coating structure (Fig. 8, c).

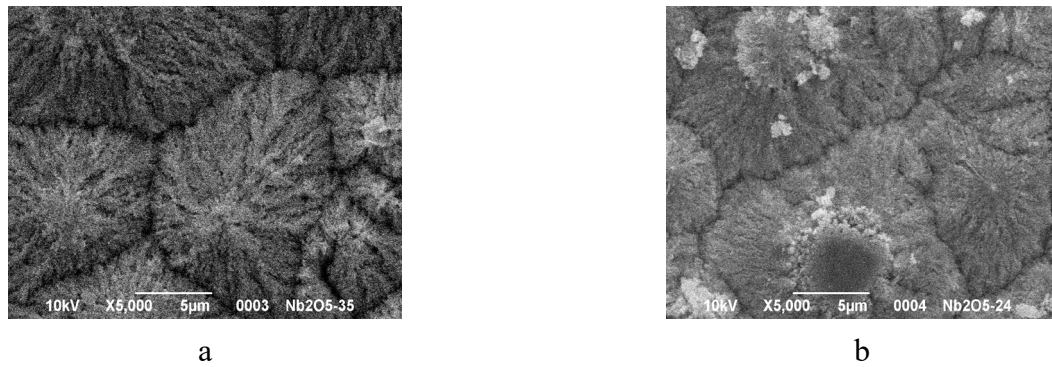


Fig. 8. SEM-micrographs of surface of crystalline niobium oxide: a – 1M H₂SO₄ + 0,5M NaF, 5 h., U = 60 V; b – 1M H₂SO₄ + 1M NaF, 5 h., U = 60 V.

Thus, the optimal solution for the rapid growth of porous crystalline oxide is a solution consisting of a background electrolyte in the form of 1M H₂SO₄ with the addition of a fluoride ion activator in the form of 0.5M NaF. The increase in the activator accelerates the formation of the crystal structure on the surface of niobium.

Determination of the optimal voltage and mode of formation of crystalline AOF

The predominant formation of nanoporous crystalline niobium oxide occurs in the voltstatic mode under the action of a strong field. Fig. 9 shows the effect of voltage on the formation of crystalline niobium oxide.

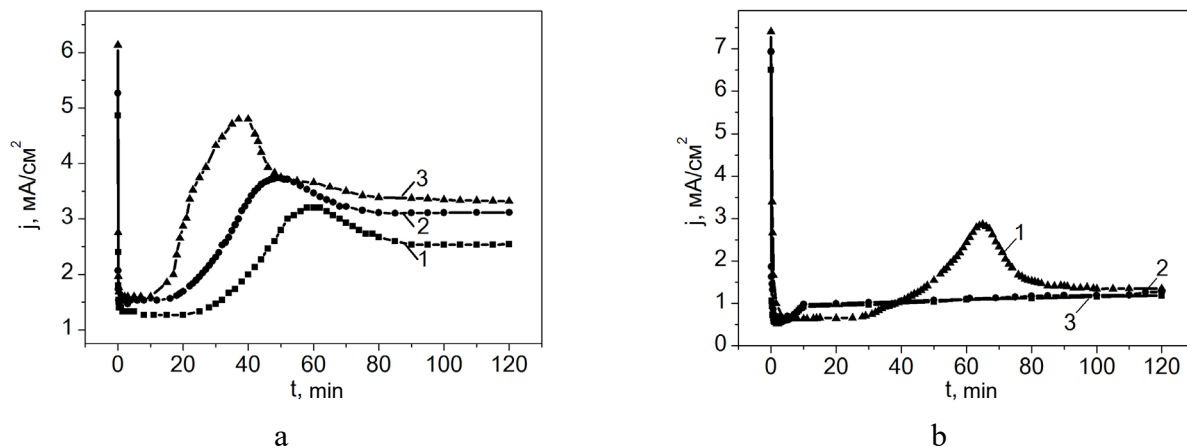


Fig. 9. Chronoamperograms of niobium electrodes synthesized under different conditions: a – 1M H₂SO₄ + 0,5M NaF (1 – 60 V; 2 – 70 V; 3 – 80 V); b – 1M H₂SO₄ + 0,5M HF (1 – 60 V; 2 – 70 V; 3 – 80 V).

Under the action of a strong electric field, the nuclei of the crystalline phase break the amorphous layer and gradually the entire surface of the sample is covered with an oxide with a crystalline structure. As the voltage of formation increases, the incubation period time decreases, which indicates a faster development of the crystalline phase (Fig. 9 3.12, a).

If we compare these graphs, we can note that in the electrolyte with the addition of HF the formation of crystalline oxide occurs only at a voltage of 80 V (Fig. 9, b, curve 1). In the electrolyte with the addition of NaF of the same concentration for the synthesis of AOF crystal structure requires a much lower voltage, namely 60 V.

Analysis of SEM-micrographs confirmed that a porous crystalline oxide is formed on the surface of niobium at a formation voltage of 60 V for 2 hours (Fig. 10, a).

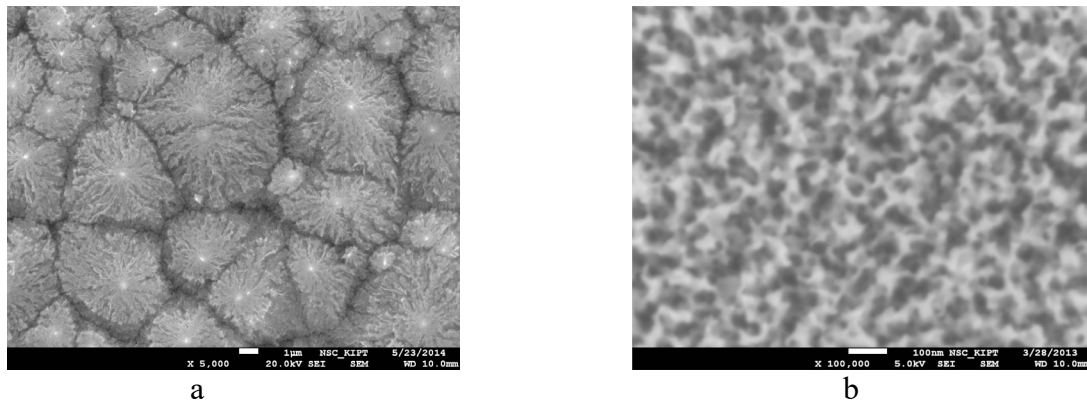


Fig. 10. SEM-micrographs of surface of porous niobium oxide synthesized at a voltage of 60 V: a – 1M H₂SO₄ + 0,5M NaF, 2 h.; b – 1M H₂SO₄ + 0,5M HF, 1 h.

Conclusion

Peculiarities of creation of porous nanostructured oxides of transition materials on the example of niobium, are considered. It is confirmed that the variation of the anodizing modes makes it possible to obtain non-porous and porous amorphous AOF and films of the crystalline type.

It is determined that the process of AOF formation on niobium, as well as its structure and properties depend on the following parameters: type of electrolyte, anodizing voltage, activator concentrations, process duration.

It is confirmed that the presence of an activator in the electrolyte is a necessary and decisive factor in the process of forming a nanostructured anode oxide layer. To obtain a nanostructured surface of niobium oxide, a necessary condition is the introduction of fluoride into the electrolyte, but also an important task is to determine the type of compound with which F⁻ ions are introduced into the electrolyte.

It has been experimentally determined that the optimal solution for the rapid growth of porous crystalline oxide is a solution consisting of a background electrolyte in the form of 1M H₂SO₄ with the addition of a fluoride ion activator in the form of 0.5M NaF. The increase in the activator accelerates the formation of the crystal structure on the surface of niobium.

It is shown that higher voltage and longer anodizing time leads to an increase in the size of microcones and their number on the niobium surface. Optimal for the formation of porous crystalline oxide is a voltage of 60 V in the electrolyte 1M H₂SO₄ + 0.5M NaF for 2 hours.

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