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EFFECT OF ANODIZING REGIMES ON THE VOLUME EXPANSION FACTOR OF THE OXIDE FILMS

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The volume expansion factor of porous alumina, formed by through anodizing of an Al foil in oxalic and sulphuric acid has been studied. The thickness of obtained porous alumina films was measured by a mechanical profilometer with a computer signal processing. The volume expansion factor of porous alumina varied from 1.35 to 1.65. Linear dependences were obtained for the volume expansion factor of porous alumina versus the anodizing voltage and the ionic current density logarithm versus the inverse volume expansion factor. Unlike oxide formation in sulphuric acid, these dependences have two subsequential rectilinear regions in oxalic acid.

Keywords: aluminum, anodizing, porous alumina, volume expansion factor.

1. Introduction

In recent years the amount of works devoted to studying porous alumina properties and its structure has increased [1-3]. This can be explained by application of anodic alumina as a template for nanosize structures, such as magnetic, electronic and optoelectronic devices [4,5]. One of the most important properties of anodic alumina is a possibility of self-organized regular formation of hexagonal oxide structure in oxalic, phosphoric and sulphuric acids [6]. As it has been shown in [7,8], the growth of self-organized arrays is observed if the volume expansion of aluminum during oxidation is about 1.2-1.4. The general regularity of porous alumina growth was noted in [7]. The linear increase of the interpore distance with the anodizing voltage obtained from disordered porous anodic alumina fits for periodic pore arrangements as well. This raises an interest to the regularities obtained for disordered pore growth.

As it is known during anodizing a porous alumina film thickens according to the Faraday law. The main regularity of alumina film growth during steady-state anodizing is that the barrier-layer thickness, cell diameter and pore diameter are all proportional to the anodizing voltage [7]. In [9] the influence of anodizing regimes of the 1.8 μm Al in oxalic acid on the volume expansion of porous alumina was studied. It was shown that the volume expansion factor of porous alumina films is proportional to the anodizing voltage as well. However, because of the limited range of anodic current densities from 1.6 to 3.7 $\text{mA}\cdot\text{cm}^{-2}$ the narrow range of change of the volume expansion factor of 1.2-1.45 was observed. This can be explained by thickness of 1.8 μm of Al film that has limited the range of studied parameters. The volume expansion of porous alumina was studied only in oxalic acid. This work is devoted to studying the volume expansion of porous alumina formed by through anodizing of the 11.5 μm Al foil in the range of current densities from 4 to 35 $\text{mA}\cdot\text{cm}^{-2}$ in oxalic and sulphuric acids.

2. Experimental

The aluminum foil (98.0% purity) $11.5 \pm 0.2 \mu\text{m}$ thick was employed as the starting material. For formation of regions of porous alumina film a dielectric mask was used. The configuration of the mask on a working side was obtained by the photolithography method. The opposite side of the foil was fully covered with the mask. Formation of a local area of porous oxide with the reproduced and controlled size allowed to ensure high accuracy of maintenance of anodic current density. For a mask made from photoresist or barrier Al oxide the main problem during anodizing in sulphuric and oxalic acid is its damage. That is why as a mask a combination of two dielectric coatings was employed: barrier Al oxide film and Ta oxide film on the working side, barrier Al oxide film and lacquer film on the opposite side of the foil. Formation of Ta oxide layer was carried out by electrochemical oxidation of the deposited Ta film. The experiments have showed that such masks possess necessary protecting properties during anodizing of Al in sulphuric and oxalic acid.

Al foil samples of a rectangular form of dimensions $6.0 \times 4.8 \text{ cm}^2$ were used. The $70 \pm 8 \text{ nm}$ Ta film was deposited in vacuum by electron-beam evaporation on Al foil working side. The following deposition regime was used: residual chamber pressure was $1.0 \cdot 10^{-4} \text{ Pa}$, the temperature of samples was 373 K , the Ta deposition rate was $0.5 \text{ nm} \cdot \text{s}^{-1}$. Formation of Ta oxide film and barrier Al oxide film on the working side of the foil, and barrier Al oxide film on the opposite side was conducted simultaneously in the 1% aqueous solution of citric acid. The process of Al anodizing was carried out at a combined regime. The first stage consisted of anodizing at potentiodynamic regime with a scanning rate of voltage of $1 \text{ V} \cdot \text{s}^{-1}$ from 0 V up to 100 V , the second stage was at potentiostatic regime at 100 V within 5 minutes.

For selective removing of the mask from the Al foil working side by the photolithography method the photoresist mask with an open region with an area of $0.75 \times 0.75 \text{ cm}^2$ was formed. The removal of Ta oxide and barrier Al oxide layers was conducted by an ionic etching with the help of an ionic source in the argon atmosphere. The following regime of the ionic etching was used: an Ar pressure was $5 \cdot 10^{-2} \text{ Pa}$, a potential was 3 kV , a current was 80.0 mA and time of the etching process was 30 minutes.

Porous anodizing of Al was conducted in a double-electrode temperature-controlled cell of the volume of about 3 litres with the graphite cathode. Porous alumina films were formed at a galvanostatic regime of anodizing over the range of current densities from 4 to $35 \text{ mA} \cdot \text{cm}^{-2}$ with stirring of an electrolyte. For porous anodizing experiments a 4% oxalic acid and 10% sulphuric acid were used. During anodizing the electrolyte temperature was 20 and 24°C for oxalic acid and 18 and 22°C for sulphuric acid. The temperature of electrolyte was kept with an accuracy of $\pm 0.5^\circ\text{C}$. The anodizing time of the Al foil was determined by a voltage jump seen on the kinetic dependence. After the end of anodizing the lacquer film was removed in order to measure the thickness of formed porous alumina film. The removal of the lacquer film was carried out in a dimethylformamide solution.

At first, the film thickness was determined by a micrometer with an accuracy of $\pm 0.5 \mu\text{m}$. For an accurate measurement of film thickness by the step height a profilometer 296 with a computer signal processing was used. For that reason the foil was glued onto the glass substrate using dry film adhesive on an epoxy base. Chemical etching of alumina film with the use of lacquer formed the step between the porous alumina surface and the epoxy surface. The etching of alumina was carried out in the following solution: NaF is 50 g, nitric acid is 35 ml and water is 60 ml.

The Al foil had some spread of thickness that limited a precision of the measurement of porous alumina thickness by the profilometer. That is why the average thickness and a deviation from its value for each sample were determined by data of five measurements in different points. The volume expansion factor of porous alumina films was calculated as the ratio of the oxide film thickness to the thickness of Al consumed.

3. Results and discussion

The experiments have showed that the total quantity of current consumed for the electrochemical oxidation of the $11.5 \mu\text{m}$ thick Al foil in oxalic and in sulphuric acid is approximately con-

stant and is equal to $40.2 \pm 1.8 \text{ C}\cdot\text{cm}^{-2}$. This allows us to make a conclusion about the constancy of current efficiency in our experiments.

The current efficiency for electrode reaction $\text{Al} \rightarrow \text{Al}^{3+}$. To determine the current efficiency the rate of Al loss, calculated as a ratio of the Al foil thickness to the time of through oxidation of Al, was used. Fig. 1 shows the rate ($\text{m}\cdot\text{t}^{-1}$) of Al loss in $\text{mg}\cdot\text{min}^{-1}$ versus current density for the 1 cm^2 of anode during anodizing in the 4% solution of oxalic acid at 24°C . For Al mass calculation the specific density equal to $2.697 \text{ g}\cdot\text{cm}^{-3}$ was used [10]. The approximation of the dependence in Fig. 1 by least-squares method has given the following equation:

$$m \cdot t^{-1} = 0.0047j \quad (1)$$

The Al mass that was spent for oxide formation can be calculated using the Faraday law:

$$m = k_0 \cdot j \cdot S \cdot t \cdot \eta \quad (2)$$

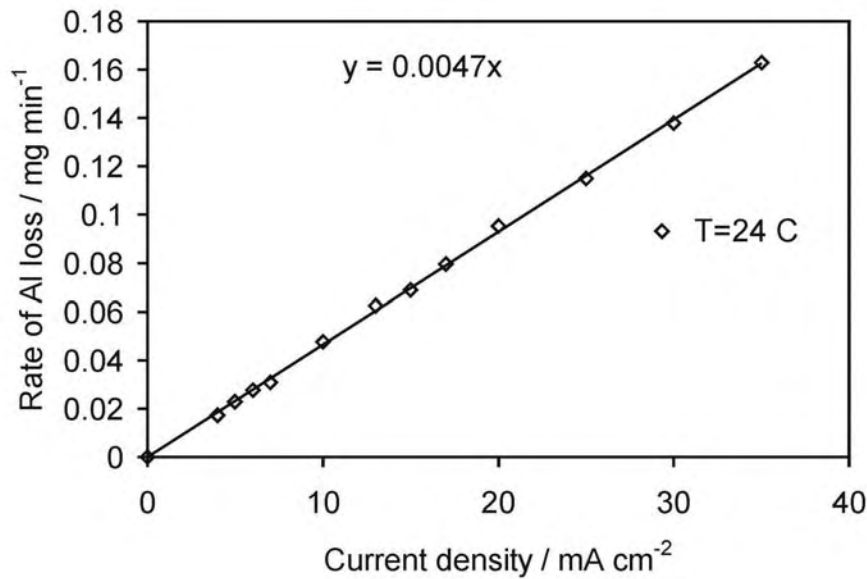
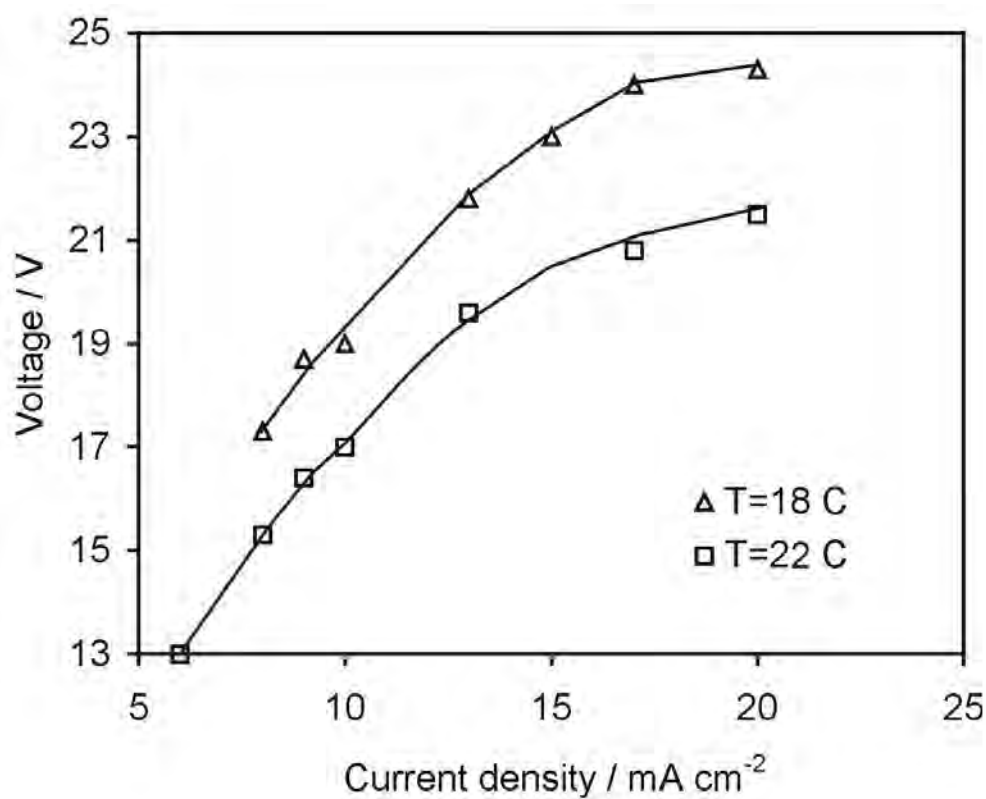


Fig. 1 The rate ($\text{m}\cdot\text{t}^{-1}$) of Al loss in $\text{mg}\cdot\text{min}^{-1}$ versus current density for the 1 cm^2 of anode during anodizing in the 4% solution of oxalic acid at 24°C .

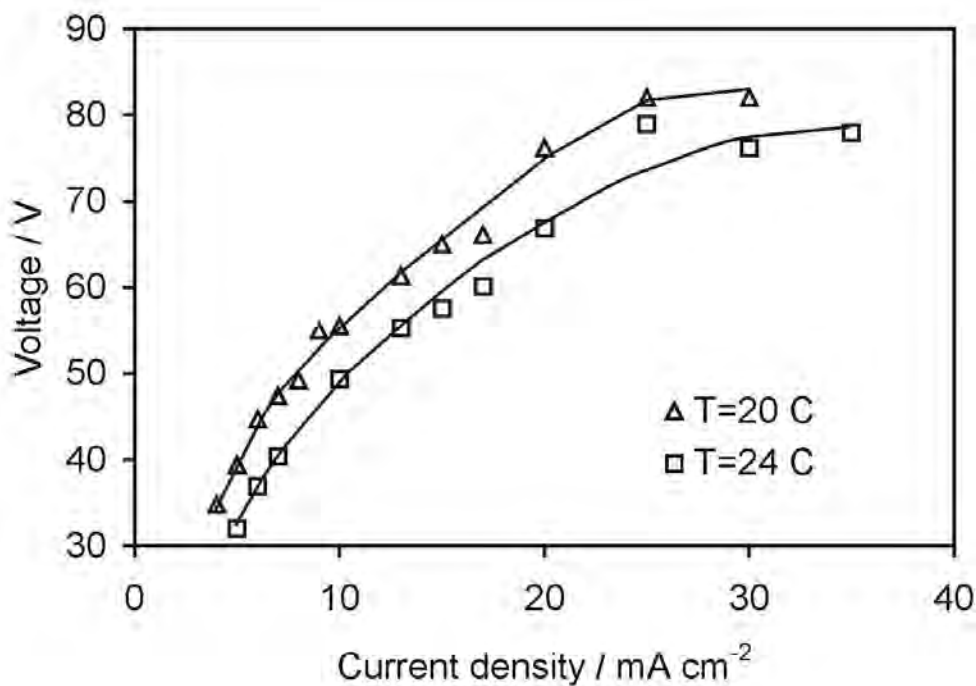
Where k_0 is the electrochemical equivalent, which for Al is $0.336 \text{ g}\cdot(\text{A}\cdot\text{h})^{-1} = 0.0056 \text{ mg}\cdot(\text{mA}\cdot\text{min})^{-1}$ [10], m is the Al mass, which was spent for oxide formation, j is the current density, S is the Al region of anodizing, t is the anodizing time, η is the current efficiency.

Comparing the experimentally obtained expression (1) with (2) the current efficiency for electrode reaction $\text{Al} \rightarrow \text{Al}^{3+}$ in oxalic acid was found to be close to 89%. As a result, there is the same value of the current efficiency in the case of sulphuric acid.

Influence of anodizing regimes on the volume expansion factor. Fig. 2 shows the anodizing voltage versus current density curves measured in sulphuric (a) and in oxalic acid (b) at different temperatures. Fig. 3 shows the volume expansion factor (k) versus the anodizing voltage in the steady-state growth region of porous alumina in sulphuric (a) and in oxalic acid (b) at different temperatures. As seen from Fig. 2 and Fig. 3, at constant current density the increase in the electrolyte temperature leads to the decrease in the anodizing voltage and in the volume expansion factor of porous alumina respectively. The observed dependences of the volume expansion factor of porous alumina films on the anodizing voltage have a linear nature. The electrolyte temperature does not change the nature of the dependence and all the points obtained for different temperatures are located at the same line in case of sulphuric acid (Fig. 3,a) and at two lines in case of oxalic acid (Fig. 3,b). Thus, the difference between sulphuric acid and oxalic acid is that on the comparable dependences for oxalic acid two linear regions are observed. For oxide formation at the anodizing voltage higher than 55 V the decrease in the slope takes place.



a



b

Fig. 2 The anodizing voltage versus current density curves measured in sulphuric (a) and in oxalic acid (b) at different temperatures.

The approximation by the least-squares method has allowed the following equations for the dependence of the volume expansion factor of porous alumina on the anodizing voltage to be established as:

In 10% sulphuric acid

$$k=0.0217 \cdot U+1.1 \quad (3)$$

In 4% oxalic acid

$$\text{I region: } k=0.0057 \cdot U+1.144 \text{ (the range of voltage from 30 to 55 V)} \quad (4)$$

$$\text{II region: } k=0.003 \cdot U+1.308 \text{ (the anodizing voltage higher than 55 V)} \quad (5)$$

Fig. 4 shows the dependences of anodic current density logarithm on the inverse volume expansion factor of porous alumina films in sulphuric (a) and in oxalic acid (b). The obtained dependences have a linear nature. These dependences are characterized by the increase in the volume expansion factor with the increase in the anodic current density. As seen from Fig. 4, each electrolyte temperature has its own dependence of anodic current density. On the dependences obtained at 20°C and 24°C the slope is simultaneously changing when the volume expansion factor reaches 1.46.

The approximation by the least-squares method for the temperature dependences in Fig. 4 has given the following equations:

Sulphuric acid

$$\ln j = -13.413 \cdot (1/k) + 11.139 \quad (T=18^\circ\text{C}) \quad (6)$$

$$\ln j = -13.426 \cdot (1/k) + 11.461 \quad (T=22^\circ\text{C}) \quad (7)$$

Oxalic acid

$$\text{I region: } \ln j = -14.148 \cdot (1/k) + 11.932 \quad (T=20^\circ\text{C, the range of } k \text{ from } 1.1 \text{ to } 1.46) \quad (8)$$

$$\text{II region: } \ln j = -27.975 \cdot (1/k) + 21.328 \quad (T=20^\circ\text{C, } k \text{ more than } 1.46) \quad (9)$$

$$\text{I region } \ln j = -14.512 \cdot (1/k) + 12.395 \quad (T=24^\circ\text{C, the range of } k \text{ from } 1.1 \text{ to } 1.46) \quad (10)$$

$$\text{II region } \ln j = -28.212 \cdot (1/k) + 21.745 \quad (T=24^\circ\text{C, } k \text{ more than } 1.46) \quad (11)$$

As can be seen from equations (6-11) for the linear dependences of $\ln j$ on $1/k$ in sulphuric acid and in oxalic acid for each region the constancy of the slope at different electrolyte temperatures is observed. The slopes of the current dependences in sulphuric acid are approximately equal to the slopes of the current dependences in oxalic acid in the first region. The slight difference between the slopes in these acids can be explained by the influence of acid anion incorporation on the volume expansion of alumina. As it is known [11] the films formed in oxalic acid contain relatively low levels of oxalate incorporation (2.4 wt.% oxalate) comparing with the films formed in sulphuric acid (12-14 wt.% sulphate). Therefore, at the same anodic current density the volume expansion factor of alumina in sulphuric acid will be higher than in oxalic acid. These peculiarities of acid anion incorporation influence the slopes of the current curves for different electrolytes. The slope of the current curves obtained in sulphuric acid at 18° and 22°C is equal to 13.42 ± 0.06 and that is less than the slope of the current curves obtained in oxalic acid (14.33 ± 0.18) at 20° and 24°C in the range of volume expansion from 1.1 to 1.46. Note that the slope of the current curve determined for oxalic acid in this work is close to 12.39 value, that has been obtained earlier in [9] for pure Al films. The decrease in the slope of the current curve in [9] can be explained by the fact that the pure aluminum has the bigger volume expansion of porous alumina during anodizing.

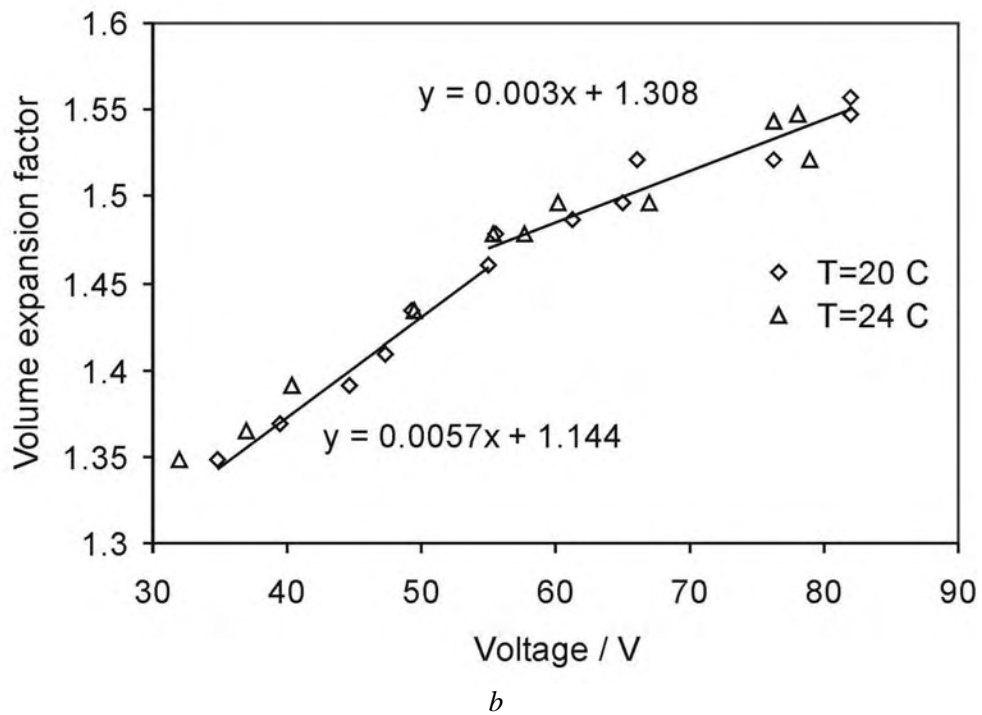
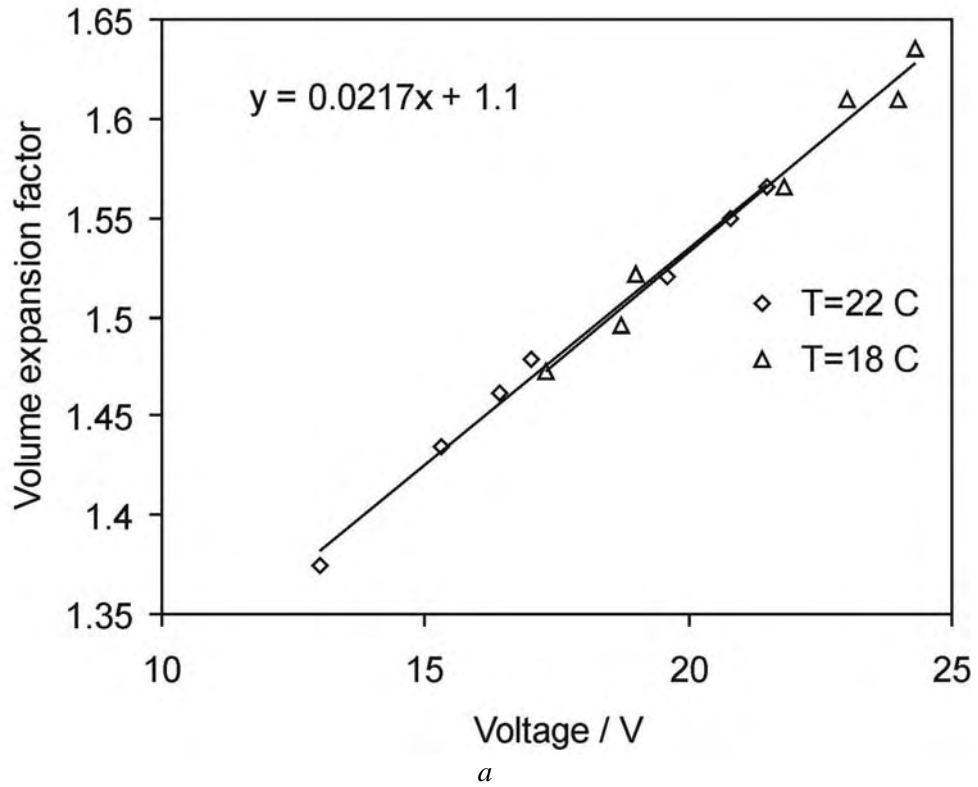


Fig. 3 The volume expansion factor (k) versus the anodizing voltage in the steady-state growth region of porous alumina in sulphuric (a) and in oxalic acid (b) at different temperatures.

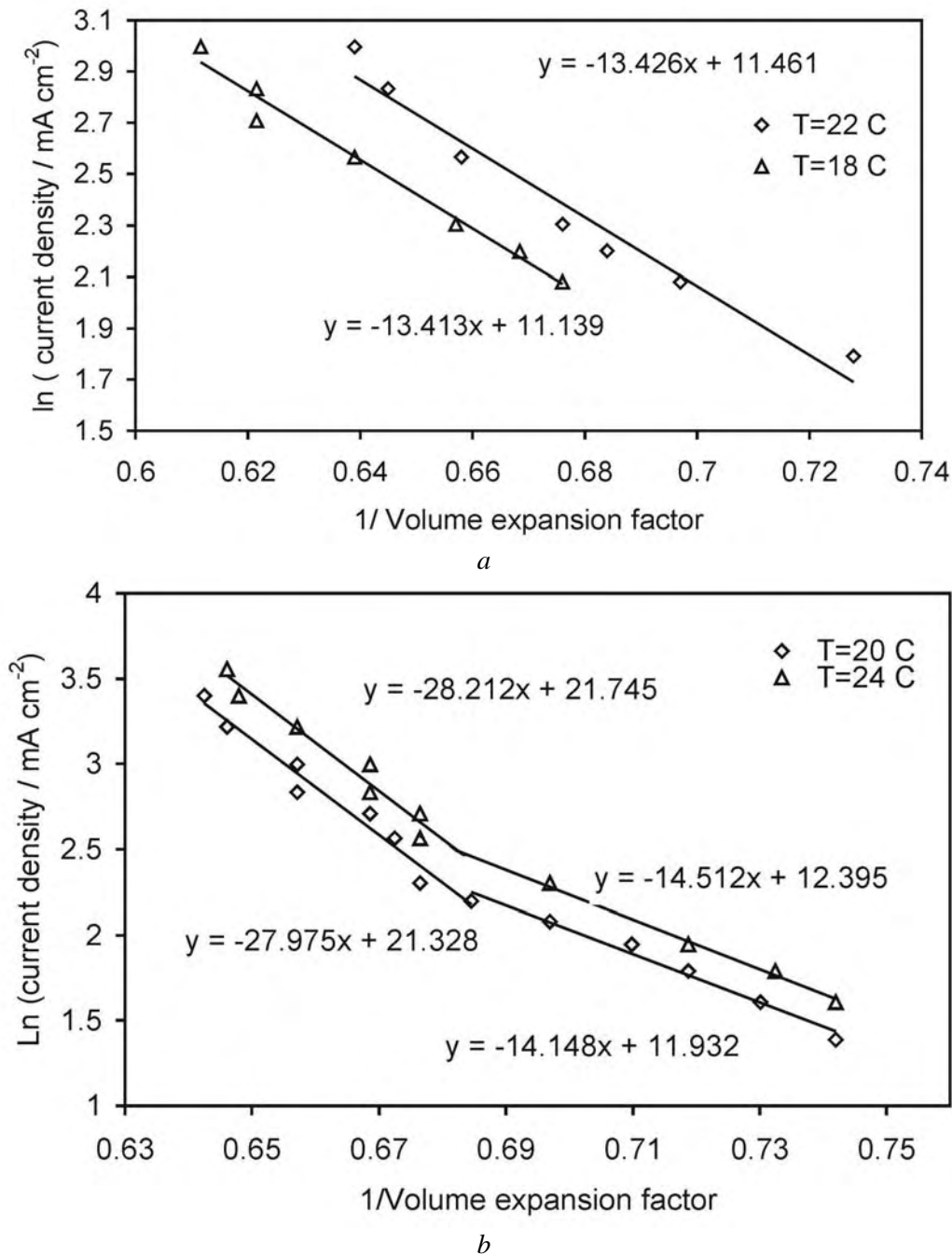


Fig. 4 The dependences of anodic current density logarithm on the inverse volume expansion factor of porous alumina films in sulphuric (a) and in oxalic acid (b).

As it is known for the steady-state anodic film formation at constant current density the cell dimensions and the barrier layer thickness are approximately constant and proportional to the anodizing voltage [7]. The mechanism controlling the formation of porous structure of oxide film is the balance between the film growth at the barrier layer and the field-assisted dissolution at the outer surface of the barrier layer. The obtained results (Fig. 4) show, that not only cell dimensions and the barrier layer thickness, but the volume expansion factor has a linear dependence on the anodizing voltage as well. As seen from Fig. 4, the dependence for oxalic acid, unlike sulphuric acid, has two linear regions. The second region of the dependence with the smaller slope starts at the anodizing voltage of 55 V. The value of the anodizing voltage for the change of the slope does not depend on the electrolyte temperature and corresponds to the volume expansion factor of 1.46.

The linear dependence of anodic current density logarithm on the inverse volume expansion factor in oxalic acid, unlike sulphuric acid, has two different regions (Fig. 4). As seen from Fig. 4 we observe a fast increase in the anodic current density when the volume expansion factor reaches a value of 1.46. The slope of the curves increases approximately by 2 times after that.

This correlates to data found in [12]. In this work for porous alumina films the measured dependences of the current density on the anodizing voltage in oxalic acid at different temperatures and the calculated with the help of the high field conduction theory [12] were compared. It was showed that for all experimental curves from a certain anodizing voltage, which does not depend on the electrolyte temperature, the fast increase of the anodic current begins. Afterwards the difference between measured and calculated dependences is observed.

Conclusions

During anodizing at constant current density the increase in the electrolyte temperature leads to the decrease in the anodizing voltage and the volume expansion factor of the porous oxide films. The volume expansion, as well as the cell dimensions and the barrier layer thickness have the linear dependence on the anodizing voltage. The dependence of the volume expansion factor on the anodizing voltage for oxalic acid, unlike sulphuric acid, consists of two subsequential rectilinear regions. The dependence in the second region (for the anodizing voltage more than 55 V, which corresponds to the volume expansion factor more than 1.46) has the slope smaller than in the first region.

It was established that the dependence of ionic current density logarithm on the inverse volume expansion factor at galvanostatic regime of anodizing of Al has a linear nature. For the obtained current dependences in oxalic and in sulphuric acid at different electrolyte temperatures a constancy of the slope is observed. The linear dependences of current density logarithm on the inverse volume expansion factor for oxalic acid, unlike sulphuric acid, have two regions.

The slope of the linear current dependence in the second region, where the volume expansion factor is more than 1.46, is two times higher than the slope in the first region.

It was established that the change in the mechanism of porous film growth in oxalic acid is observed at the anodizing voltage more than 55 V (the volume expansion factor is 1.46).

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