



Effect of Joule Heating on Formation of Porous Structure of Thin Oxalic Acid Anodic Alumina Films

Katsiaryna Chernyakova,¹ Igor Vrublevsky,¹ ^{1,z} Vaclovas Klimas,² and Arunas Jagminas²

¹Belarusian State University of Informatics and Radioelectronics, 220013 Minsk, Belarus

²Center for Physical Sciences and Technology, LT-10257 Vilnius, Lithuania

The effect of electrolyte temperature and anodizing voltage on the surface morphology of thin oxalic acid anodic alumina films formed on the SiO₂/Si and glass-ceramic substrate was studied. It was shown when anodizing voltage increased from 10 to 20 V pore diameter increased from 12.2 to 15.5 nm and from 14.5 to 17.7 nm for the films formed on SiO₂/Si and glass ceramic substrates, respectively. For the films formed at anodizing voltage (U_a) 30 and 40 V, pore diameter was 20.5 and 25.5 nm, respectively, and it was independent of the substrate type. It was demonstrated that when thin aluminum films were oxidized in oxalic acid, anodizing voltage of 30 V was a turning point at which the mechanism of the formation of anodic porous structure changed. By performing the experiments on the substrates with different thermal conductivity, we showed that at $U_a < 30$ V generated in the barrier layer Joule heating was absorbed by the substrate, but at $U_a > 30$ V the heat warmed up the electrolyte at the pore bottom that resulted in the changes of morphology of the films. We also suggested the empiric equation that connected pore diameter, anodizing current and generated Joule heating.

© 2018 The Electrochemical Society. [DOI: 10.1149/2.1001807jes]

Manuscript submitted January 24, 2018; revised manuscript received April 27, 2018. Published May 11, 2018.

Currently, nanoporous alumina is used to form structurally perfect templates used in optics, photonics, electronics and medicine.¹⁻⁴ Nanoporous alumina with an ordered pore arrangement and controlled structural parameters, such as pore diameter and interpore distance, can be obtained by electrochemical oxidation of aluminum in aqueous solutions of various acids.⁵⁻⁹ The properties of nanoporous alumina can be easily changed by varying the synthesis modes: the composition and temperature of the electrolyte, anodizing voltage, current and time.¹⁰⁻¹² In the anodic alumina coating production solutions of sulfuric, phosphoric and oxalic acids are frequently used as electrolytes. However, most studies of the properties of anodic alumina are performed on samples obtained in the solutions of oxalic acid.^{6,13-15}

Using anodic alumina films having pore diameter less than 10 nm will significantly expand the application areas of the nanostructures on their basis. These films can be synthesized in a solution of oxalic acid at the reduced anodizing voltage (<30 V). It has been found that in a wide range of anodizing voltages (40–100 V) the pore diameter exponentially increases with increased anodizing voltage.^{16,17} However, during oxidation of aluminum in solutions of oxalic acid at a voltage of 30 V and lower, the pore diameter linearly grows with increased anodizing voltage. This phenomenon has been observed in Refs. 10,18–22, but its origin has not been established yet.

Usually, the effect of temperature on the process of electrochemical aluminum oxidation is studied by changing the temperature of the electrolyte, but the effect of local anode overheating when the current passes has so far been insufficiently investigated. In Refs. 23,24, it has been shown that for sulfuric acid anodic alumina films formed at electrolyte temperature range 5–55°C neither pore diameter nor interpore distance has been changed. Studying the porous structure of thin anodic alumina film formed in 0.3 M aqueous solution of oxalic acid at anodizing voltage 20 V and temperature 20°C on silicon (SiO₂/Si) and glass ceramic substrates we have found that pore diameter was 15.1 and 17.6 nm, respectively.²⁵ This fact was explained by the difference in the thermal conductivity of silicon (149 W m⁻¹ K⁻¹) and glass ceramic (1.4 W m⁻¹ K⁻¹), as it resulted in the various rate of Joule heating transfer generated in the barrier layer of porous alumina which affected the temperature of the electrolyte at the bottom of the pore, and, as a consequence, the dissolution rate of the oxide and pore diameter.

In this study, we present the results of further investigations of the effect of anodizing modes and Joule heating generated on the formation of porous structure of thin anodic alumina films. First we obtained the films at electrolyte temperature range 5–40°C then in order to determine the influence of local temperature on the mor-

phology of the films synthesized on substrates with different thermal conductivity we studied the effect of changed anodizing voltage (range 10–30 V and 40 V).

Experimental

Thin aluminum films (about 100 nm in thickness) were obtained on silicon coated with silicon dioxide (SiO₂/Si, 60 nm thick SiO₂ layer on 375 μm thick Si substrate) and glass ceramic substrates by vacuum thermal evaporation. The trademark of glass-ceramic substrate (Sitall) used in our experiments was CT-50-1, Russia (60.5 wt% SiO₂, 13.5 wt% Al₂O₃, 8.5 wt% MgO, 7.5 wt% CaO, 10 wt% TiO₂). The thermal conductivity of silicon substrate (149 W m⁻¹ K⁻¹) was significantly higher than that of glass ceramic substrate (1.4 W m⁻¹ K⁻¹).

Then square pieces with an area not more than 7.2 cm² were cut and anodized in a 0.3 M aqueous solution of oxalic acid at constant voltage in the range 10–40 V using power supply PI50-1. The anodizing area of ca. 3.14 cm² was set out by a Viton-o-ring. The process was carried out in two electrode polytetrafluoroethylene cell similar to the one described in Ref. 26 at constant temperature in the range 5–40°C. The electrolyte temperature was fixed by cryostat WK 230 (Lauda). Platinum net was applied as the counter electrode. The electrolyte was vigorously stirred. After anodizing the samples had the surface appearance shown in Figure 1.

The morphology and pore diameter were studied by scanning electron microscopy (SEM) using electron microscope model Quatra 200F (FEI) with subsequent statistical analysis of the images by ImageJ software.

A major pore diameter (d_{pore}), Figures 2a and 2b (SiO₂/Si substrate, 0.3 M oxalic acid, $T = 20^\circ\text{C}$), was determined by procedure described in Ref. 25. To calculate a cell diameter (D_{cell}) the following algorithm was applied:

- 1) determination of pore centers with SEM images;
- 2) segmentation of the image relative to the pore centers (Figure 2c);
- 3) calculation of D_{cell} using Equation 1:

$$D_{\text{cell}} = \frac{2}{3} \sqrt{2\sqrt{3}S} \quad [1]$$

where S is the area of each segmented cell assuming the hexagonal arrangement of the pores.

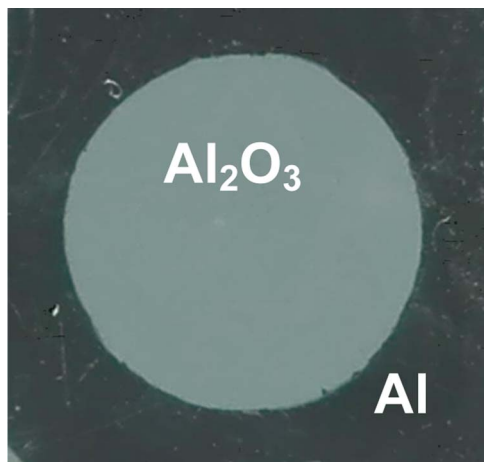


Figure 1. Surface appearance of the as-anodized alumina formed by anodizing in a 0.3 M aqueous solution of oxalic acid at 15 V and 20°C of the aluminum deposited onto the glass ceramic substrate.

Then, based on the data obtained, we determined interpore distance (D_{inter}) by Equation 2:

$$D_{\text{inter}} = \frac{\sqrt{3}}{2} D_{\text{cell}}. \quad [2]$$

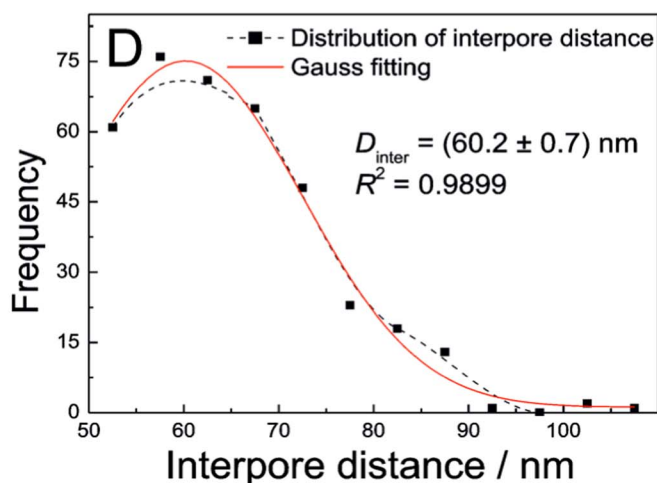
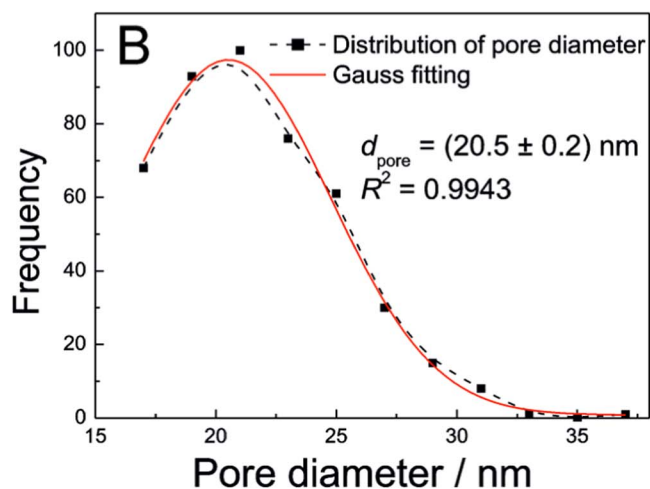
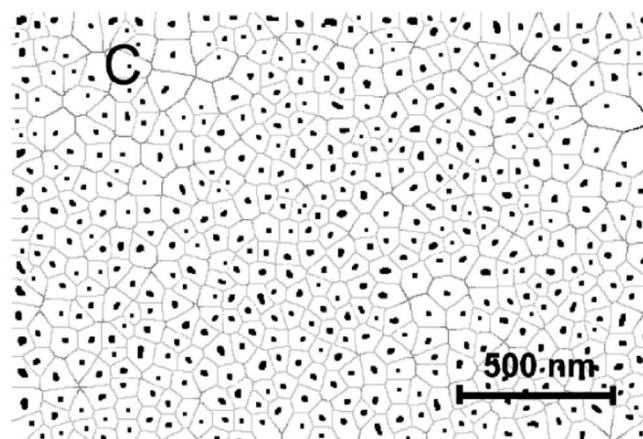
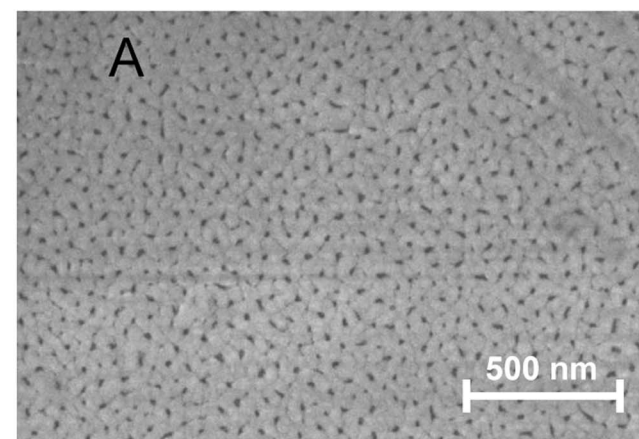


Figure 2. Representation of the image processing steps: the original image (a); Gaussian distribution of the pore diameter (b); segmented image showing the cells with the computed centers (c); Gaussian distribution of interpore distance (d).

The D_{inter} values were taken in order to plot histograms, which were fitted by Gauss curves (Figure 2d). The maximum in interpore distance distribution curve corresponded to the average value of D_{inter} . For obtaining accurate results, we analyzed each image minimum 10 times. The error in the determination of d_{pore} and D_{inter} was not greater than 1% and 5%, respectively.

Results and Discussion

Effect of electrolyte temperature.—To study the effect of the electrolyte temperature on the morphology of the surface of thin films of oxalic acid anodic alumina, we chose SEM images of the films formed at 30 V. As in this case, the pore diameter was larger than in the samples obtained at lower voltages, which simplified the processing of images in ImageJ and increased the accuracy of the results. Besides, in all the experiments, the time for the complete oxidation of aluminum did not exceed 180 s. This guaranteed that the oxide was not subjected to a prolonged aggressive impact of the electrolyte and, in turn, prevented pore etching at the oxide | electrolyte interface.

According to the SEM data, d_{pore} and D_{inter} are (20.5 ± 0.5) nm and (62.5 ± 2.5) nm, respectively, for the films formed at temperature range 5–40°C. Both d_{pore} and D_{inter} are independent of the electrolyte temperature (Figure 3). Though, this result agrees with the data obtained by other authors,^{23,24,27,28} it stays still quite unexpected, since an increase in the temperature of the electrolyte in the electrochemical cell should have led to the increase in the activity of the electrolyte and hence to the pore widening. In Ref. 25 it was shown that the observed effect resulted from the difference in the electrolyte temperature at

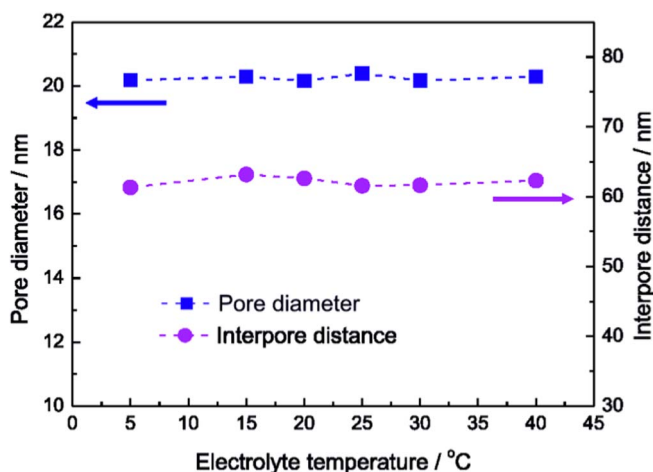


Figure 3. Evolution of pore diameter and interpore distance as a function of the electrolyte temperature for nanoporous alumina films formed in a 0.3 M oxalic acid at 30 V.

the pore bottom and in the electrochemical cell. At the pore bottom, it is much higher than in the cell. Therefore, we can assume that at the pore bottom, the electrolyte temperature depends only on the amount of Joule heating evolved in the barrier layer of the alumina. In this case, an increase in the anodizing voltage leads to the increase in the amount of Joule heating generated and, as a result, to the pore widening and the change in the D_{inter} . Based on these ideas we attempt to analyze and explain the experimental data obtained depending on the anodizing voltage applied.

Effect of anodizing voltage.—When anodizing voltage increases from 10 to 20 V pore diameter increases from 12.2 to 15.5 nm and from 14.5 to 17.7 nm for the films formed on SiO_2/Si and glass ceramic substrates, respectively. For the films formed at U_a 30 and 40 V, d_{pore} is 20.5 and 25.5 nm, respectively, and it is independent of the substrate type. It should be noted that at $U_a < 30$ V for the films obtained on glass ceramic substrate d_{pore} is greater than for the ones obtained on SiO_2/Si (Figure 4).

Thus, at low anodizing voltages d_{pore} depends on the type of substrate on which the alumina films have been obtained. As, during the aluminum anodizing, at the bottom of the pore the electrolyte is

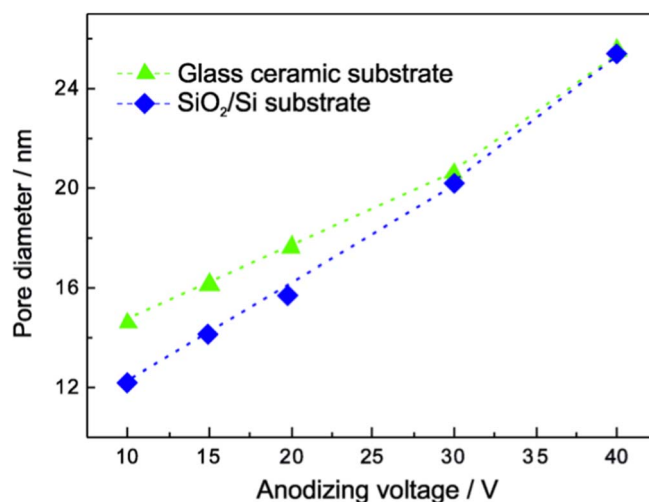


Figure 4. Evolution of pore diameter as a function of the anodizing voltage for nanoporous alumina films formed in a 0.3 M oxalic acid.

heated by the generated Joule heating, and this causes a continuous circulation of the electrolyte in the pore resulted from the diffusion (Figure 5). The more heat is released, the higher circulation speed of the electrolyte is: at $U_a < 30$ V it is not high, so the main role in the heat dissipation will play the substrate on which the oxide film is formed. This is confirmed by the experimental data as the thermal conductivity of glass ceramic is less than the one of silicon, therefore, due to the high dissolution rate of the oxide, the pore diameter for the films formed on glass ceramic substrate is greater than the one on SiO_2/Si . However, at high U_a , when the electrolyte circulation speed noticeably increases the ways of heat dissipation also changes. In this case, the thermal conductivity of the substrate does not play an important role that we have observed in our experiments: at $U_a > 30$ V d_{pore} depends only on the anodizing voltage (See Figures 4).

So, when thin aluminum films are anodized in the aqueous solution of oxalic acid, $U_a = 30$ V is a turning point in which the mechanism of formation of the porous structure of anodic aluminum oxide films changes. This conclusion can be confirmed by the other experimental data, such as the dependence of D_{inter} and J_a on U_a (Figures 6 and 7). As can be seen from Figure 6, D_{inter} linearly increases with the increased anodizing voltage and does not depend on the substrate

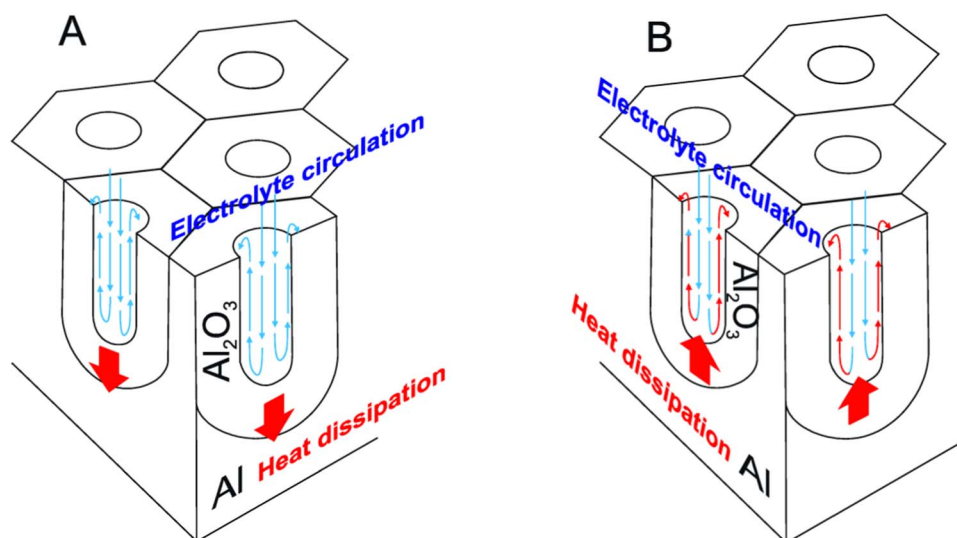


Figure 5. Schematic illustration of Joule heating dissipation during anodizing of thin aluminum films in aqueous solution of oxalic acid at $U_a < 30$ V (a) and $U_a > 30$ V (b).

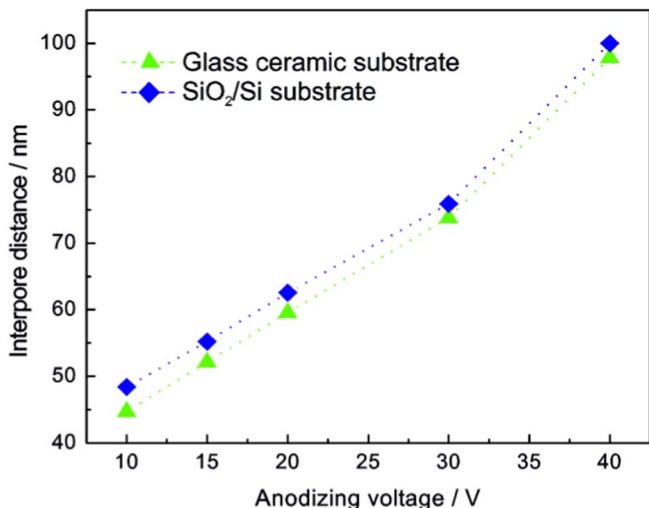


Figure 6. Evolution of inter pore distance as a function of anodizing voltage for nanoporous alumina films formed in a 0.3 M oxalic acid.

type on which the oxide was formed. Moreover, at anodizing voltage range 10–30 V the slope (k) equals to 1.38 that is less than at 30–40 V ($k = 2.41$). The same peculiarity of D_{inter} changes was observed in Refs. 13,20,29 At the anodizing voltage range 10–30 V, the evolution of D_{inter} as a function of U_a is described by Equation 3:

$$D_{\text{inter}} = 1.38U_a + 37.4, \quad [3]$$

by Equation 4 at $U_a > 30$ V:

$$D_{\text{inter}} = 2.41U_a + 3.5. \quad [4]$$

The experimental data obtained confirmed that when thin aluminum films are oxidized in oxalic acid $U_a = 30$ V is a turning point at which the mechanism of porous structure formation of anodic alumina changes. At low values of U_a (<30 V) the heat generated is absorbed by the substrate. At higher U_a values, the amount of Joule heating noticeably increases that results in the rise in the electrolyte temperature and in its circulation speed, at the same time, the etching of pores and increase in their diameter take place. Moreover, Joule heating released in the barrier layer of growing anodic alumina film plays a key role in the processes of the formation of porous structure.

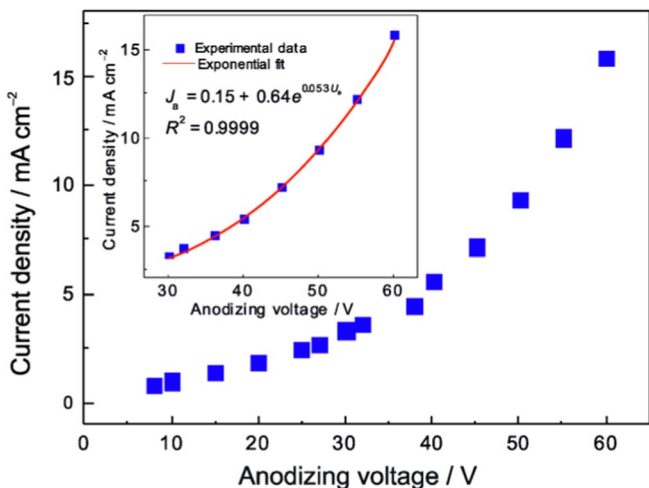


Figure 7. Evolution of current density as a function of anodizing voltage for the thin aluminum film oxidation in a 0.3 M oxalic acid at 20°C. The inset shows the exponential fitting of the current–voltage curve at $U_a > 30$ V.

In the anodizing voltage range 10–30 V, the changes in J_a versus U_a obeys Ohm's law, but, at $U_a > 30$ V, this relationship is broken and becomes exponential (Figure 7). It also agrees with data obtained by S. Ono and N. Masuko.³⁰

In our research, we also attempted to explain observed exponential behavior of d_{pore} and J_a , taking into account the role of Joule heating. During aluminum anodizing in oxalic acid solution, at the pore bottom the generated Joule heating warms up the electrolyte at the pore bottom and increases its chemical activity. This results in the pore widening.

Consider the situation when during the aluminum anodizing the work of an external electric field completely uses up to the release of Joule heating (Q) and the specific heat of the electrolyte (c) is independent of the temperature in the selected range:

$$Q = IUt = cm\Delta T, \quad [5]$$

where U is anodizing voltage; I is anodizing current; t is anodizing time; m is the mass of the electrolyte heated by ΔT in the pore; ΔT is the increase in the electrolyte temperature resulted from heating at the pore bottom (the difference between the final and initial electrolyte temperature).

$$m = \frac{1}{2} \left(\pi \frac{d_{\text{pore}}^2}{4} \right) N \rho v t = \frac{1}{8} \pi d_{\text{pore}}^2 N \rho v t \quad [6]$$

where d_{pore} is pore diameter; v is the speed of electrolyte circulation; ρ is the specific electrolyte density; N is the number of pores; t is anodizing time.

According to^{10,31} with increased anodizing voltage the porosity and number of pores are almost unchanged so Equation 5 can be written as follows:

$$IU = \frac{1}{8} \pi c \rho d_{\text{pore}}^2 N v \Delta T \quad [7]$$

Since the increase in electric power by $\delta(IU)$ leads to an increase in the temperature of the electrolyte at the bottom of the pore by δT , the Equation 7 can be written:

$$\delta(IU) = \frac{1}{8} \pi c \rho d_{\text{pore}}^2 N v \delta T. \quad [8]$$

As when $U_a > 30$ V the anodizing current exponentially depends on the anodizing voltage ($I = I_0 e^{\beta U}$) then:

$$\delta(IU) = \delta(I_0 e^{\beta U}) = U I_0 \beta e^{\beta U} \delta U + I_0 e^{\beta U} \delta U, \quad [9]$$

where β and I_0 are oxide specific constants.³²

As far as $U I_0 \beta e^{\beta U} \delta U \gg I_0 e^{\beta U} \delta U$ then

$$\delta(IU) = U I_0 \beta e^{\beta U} \delta U. \quad [10]$$

When the electrolyte temperature increased the rate of oxide dissolution also grew according to the Arrhenius equation:

$$k = A e^{-E_a/RT}, \quad [11]$$

where k is rate constant of the alumina dissolution; A is pre-exponential factor that characterizes the frequency of collisions of the reacting molecules; E_a is activation energy; R is universal gas constant.

Substitute Equation 11 into one-term Taylor series:

$$k = A \left(1 - \frac{E_a}{RT} \right). \quad [12]$$

By differentiating left and right sides of the Equation 12, we find that

$$\delta k = \frac{A E_a}{RT^2} \delta T. \quad [13]$$

According to the mass action law $r \sim k$, as well with increased electrolyte temperature its chemical activity also grows that results in the increase in the rate of oxide dissolution (r), i.e., $d_{\text{pore}} \sim r$. Therefore, Equations 13 can be written as follows:

$$\delta d_{\text{pore}} = \frac{A E_a}{RT^2} \delta T. \quad [14]$$

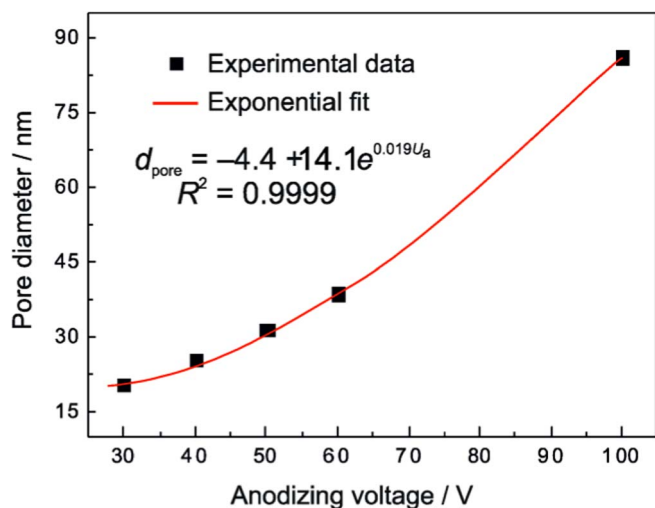


Figure 8. Evolution of pore diameter as a function of anodizing voltage for the thin aluminum film oxidation in a 0.3 M oxalic acid at 20°C.

Then in a view of Equations 10 and 14 the Equation 8 can be written as:

$$UI_0\beta e^{\beta U}\delta U = \frac{1}{8} \frac{c\rho\pi RT^2}{AEa} Nvd_{\text{pore}}^2 \delta d_{\text{pore}} = \alpha vd_{\text{pore}}^2 \delta d_{\text{pore}}. \quad [15]$$

It is known that in the process of aluminum anodizing the rate of chemical dissolution of the oxide is equal to the rate of formation of anodic alumina, therefore, for a given anodizing voltage, the thickness of the barrier layer of the porous anodic oxide remains constant. Consequently, the speed of electrolyte circulation in the pore is directly proportional to the anodizing voltage. Then Equation 15 can be simplified as follows:

$$\beta I_0 e^{\beta U} \delta U = \alpha d_{\text{pore}}^2 \delta d_{\text{pore}}. \quad [16]$$

By integrating the left and right sides of the Equation 16, we find:

$$I_0 e^{\beta U} + C = \frac{1}{3} \alpha d_{\text{pore}}^3, \quad [17]$$

where C is constant of integration.

As $C \rightarrow 0$ Equation 17 can be written:

$$d_{\text{pore}} = \sqrt[3]{\frac{3I_0}{\alpha}} e^{\frac{1}{3}\beta U}. \quad [18]$$

The experimental value of the coefficient β determined by plotting J_a from U_a equals 0.053 (Figure 7, insert). The value of β calculated by plotting d_{pore} as a function of U_a is close to 0.053 ($0.019 \times 3 = 0.057$) (Figure 8). According to the data obtained the Faraday current efficiency for pure aluminum in case of oxalic acid anodizing is close to 100% that agrees with the results reported in Refs. 33,34.

Conclusions

It was established that at low anodizing voltages d_{pore} depended on the type of substrate on which the alumina films was been obtained. As, during the aluminum anodizing, at the bottom of the pore the electrolyte was heated by the generated Joule heating, and this caused a continuous circulation of the electrolyte in the pore resulted from the diffusion. The more heat was released, the higher circulation speed of the electrolyte was: at $U_a < 30$ V it was not high, so the main role in the heat dissipation will play the substrate on which the oxide film was formed. It was explained by the difference in the thermal conductivity of silicon and glass ceramic, the thermal conductivity of glass ceramic was less than the one of silicon, therefore, due to the high dissolution rate of the oxide, the pore diameter for the films formed on glass ceramic substrate was greater than the one on SiO₂/Si. At high U_a ,

when the electrolyte circulation speed noticeably increased the ways of heat dissipation also changed. In this case, the thermal conductivity of the substrate did not play an important role: at $U_a > 30$ V d_{pore} depended only on the value of anodizing voltage.

It was demonstrated that when thin aluminum films were oxidized in oxalic acid anodizing voltage of 30 V is a turning point at which the mechanism of the formation of anodic alumina porous structure changed. By performing the experiments on the substrates with different thermal conductivity, we showed that at $U_a < 30$ V generated in the barrier layer Joule heating was absorbed by the substrate, but at $U_a > 30$ V the heat warmed up the electrolyte that resulted in the changes of morphology of the films. We also suggested the empiric equation that connected pore diameter, anodizing current and Joule heating generated.

Acknowledgment

The authors gratefully acknowledge Arnas Naujokaitis for SEM observations.

ORCID

Igor Vrublevsky  <https://orcid.org/0000-0002-6796-8994>

References

1. A. M. Md. Jani, D. Losic, and N. H. Voelcker, *Prog. Mater. Sci.*, **58**, 636 (2013).
2. A. Santos, *J. Mater. Chem. C*, **5**, 5581 (2017).
3. W. Lee and S.-J. Park, *Chem. Rev.*, **114**, 7487 (2014).
4. A. Santos, T. Kumeria, and D. Losic, *Trends Analytic Chem.*, **44**, 25(2013).
5. S. Ono, M. Saito, and H. Asoh, *Electrochim. Acta*, **51**, 827 (2005).
6. O. Jessensky, F. Muller, and U. Gosele, *Appl. Phys. Lett.*, **72**, 1173 (1998).
7. A. Jagminas, D. Bigeliene, I. Mikulskas, and R. Tomašiūnas, *J. Cryst. Growth*, **233**, 591 (2001).
8. H. Masuda and K. Fukuda, *Science*, **268**, 1466 (1995).
9. A. Mozalev, I. Mozaleva, M. Sakairi, and H. Takahashi, *Electrochim. Acta*, **50**, 5065 (2005).
10. S. Ono and N. Masuko, *Surf. Coat. Technol.*, **169–170**, 139 (2003).
11. I. A. Vrublevsky, A. I. Jagminas, and K. V. Chernyakova, *J. Electrochem. Soc.*, **160**, C285 (2013).
12. R. Elaiash, M. Curioni, K. Gowers, A. Kasuga, H. Habazaki, T. Hashimoto, and P. Skeldon, *J. Electrochem. Soc.*, **164**, C831 (2017).
13. W. J. Stepniowski, M. Norek, M. Michalska-Domańska, and Z. Bojar, *Mater. Lett.*, **111**, 20 (2013).
14. Li. Wang, G. Li, X. Liu, S. Xia, and H. Jia, *J. Electrochem. Soc.*, **164**, E117 (2017).
15. G. D. Sulka and W. J. Stepniowski, *Electrochim. Acta*, **54**, 3683 (2009).
16. T. Kikuchi, D. Nakajima, O. Nishinaga, S. Natsui, and R. O. Suzuki, *Curr. Nanosci.*, **11**, 560 (2015).
17. Alaa M. Abd-Elnaiem, A. M. Mebed, A. Gaber, and M. A. Abdel-Rahim, Effect of the Anodization Parameters on the Volume Expansion of Anodized Aluminum Films, *Int. J. Electrochem. Sci.*, **8**, 10515 (2013).
18. S. Shingubara, O. Okino, Y. Sayama, H. Sakaue, and T. Takahagi, *Jpn. J. Appl. Phys.*, **36**, 7791 (1997).
19. S. Shingubara, O. Okino, Y. Sayama, H. Sakaue, and T. Takahagi, *Solid-State Electron.*, **43**, 1143 (1999).
20. W. J. Stepniowski, A. Nowak-Stepniowska, M. Michalska-Domańska, M. Norek, T. Czujko, and Z. Bojar, *Polish J. Chem. Technol.*, **16**, 63 (2014).
21. J. A. Wahab, M. N. Derman, and Z. C. Daud, The Effect of Electrolyte Temperature on Formation of Porous Aluminium Oxide Films Anodising Process, *Adv. Environ. Biol.*, **7**, 3708 (2013).
22. S.-K. Hwang, S.-H. Jeong, H.-Y. Hwang, O.-J. Lee, and K.-H. Lee, *Korean J. Chem. Eng.*, **19**, 467(2002).
23. T. Aerts, Th. Dimogerontakis, I. De. Graeve, J. Fransaer, and H. Terryn, *Surf. Coat. Technol.*, **201**, 7310 (2007).
24. W. J. Stepniowski and Z. Bojar, *Surf. Coat. Technol.*, **206**, 265 (2011).
25. I. Vrublevsky, A. Ispas, K. Chernyakova, and A. Bund, *J. Solid State Electrochem.*, **20**, 2765 (2016).
26. A. Ispas, A. Bund, and I. Vrublevsky, *Electrochim. Acta*, **55**, 4180 (2010).
27. L. Cantelli, J. S. Santos, and F. Trivinho-Strixino, *J. Electroanal. Chem.*, **780**, 386 (2016).
28. C. H. Voon, M. N. Derman, U. Hashim, K. R. Ahmad, and K. L. Foox, *J. Nanomater.*, **2013**, Article ID 167047, 8 (2013).
29. L. Zaraska, G. D. Sulka, J. Szeremeta, and M. Jaskuła, *Electrochim. Acta*, **55**, 4377 (2010).
30. S. Ono and N. Masuko, *ECS Transactions*, **75**, 23 (2017).
31. K. Ebihara, H. Takahashi, and M. Nagayama, *J. Met. Finish. Soc. Jpn.*, **34**, 548 (1983).
32. S. Ruesse, M. M. Lohrengel, and J. W. Schultze, *Solid State Ionics*, **72**, 29 (1994).
33. F. Li, L. Zhang, and R. M. Metzger, *Chem. Mater.*, **10**, 2470 (1998).
34. A. Mozalev, A. Poznyak, I. Mozaleva, and A. W. Hassel, *Electrochem. Commun.*, **3**, 299 (2001).