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TRANSLATION

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By

N. D. Tomashov and P. P. Zalivalov

FOREIGN TECHNOLOGY DIVISION

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THE CELLULAR STRUCTURE OF THICK-LAYERED ANODIC OXIDE FILMS

By

N. D. Tomashov and F. P. Zalivalov

Thick-layered oxide films (of a thickness of 25 to 200 microns) anodically formed on the surface of aluminum and its alloys have great practical significance due to such valuable properties as high resistance to wear by attrition, high heat and electrical insulation qualities, condiderable toughness in meshing with other metals, and high resistance to corrosion [1—3]. The properties of anodic oxide films are determined by their structure, which in turn depends on the conditions of the electrolysis.

A considerable amount of work has been devoted to the investigation of the structure of anodic films obtained on pure aluminum by foreign and domestic authors [4—8], according to which the structure of these films represents a dense packing of oxide units of hexagonal form set perpendicularly to the surface of the metal and solidly welded to each other by their lateral faces (Fig. 1). Each unit (or cell) consists of a centrally located pore, the walls of the oxide cell, and a thin layer of oxide of the barrier type (barrier film) as its basis. The diameter of the pore is determined mainly by the character of the electrolyte and does not depend on other conditions of the anode process.

The study of the structure of the anodic oxide films, along with a great deal of theoretical interest, has direct practical significance, inasmuch as it enables one to mark out ways for the creation of new coatings with properties given beforehand and also to proceed to the explanation of the structure and properties of anodic films obtained on aluminum allows. The purpose of this present work is centered in the determination of the quantitative interconnection between the thickness of the barrier layer of the film and the dimensions of the oxide cells.

For objects of research there were chosen specimens of aluminum of the brand AV000 (99.99% Al) which were then anodically oxidised (anodised) in 4-n H_2SO_4 with current densities of 2.5, 5, and 10 amp/dm^2 and the shaping voltages corresponding to them (E) 22, 25, and 27 v. The temperature of the electrolyte during the anodising was maintained at about — 2 . For comparison we researched the structure of the anodic cell obtained in the ordinary procedure of the anodic process: density of the current 1 amp/dm^2 (shaping voltage 10v), temperature of electrolyte 20 . The procedure and conditions of the anodising are described more in detail in other reports [9, 10]. The dimensions of the oxide cells are determined from photographs obtained with the electron microscope EM-3 with the aid of collodion and carbon replicas [8]. The thickness of the barrier layer of the anodic film was determined by the electrochemical method [11], based on the measurement of the dependence, voltage-amperage in alkalised 3-percent solution of tartaric acid (pH = 5.5) in which the rate of the growth of the barrier is equal to 14 Å/v. In accordance with these data the thickness of the barrier layer (A) is equal to the fourteenfold maximum terminal voltage of the circuit in volts at which the current does not rise sharply. The latter is observed at the rise above the

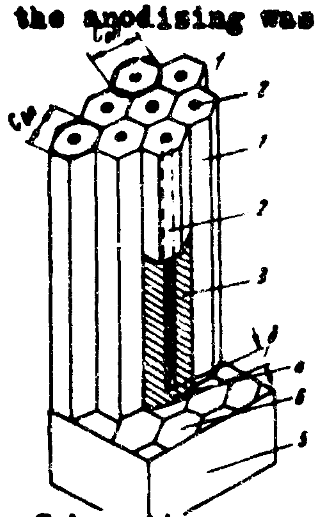

Fig. 1. Schematic presentation of the structure of the cells obtained in anodic oxidation of aluminum sulfuric acid. 1—oxide cell, 2—pore, 3—wall of oxide cell, 4—barrier layer, 5—aluminum, 6—impressions of oxide cells on surface of aluminum after removal of anode film: C is dimension of oxide cell equal to diameter to circle inscribed in hexagon, C is the same but for circumscribed

cont. Fig. 1.

circle, δ--thickness of barrier layer

voltage at which there was formed the given barrier layer.

In the article two questions are considered.

1. Keeping in mind that the oxide film is formed in the barrier layer it is natural to assume a definite dependence between the thickness of the barrier layer and the size of the oxide cell (See Fig. 1). The first attempt to find such a dependence was made on the basis of theoretical premises in the report [4] in which the relationship between the size of the cell $C_{B\Pi}$, equal to the diameter of the circle inscribed in the hexagonal cell and the thickness of the barrier layer δ is expressed by the formula $C_{B\Pi} = \sqrt{2\delta}$. In the following work [5] the connection between the size of the cell and the thickness of the barrier layer, which was obtained on the basis of experimental data, is determined by the equation $C_{B\Pi} = 1.67\,\delta + p$, where p is the size (diameter) of the pore. In the work [7] it is pointed out that in accordance with calculations the distance between the pores cannot exceed twice the thickness of the barrier layer and ordinarily is equal to its thickness, i. e., one can write that $C_{B\Pi} \approx \delta$. By rewriting the above-presented equations $C_{B\Pi} = \sqrt{2\delta}$, $C_{B\Pi} = 1.67\,\delta + p$ and $C_{B\Pi} \approx \delta$ in the form of a ratio of the thickness of the wall of the oxide cell $\frac{(C_{B\Pi} - p)}{2}$ to the thickness of the barrier layer (δ) we shall have correspondingly

$$\frac{C_{вп} - p}{2\delta} < 0{,}7, \quad \frac{C_{вп} - p}{2\delta} = 0{,}835 \text{ и } \frac{C_{вп} - p}{2\delta} < 0{,}5,$$

i. e., the ratio $\frac{C_{B\Pi} - p}{2}$ which characterizes the connection of the thickness of the wall of the oxide cell with the thickness of the barrier layer in all cases less than unity.

In Table 1 there are shown the figures for the dimensions of the described cells of anodic films and the thickness of the barrier layer corresponding to them, which were obtained experimentally for four procedures of anodic oxidation of aluminum. Since the cell has a six-sided form in the table there are given two dimensions of the oxide cell: one equal to the diameter of a circle described in the hexagon ($C_{\text{вп}}$) and another equal to the diameter of a circumscribed circle ($C_{\text{оп}}$).

The ratio of the thickness of the wall of the oxide cell to the thickness of the barrier layer, i. e., the magnitude $\frac{C_{\text{вп}} - p}{2\delta}$ as is seen from Table 1, lies within the limits of 0.802 to 0.811. The ratio $\frac{C_{\text{оп}} - p}{2\delta}$ computed from the cell equal to the diameter of circle circumscribing the hexagon is equal to 0.958—9.994, i. e., to the greatest degree approaches unity. In fact the most probable ratio, so it seems, will be the equality $\frac{C'_{\text{оп}} - p}{2\delta} = 1$, where $C'_{\text{оп}}$ is the maximum possible dimention of the cell (according to the circumscribed circle). Then the greatest magnitude of the size of the cell in accordance with inscribed circle ($C'_{\text{вп}}$) will be equal to $C'_{\text{вп}} = \frac{C'_{\text{оп}}}{k}$ where k is the coefficient which determines for the correct hexagon the ratio of the diameter of the circumscribed circle to the diameter of the inscribed circle ($k = 1.154$). In this way one may conclude that the basic relationship which determines the structural parameters of the thick-layer anodic film is the equation $\frac{C'_{\text{оп}} - p}{2\delta} = 1$. The figures of the dimensions of the oxide cell are determined in the following form: $C'_{\text{оп}} = 2\delta + p$ and $C'_{\text{вп}} = \frac{C'_{\text{оп}}}{k}$. All other relationships prove to be more or less precise approximations to these equations.

As an example which confirms the close connection of the thickness of the barrier layer with the size of the oxide cell one may use the temperatures given in accordance with the effect on them. As is seen from Fig. 2 and Fig. 3, with the rise in the temperature of the electrolyte, there is a drop in the thickness of the barrier layer and the size of the oxide cell. Since the two experiments were set up in somewhat different conditions they do not allow a numerical comparison of these values. However, the conformity to law in the two cases is identical.

2. In the research of the cellular structure of the thick-layered anodic films the most characteristic form of the mutual orientation is the strict

Table 1

Structural characteristics of anodic oxide films obtained on aluminum with ordinary and thick-layered anodizing in 4-n H_2SO_4

Method of anodizing and overall thickness of anode layer in microns	Density of the anodic flow D_a amp/dm²	Shaping voltage E в	Size of oxide cell Å		Thickness of barrier layer of film (δ) Å	Ratio of thickness of wall of oxide cell to thickness of barrier layer	
			Computed by inscribed circle $C_{вп}$	Computed by circumscribed circle $C_{оп}$		$\frac{C_{вп}-p^*}{2\delta}$	$\frac{C_{оп}-p}{2\delta}$
Ordinary anodizing							
t = 20°,	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
a** = 7 microns							
Thick-layered anodizing	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
t = —2°,	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
a = 100 microns	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

---

* Dimension (diameter) of pore for all presented procedures of anodizing, constant and equal to 20 Å

**a — overall thickness of anodic film

orderliness (regularity) in the arrangement of the oxide cells. This can be seen from Fig. 4, a and b, where there are presented the electron-microscope pictures obtained by us of the cellular structure in two mutually perpendicular planes. As is seen from Fig. 4, a, each cell, judging by its impression on the photograph, borders on six adjoining cells, forming a solid packing of hexagons, reminding one of a beehive. As is known the most solid packing of spheres is such an arrangement of them that each sphere has six neighbors in contact with it. There is no other way of arranging a solid layer of spheres, and the bases of oxide cells represent spheres, close in their geometry to hemispheres. Therefore the form of the oxide cells corresponds to the form of hexahedrons.

In accordance with our concept the orderly cellular structure is formed in the following way. In the beginning after the formation of the thin nonporous oxide film of the barrier type on the surface of the metal in the process of its anodising there are formed separate cells corresponding to those places in the film where the pores are formed. The presence of such places is determined by some kind of defects in the barrier film which more easily are subjected to the caustic action of the

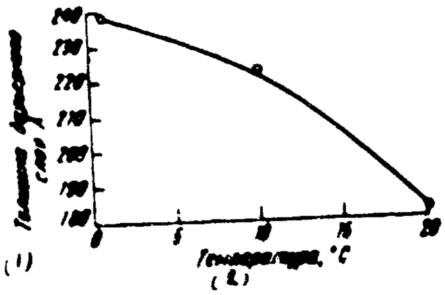

Fig. 2. Effect of temperature of electrolyte on the thickness of the barrier layer obtained on pure aluminum in 4-n H_2SO_4

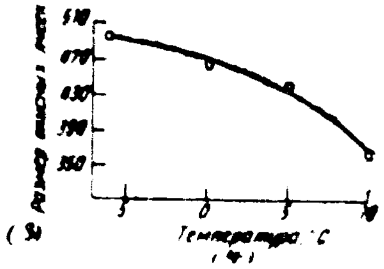

Fig. 3. Effect of temperature on size of oxide cells of anodic oxide film obtained under following conditions: 99.99-percent Al, 4-n H_2SO_4, D_a = 2.5 amp/dm^2, T = 60 min

Legend: (1) thickness of barrier layer, (2) temperature, (3) size of oxide cells, (4) temperature.

electrolyte.

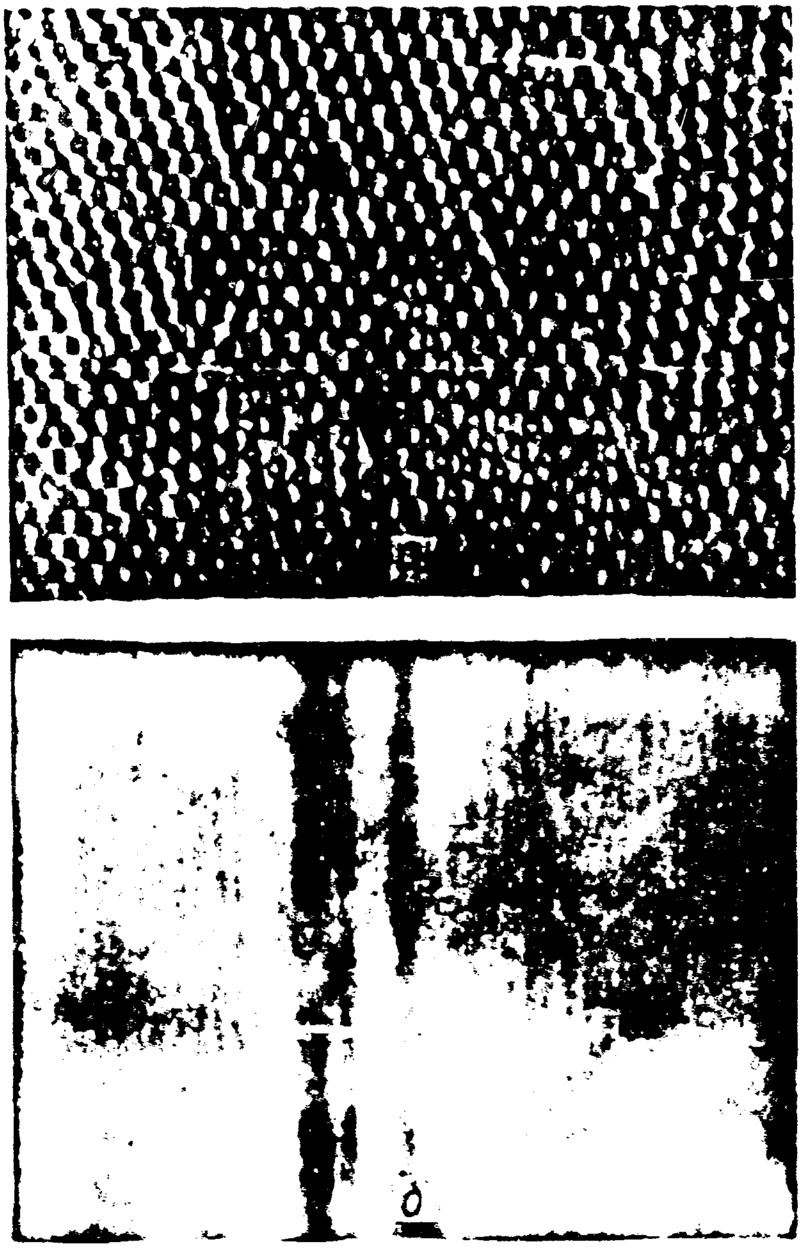

Fig. 4. Electron-microscope photographs obtained of the surface of the aluminum after removing the anode film (a) and from the surface of the longitudinal shear of the film (b). The film was obtained in 4-n. H_2SO_4 at D_a + 5 amp/dm^2. Collodion-carbon impression: a - x22,000; b - x16,000.

As the shaping voltage between the existing cells increases new cells are formed gradually filling the whole surface of the metal. Apparently, even an earlier formed hemisphere of a cell cannot grow unlimitedly, since its dimensions will be determined by the applied voltage and the conductivity of the film. However, without doubt in the initial moment of the formation of the film the dimensions of the cells will be naturally somewhat different from each other, since later the formation of cells will give less time for their growth, and the centers of the cells will be arranged chaotically without any definite orientation. Such a situation refers to the initial period of the formation of the porous part of the film.

After the separate cells look together and cover the whole surface of the metal the cells can then only grow in depth. Under these conditions, apparently, each oxide cell which has a lesser hemisphere (having delayed from the beginning of the growth) will have more possibility for growth since these cells are distinguished by the lesser thickness of the barrier layer.

In this way in the beginning of the process of the formation of the porous part of the film there is observed a certain disorder, irregularity in the structure of the oxide cells.

One may assume two variants of the transition to the strictly orderly cellular structure. The first consists in the "squeezing" of some cells by others, i. e., separate cells will in the process of their growth in depth gradually crowd their neighbors, lining up as to dimensions and and regrouping so as to create as much as possible a more compact packing. But in this case the number of cells coming into existence at the very beginning should be preserved throughout the whole anodic process. Since the number of first cells can in general be indefinite (i. e., their number to a greater or lesser degree differs from the number of cells corresponding to an orderly structure), therefore the average dimensions of the cells in each separate case should vary, which, as is known, is not so in practice.

The second, as it seems to us, more real variant consists in the reorganisation of the cells themselves in the process of their growth. In this case the rearranging of the cells results in this that out of a greater number of cells a smaller number is formed--too often the arranged cells will blend. Such a reorganisation is schematically presented in Fig. 5. As a result the cells are aligned in accordance with their dimensions. But in this case the cells will tend to align themselves not in a general way but around a definite maximum dimension determined by the equation $\frac{C\delta_m - p}{2\delta} = 1$. Only after this each cell gets equal possibility for its growth. And as soon as the dimensions of the cells become identical the scheme of their arrangement takes on a strictly orderly appearance. This will correspond to the stabilization of the structure of the anodic film.

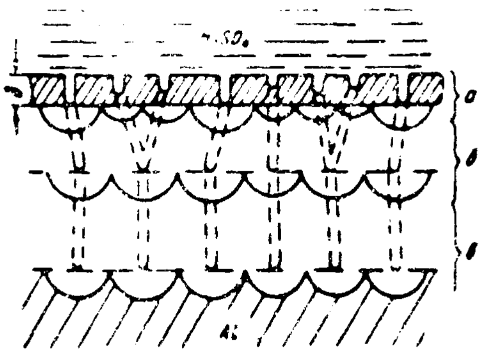

Fig. 5. Scheme of the arrangement of the orderly cellular structure on the surface of aluminum with uniform structure of the metal: a—initial moment (disorderly structure); b—rearrangement of the structure, c—orderly (regular) structure.

The possibility of such a reorganization was shown in the following experiment. At the time of the anodising the density of the current changed (from 2.5 to 10 amp/dm^2 and vice versa). After this the electron-microscopy investigated the cellular structure on the boundary separating the metal and the cells (after removal of the film). As is seen from Table 2 with the change in the density of the current there was a change also in the dimensions of the oxide cells (and consequently of their number), i. e., there occurs a reorganisation in the structure of the film itself (the plus sign indicates increase in the size of cells; the minus sign, decrease).

Table 2

Dimensions of Oxide Cells with Change of Density of Current in the Process Oxidation of Aluminum (4-n. H_2SO_4, t = —2°)

density of current amp/dm^2	time of anodic oxidation, min	size of cells Å	Change in size of cell, Å	
			theoretical	observed
2.5	10	480	—	—
10	10	550	—	—
2.5→10	10→10	560	+70	+80
10→2.5	10→10	490	-70	-60

In this way the reorganization of the structure of the oxide cells in the process of anodic oxidation is quite possible.

Conclusions

1. It has been shown that the basic ratio which determines such structural parameters of a thick-layer anodic film as the size of the oxide cell (C'_{on}) and the thickness of the barrier layer is the equation

$$\frac{C'_{on} - p}{2\delta}$$

where p is the diameter of the pore.

2. There has been presented the mechanism for the formation of the orderly cellular structure according to which with the shaping of the oxide cells there occurs not only a qualitative (change of dimensions) but also a quantitative reorganization of the cellular structure.

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