GENERAL GROWTH PATTERN OF ANODIC ALUMINUM OXIDES

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Abstract – One of the effective methods for the formation of coatings with required functional properties on the aluminum surface is the anodization. Usually anodic aluminum oxides are divided into dense (barrier) and porous. This work shows that such the division is very conditional. In any electrolyte, the alumina film origin and growth is defined by two factors. These are the rate of Al→Al$_2$O$_3$ transformation at the aluminum/alumina interface (V_0) and the rate of the alumina dissolution at the alumina/electrolyte interface (V_d). In all cases $V_0 \gg V_d$. When $V_d \to 0$, a preferential growth of dense alumina takes place. However, V_d is never equal to zero, even in water. It depends on the electrolyte composition, concentration and temperature and ion current density (J_i). With specified electrolyte, temperature and anodization voltage, only the anodization time defines either dense or porous alumina will be formed.

I. INTRODUCTION

Anodization is one of the effective methods for the formation of alumina films with required functional properties on the aluminum surface. Note the following advantages of this method [1]. Firstly, the film is grown directly from the metal body instead of outer deposition, so the adhesion problems stand no longer. Secondly, the quality of the alumina film grown can be controlled by the variation of the electrolyte nature and quantitative composition as well as varying the conditions and electrical parameters of the anodization process. To work in practice the method advantages in full, a comprehensive study into the mechanism and formation conditions of desired alumina films is needed. The research in this field can open new potentialities in the formation of coatings with a specified set of functional properties.

II. RESULTS AND DISCUSSION

Usually anodic aluminum oxides are divided into dense (barrier) and porous. But such the division is very conditional. When aluminum is anodized in any electrolyte, the alumina film origin and growth is defined by two factors. These are the rate of Al→Al$_2$O$_3$ transformation at the aluminum/alumina interface (V_0) and the rate of the alumina dissolution at the alumina/electrolyte interface (V_d). In all cases $V_0 \gg V_d$. At $V_d \to 0$, a preferential dense alumina growth takes place. However, V_d is never equal to zero, even in water. It depends on the electrolyte composition and concentration, temperature and ion current density (J_i). With the specified electrolyte, temperature and anodization voltage, only the anodization time defines either dense or porous alumina will be formed.

It should be noted that the anodic alumina formation is possible only in the presence of ion current due to which an oxygen ion delivery to the aluminum/alumina interface is provided. When voltage is applied between the anode and cathode, a common current through the alumina film is equal to sum of ion (J_i) and electron (J_e) currents. The electron current does not participate in the oxide formation and is defined only by the oxide structure characteristics (lattice damages, ion inclusions, etc.). Its value is much less than the ion current value. So, in the presence of J_i, the electron current is neglected.

Definite rates V_0 and V_d are characteristic for any definite electrolyte. And with the electrolyte, temperature and anodization voltage specified, only the anodization time defines either dense or porous alumina will be formed. So, if the anodization time is so short that the thickness of the anodic film dissolving at the alumina/electrolyte interface is negligible, dense alumina may be said to be formed. Denote this time by t_{dense}. Of course, this time is defined by the ratio of the growing film thickness h_0 to the thickness of the film part dissolved h_d, i.e. by any factor $k_0 = h_d/h_0$. in ideal case, $k_0 = 0$. So, permissible anodization time can be determined by specifying k_0. When the anodization time is longer than t_{dense}, porous alumina may be said to be formed.

It is known that the porous alumina growth rate is defined by the dissolution rate at the pore bottom, which depends on the ion current density - other things being equal. When the ion current density increases, the dissolution rate $V_d \to V_0$. When $V_d \approx V_0$, a well-known aluminum polishing process takes place.

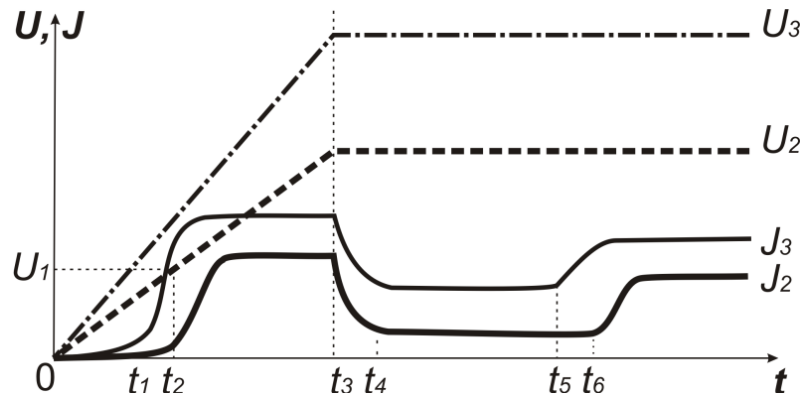Fig. 1 shows the growth kinetics of dense anodic alumina.

Figure 1 – Growth kinetics of dense anodic alumina in the range of low oxide dissolution rates

Because 5 – 7 nm thick dense native oxide is at the aluminum surface, only the electron current flows through the oxide at the initial anodization stage to t_1 and t_2. When the anodization voltage increases up to U_1, the electrochemical breakdown of the native oxide film begins and the ion current appears which increases sharply at $t > t_1$ or $t > t_2$. A value U_1 is evaluated as $U_1 = h_{initial}/k_0$, where $h_{initial}$ is a thickness of the initial native alumina (nm) and k_0 is a well-known anodization constant equal to 1.4 nm/V. The ion current is constant up to the moment t_3 and higher is voltage scan rate, higher is a value of this current.

At the moment t_3 the voltage U_2 = const and the ion current falls. Some increase of the oxide effective thickness is observed during the current fall time. After t_4 only the electron current takes place and the alumina films stops growing. It is considered that this electron current is less than 0.1 from the current at t_3. A period $\Delta t = t_4 - t_3$ is about 10 min. The current is practically constant for a long time up to t_5 (or t_6). However, the alumina film undergoes a certain change associated with its electrochemical dissolution at that. Practically, the oxide surface is not ideal, i.e. defect regions (crystal lattice damages, ion inclusions, etc.) are observed. As a rule, the dissolution rate is higher in these regions, so they are considered as pore nuclei. With time, pores grow deep into the oxide film and its diameter increases. At some moment walls of neighboring pores come to the contact and pores start grow only into the oxide depth.

Up to this moment all processes take place without the participation of the ion current. But the moment comes when the pore growth into the oxide depth results in such the oxide thickness at the pore bottoms that the electrochemical breakdown happens and the ion current appears within the pores, i.e. a classical growth of porous alumina begins. This corresponds to the t_5 and t_6 moments in Fig. 1. The alumina dissolution rate at the pore bottoms is very low in the electrolytes for the dense anodization, so the growth rate of porous alumina in such electrolytes is very low.

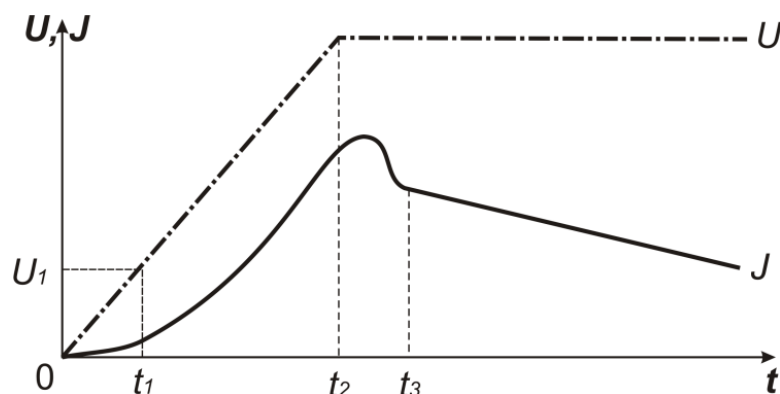Fig. 2 shows the growth kinetics of porous anodic alumina in the range of high oxide dissolution rates.

Figure 2 – Growth kinetics of porous anodic alumina in the range of high oxide dissolution rates

Only the electron current flows through the oxide to the moment t_1 as in the case shown in Fig. 1. When the anodization voltage increases up to the electrochemical breakdown voltage of the native oxide film at the aluminum surface U_1, the ion current appears which increases. In contrast to the case in Fig. 1, this current increases steadily up to the moment t_2 when the constant anodization voltage is observed. At this time ($t \geq t_1$) the pores nucleation takes place. In the time of $t_1 \rightarrow t_2$ the pore restructuring happens. Number of pores decreases with the anodization voltage in compliance with the well-known fact that the pore diameter and cell size are proportional to the anodization voltage. In the $t_2 - t_3$ time range a fixed amount of pores per the aluminum unit surface area is established. At $t \geq t_3$, pores grow into the oxide depth and the current decreases due to the voltage drop in the pore channels.

The growth kinetics form shown in Fig. 2 is independent of the electrolyte (sulfuric, oxalic, phosphoric and other acids) though quantitative values of the parameters at various time moments are different.

III. CONCLUSION

Thus, the division of anodic alumina film into dense and porous is very conditional. In any electrolyte, the alumina film origin and growth is defined by two factors. These are the rate of $Al \rightarrow Al_2O_3$ transformation at the aluminum/alumina interface and the rate of the alumina dissolution at the alumina/electrolyte interface. When the dissolution rate tends to zero, a preferential growth of dense alumina takes place. It depends on the electrolyte composition and concentration, temperature and ion current density. With the specified electrolyte, temperature and anodization voltage, only the anodization time defines either dense or porous alumina will be formed.

REFERENCES

[1] V. A. Sokol, *Anodic alumina*. Minsk, Belarus: Bestprint, 2011, 431 p.