

## CONTINUOUS CONSTANT VOLTAGE ANODIZING OF ALUMINUM

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**Abstract:** *The kinetics of continuous constant voltage ( $U_V = \text{const}$ ) anodizing of aluminum (AA1050) in an electrolyte, with no dissolving action (aqueous borate electrolyte) on the formed anodic alumina was studied in the present work. The recorded  $J_{\text{total}}(t)$ -dependencies are interpreted on the basis of the notion that the total current ( $J_{\text{total}}$ ) flowing in the Al/Al<sub>2</sub>O<sub>3</sub>/Electrolyte system includes an ionic ( $J_i$ ) and an electronic ( $J_e$ ) component, i.e.:  $J_{\text{total}} = J_i + J_e$ . The dependences of these two components on the electric field strength ( $E$ ) and temperature ( $T$ ) are discussed considering existing theoretical concepts. The analysis of the kinetics undoubtedly shows that the presence of an electronic component in the total current flowing under conditions of continuous constant voltage anodizing in the (+)/Valve metal/Anodic oxide/Electrolyte systems should not be neglected.*

**Keywords:** *barrier anodic Al<sub>2</sub>O<sub>3</sub> film, constant voltage anodization, ionic and electronic current component*

### INTRODUCTION

It is known that the anodic oxide films on valve metals, including these on aluminum can also be formed in constant voltage mode. In general, constant voltage anodizing is the more common technological method for the industrial production of such anodic oxide films. The process of constant voltage anodizing ( $U_V = \text{const}$ ) is more difficult to interpret than the galvanostatic one ( $J = \text{const}$ ) due to its non-stationarity. The process takes place at a constantly decreasing value of the electric field ( $E$ ). However, film formation in both regimes is thought to proceed by the same mechanism (Fromhold A. T. Jr. & Cook E. L. 1967). The main goal of the present study is to obtain data on the kinetics of continuous tensiostatic anodizing of aluminum in a classical non-dissolving the oxide electrolyte and to evaluate the influence of the ionic ( $J_i$ ) and electronic ( $J_e$ ) component comprising the total current density ( $J_{\text{total}}$ ).

### EXPERIMENTAL

The electrodes were cut from technical aluminum (AA1050) with a working area of 4 cm<sup>2</sup>. Prior to the actual anodic polarization, the samples were subsequently treated by consecutive etching for two minutes in alkaline (50 g dm<sup>-3</sup> NaOH, at 50 °C) and in acidic (1: 1, HNO<sub>3</sub>: H<sub>2</sub>O, at 20 °C) media. After each treatment, the samples were washed thoroughly with tap and bi-distilled water. A classic aqueous borate electrolyte (ABE) for barrier anodizing was used as the contact electrolyte. Its composition is 2.5% aqueous boric acid solution neutralized with NH<sub>4</sub>OH to a pH

value of 6. The anodizing was performed at 293 K in a two-electrode electrolytic cell with a platinum mesh, as a counter-electrode.

The anodic potential was increased in galvanostatic mode ( $10 \text{ mA cm}^{-2}$ ) until a preset voltage ( $U_V = 100 \text{ V}$ ) was reached. The power supply of the electrolytic cell was then switched to a stabilized rectifier, where the same voltage had been set in advance. The current density ( $J_{\text{total}}$ ) with time ( $t$ ) was recorded from the initial moment of switching to constant voltage regime. The  $J_{\text{total}}(t)$  dependence data were registered on a digital multimeter connected to a personal computer.

## RESULTS AND DISCUSSION

### Kinetics of continuous constant voltage anodizing

The kinetic curve for the anodization process carried out at constant voltage ( $U_V = 100 \text{ V}$ ) and temperature (293 K) for  $10^6 \text{ sec}$  is shown in Figure 1. Various  $J(t)$ -dependences have been proposed in order to describe the kinetics of constant voltage anodizing by different authors: an exponential (Fromhold A. T. Jr. & Cook E. L. 1967), a linear (Dreiner R. 1964) and others.

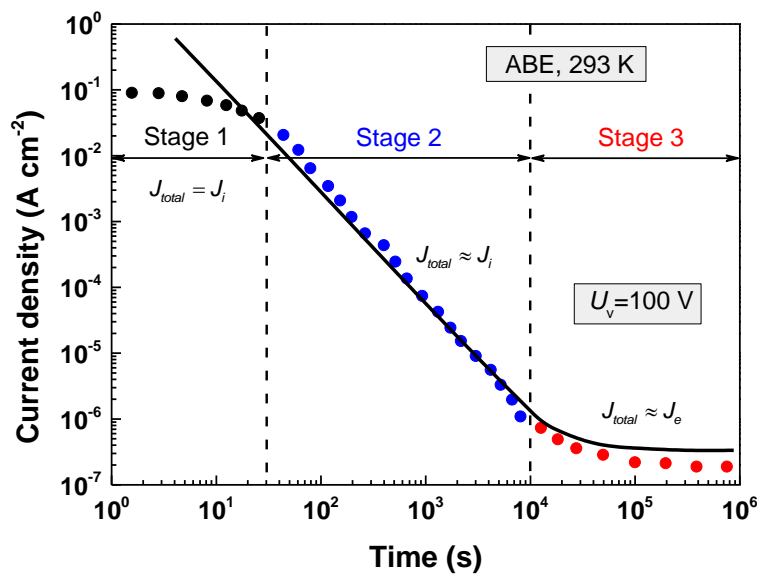


Fig. 1.  $J_{\text{total}}(t)$ -dependence recorded during constant voltage anodization of AA1050 in ABE (symbols) and calculated values (solid line)

Since the formation and growth of the anodic  $\text{Al}_2\text{O}_3$  in the (+)  $\text{Al}/\text{Al}_2\text{O}_3/\text{Electrolyte}$  system is an electrochemical process (Girginov Ch. & Kozhukharov S. 2020), the total current flowing ( $J_{\text{total}}$ ) should be analyzed. It includes three components:  $J_{\text{total}} = J_i + J_e + J_{\text{diss}}$ . The ionic current ( $J_i$ ) is associated with the migration of ions and is responsible for the growth of the anodic film. This type of current appears as a result of the migration of both  $\text{O}^{2-}$  anions from the electrolyte, and  $\text{Al}^{3+}$  cations from the metallic substrate. The electron current ( $J_e$ ) is being injected into the oxide layer, across the oxide/electrolyte interface from the electrolyte and does not affect the thickness of the anodic oxide film. The dissolution current ( $J_{\text{diss}}$ ) can reach significant values when anodizing is performed in film-dissolving electrolytes, where porous  $\text{Al}_2\text{O}_3$  matrices are being formed. The formation and/or polarization of barrier anodic films is usually performed in electrolytes that are not aggressive (Girginov Ch. & Kozhukharov S. 2020) towards the formed  $\text{Al}_2\text{O}_3$ . In these cases, no dissolution current flows ( $J_{\text{diss}} = 0$ ), hence  $J_{\text{total}} = J_i + J_e$ . In this sense, the interpretation of the kinetics of constant voltage anodizing when barrier films are formed should only be based on the flow of  $J_i$  and  $J_e$ . These two current components depend on the field strength ( $E$ ) and temperature ( $T$ ). An illustration of such anodic polarization process is shown in Figure 2.

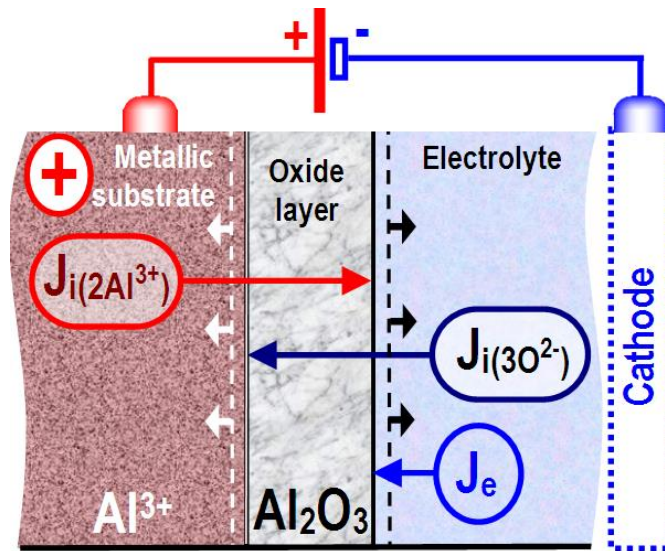


Fig. 2. Schematic view of the currents flowing through the (+)Al/Al<sub>2</sub>O<sub>3</sub>/Electrolyte system

### Currents flowing during barrier anodization

#### *Ionic current in the (+) Al/Al<sub>2</sub>O<sub>3</sub>/electrolyte System*

Three basic equations have been developed for the description of the  $J_i(E, T)$ -dependence recorded during anodization of valve metals, including aluminum:

- **Güntherschulze-Betz equation** At defined temperature ( $T$ ), the values of the field strength ( $E$ ) depend only on the current density ( $J_i$ ):

$$J_i = A_G \exp(B_G E), \quad (1)$$

where  $A_G$  and  $B_G$  are constants, which are always positive (Güntherschulze A. & Betz H. 1934).

- **Tafel-Frenkel equation**

$$J_i = A_i \exp\left(-\frac{B_i - \alpha_i E}{k_B T}\right). \quad (2)$$

In this equation, the values of the constants when anodizing aluminum in aqueous borate electrolyte (ABE) in the temperature interval from 273 to 313 K are:  $A_i = 1.644 \times 10^{10} \text{ A cm}^{-2}$ ,  $B_i = 1.495 \text{ eV}$  and  $\alpha_i = 9 \times 10^{-8} \text{ cm}$ . These values have been determined by (Andreeva L. & Ikonopisov S. 1970), where the value used for the Boltzmann constant is  $k_B = 8.61 \times 10^{-5} \text{ eV K}^{-1}$ .

- **Young equation** Another recognized expression for the  $J_i(E, T)$ -dependence has been proposed by Young:

$$J_i = A_i \exp\left(-\frac{B_i}{k_B T}\right) \exp\left(\frac{\alpha_i E - \beta_i E^2}{k_B T}\right). \quad (3)$$

Here also the constants  $A_i$ ,  $B_i$ ,  $\alpha_i$  and  $\beta_i$  possess positive values.

#### *Electronic current in the (+)Al/Al<sub>2</sub>O<sub>3</sub>/electrolyte System*

Different concepts about the mechanism of occurrence and flow of the electronic currents in the system (+)/Valve metal/Anodic oxide/Electrolyte have been developed. Based on these perceptions (*Poole-Frenkel*, *Schottky*, *Christov*) one and the same type of equation was found to describe the dependence of the electronic current ( $J_e$ ) on the electric field strength ( $E$ ):

$$J_e = \alpha_e \exp(\beta_e E^{1/2})_T. \quad (4)$$

Depending on the different models, the expressions for the  $\beta_e$  constant in the three models differ in analytical form (Girginov Ch. & Kozhukharov S. 2020). Data for the electronic conductivity in (+)Al/Al<sub>2</sub>O<sub>3</sub>/Electrolyte system were obtained from (Ikonopisov S. 1969) when polarizing in an aqueous borate electrolyte (ABE). The value of the constant  $\beta_e$  changes within the interval ( $3.29 \times 10^{-3} - 3.42 \times 10^{-3} \text{ V}^{1/2} \text{ cm}^{-1/2}$ ), whereas for the constant  $\alpha_e$  these values are determined to be enclosed between  $0.60$  and  $1.84 \times 10^{-11} \text{ A cm}^{-2}$ .

Three stages have been identified in the recorded  $J_{\text{total}}(t)$ -dependence (Fig. 1):

- Stage I: This stage represents a short initial phase of quasi-galvanostatic anodization, where the electronic component ( $J_e$ ) can be completely discarded ( $J_{\text{total}} = J_i$ );
- Stage II: During this period the current density is predominantly ionic ( $J_{\text{total}} \approx J_i$ );
- Stage III: In that phase a significant alteration of the shape of the kinetic curve is observed. This alteration is due to the fact that the current after prolonged anodization at constant voltage is prevalingly electronic ( $J_{\text{total}} \approx J_e$ ). Furthermore, the “tails” of the curves are expected to be different for the different contact electrolytes, since the electronic current depends on their nature and concentration.

### Field strength, ionic and electronic currents during anodizing

Using the *Tafel-Frenkel* equation (2) and the corresponding values of the constants, the change in the value of the electric field ( $E$ ) with anodizing time ( $t$ ) was calculated. By plugging in the obtained values for  $E$  in Eq. (4) values for the electronic component of the current ( $J_e$ ) were also determined. These calculations enable to plot and compare the dependences  $J_i(t)_T$  and  $J_e(t)_T$  presented in Fig. 1 with a solid line. It can be noted that they very well describe the experimentally recorded  $J_{\text{total}}(t)$ -dependence (depicted with symbols). For the same electrolyte (ABE) (Ikonopisov & Machkova 1984) have determined ranges of field strengths, where the individual components of the current ( $J_i$  and  $J_e$ ) are deterministic for the value of the total current ( $J_{\text{total}}$ ):

$$\begin{aligned} \text{at } E > 7 \times 10^6 \text{ V cm}^{-2}, J_{\text{total}} &\approx J_i & (J_i = 50 J_e); \\ \text{if } E < 5 \times 10^6 \text{ V cm}^{-2}, J_{\text{total}} &\approx J_e & (J_e = 50 J_i); \\ \text{in the interval } E = (5 \times 10^6 - 7 \times 10^6) \text{ V cm}^{-2}, & & (J_i = J_e). \end{aligned}$$

The defined (Ikonopisov S. & Machkova M. 1984) regions of the respective current components give a completely logical explanation of the acquired  $J_{\text{total}}(t)$ -dependence of continuous constant voltage anodizing of aluminum in aqueous borate electrolyte (ABE). Obviously, when using a different electrolyte for barrier anodizing of aluminum, changes can be expected in the range of fields ( $E$ ) in which the value of the respective current component ( $J_i$  or  $J_e$ ) will prevail. This is due to the fact that according to *Christov's* model (Christov S. 1979) the electronic current depends on the nature and concentration of the contact electrolyte. It is worth noting that similar kinetics of continuous constant voltage anodizing have been observed in the anodic polarization of other metals (Girginov Ch. & Petkova S. 2013).

### CONCLUSION

Under constant voltage anodization conditions in the initial stages of the process, the predominant contribution to the total current density ( $J_{\text{total}}$ ) is the ionic component ( $J_i$ ). It is associated with ion transport (migration of both  $\text{O}^{2-}$  anions from the electrolyte and  $\text{Al}^{3+}$  cations from the metallic substrate). As the anodic polarization progresses (upon reaching a certain value ( $E$ ) of the electric field), a region in which  $J_i \approx J_e$  is established. Finally, at already relatively low values of the electric field, a stage where  $J_{\text{total}} \approx J_e$  is reached. These circumstances definitely show that in the interpretation of the kinetics of continuous constant voltage anodizing in the (+)/Valve metal/Anodic oxide/Electrolyte systems, the presence of an electronic component in the flowing total current cannot be neglected.

### Acknowledgement

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