

## Research Article

# Surface of Alumina Films after Prolonged Breakdowns in Galvanostatic Anodization

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Breakdown phenomena are investigated at continuous isothermal (20°C) and galvanostatic (0.2–5 mA cm<sup>-2</sup>) anodizing of aluminum in ammonium salicylate in dimethylformamide (1M AS/DMF) electrolyte. From the kinetic  $U_f(t)$ -curves, the breakdown voltage ( $U_B$ ) values are estimated, as well as the frequency and amplitude of oscillations of formation voltage ( $U_f$ ) at different current densities. The surface of the aluminum specimens was studied using atomic force microscopy (AFM). Data on topography and surface roughness parameters of the electrode after electric breakdowns are obtained as a function of anodization time. The electrode surface of anodic films, formed with different current densities until the same charge density has passed (2.5 C cm<sup>-2</sup>), was assessed. Results are discussed on the basis of perceptions of avalanche mechanism of the breakdown phenomena, due to the injection of electrons and their multiplication in the volume of the film.

## 1. Introduction

Breakdown voltages are an important feature of the process of formation of anodic oxide films on valve metals. The increase in thickness of barrier anodic films is limited by the occurrence of electric breakdowns [1, 2]. Breakdown phenomena in the formation of barrier anodic films are most successfully interpreted by the models [3–5] of an avalanche mechanism. According to these models breakdowns are a result of injection of electrons from the electrolyte [6] in the anodic film and their multiplication during growth of the film [3]. This fact is supported by the established strong dependence of the breakdown voltage value on the nature and concentration of the contact electrolyte [7–9]. Breakdown phenomena can be observed both in galvanostatic and potentiostatic modes of anodic polarization. However, breakdowns are typically recorded in galvanostatic-isothermal regimes, where the formation voltage ( $U_f$ ) increases linearly with time ( $t$ ), respectively, with the charge density passed ( $Q_f$ ) until the “first spark voltage” ( $U_{FS}$ ) is reached. At  $U_{FS}$  the first oscillation in formation voltage is registered. Later the breakdown voltage value ( $U_B$ ) is reached [10], where there are regular oscillations in the formation voltage. Each

oscillation corresponds to one spark, which leaves a trace of a thicker film on the electrode surface. After prolonged breakdowns the surface looks microscopic rough and the film is colored gray [8]. Shimizu et al. [11] have studied the surface of the aluminum electrodes after the occurrence of breakdowns using high-resolution scanning electron microscopy. According to them, as a result of breakdowns craters are formed, which in turn are immediately filled with newly formed oxide. In the study of anodizing breakdowns, it is necessary to take into account the presence of the electrolyte contact [12]. It is of certain interest to study changes in the electrode surface as a result of breakdowns, occurred during anodization at different current densities.

## 2. Experimental

The samples were cut from sheets of aluminum (99.5%) with a working area of 4 cm<sup>2</sup>. The specimens were annealed at 400°C for 3 hours, electropolished in a mixture of 210 mL H<sub>2</sub>O, 40 g CrO<sub>3</sub>, 450 g H<sub>3</sub>PO<sub>4</sub> (85%) and 150 g H<sub>2</sub>SO<sub>4</sub> (96%) at a current density of 0.2 A cm<sup>-2</sup>, at 80°C, for 3 minutes, and followed by rinsing with distilled water and drying. Before anodization, the initial air-formed layer was removed by

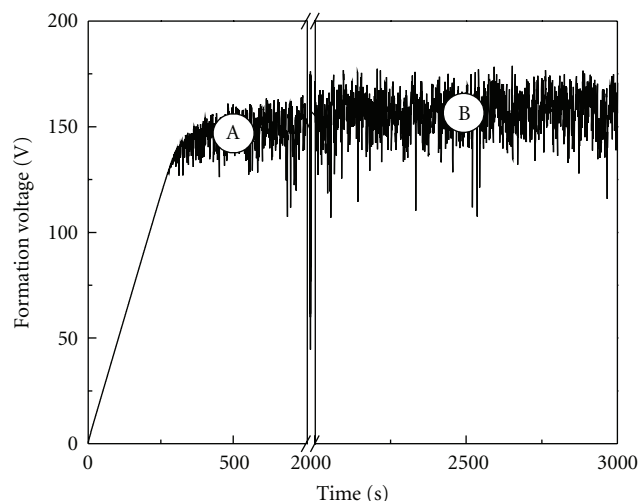


FIGURE 1: Kinetic curve of galvanostatic anodizing in 1 M AS/DMF ( $1 \text{ mA} \cdot \text{cm}^{-2}$ ,  $20^\circ\text{C}$ ).

immersing the samples in an aqueous solution of 1.8%  $\text{CrO}_3$  and 7%  $\text{H}_3\text{PO}_4$  (85%), at  $75^\circ\text{C}$ , for 3 min.

The film formation was carried out isothermally ( $20^\circ\text{C}$ ) with different current densities ( $0.2\text{--}5 \text{ mA} \cdot \text{cm}^{-2}$ ) to pass the same charge density ( $2.5 \text{ C cm}^{-2}$ ). Ammonium salicylate in dimethylformamide (1 M AS/DMF) was used as a formation electrolyte. The usual electrolytic cell with thermostatic regulation and electronic apparatuses for galvanostatic anodization were used. Kinetic  $U_f(t)$ -curves were registered with a precision multimeter (Mastech MS 8050). The frequency and amplitude of oscillations of  $U_f$  during the breakdown phenomena is assessed for different current densities. The surface of the aluminum specimens was studied using atomic force microscopy (Nanosurf EasyScan 2 AFM).

### 3. Results and Discussion

Breakdown phenomena in barrier anodizing can reasonably be interpreted by models, predicting avalanche mechanism [3–5]. According to them, breakdowns are result of injection of electrons from the electrolyte at the phase boundary electrolyte/anodic film. Christov [6] has introduced a model, where the electrolyte is considered as a semiconductor and the redox couples in it were assumed to play the role of electron donors. Only this model is able to explain the dependence of the electronic current ( $J_e$ ) on the nature and concentration of the contact electrolyte.

The breakdown occurs when the thickness of the film at some point reaches a value sufficient to increase the electronic current to a critical value [3]. After reaching the breakdown voltage ( $U_B$ ), the breakdown condition is statistically satisfied for the whole electrode surface. However, a breakdown occurs only in one point of the electrode surface. The electron avalanche causes destruction (evaporation and/or plasmation) of the film at that point. The crater in the film at the broken oxide is obliterated by the rapid formation of new anodic film that is thicker than the rest. Thus, the probability for a second break in the same place is much smaller. The film on the remaining surface continues

to grow, leading to continuous breaking and subsequent obliteration of the broken oxide.

Assuming this picture [8] of occurrence of breakdowns, it can be expected that roughness of the electrode surface will be significantly influenced by the anodizing conditions (duration, current density).

**3.1. Breakdowns at Prolonged Galvanostatic Anodization.** A typical kinetic  $U_f(t)$ -curve at prolonged galvanostatic anodization is presented in Figure 1.

After reaching a certain breakdown voltage ( $U_B$ ) breakdowns continue with regular oscillations in voltage. On Figure 2 fragments of the kinetic curve at two different times in the field of breakdown occurrence are presented.

The frequency and amplitude analysis of the oscillations shows that they do not change significantly with the prolonged breaking down of the film. This result is not surprising, given that the value of breakdown voltage does not change over time.

Using AFM technique, the electrode surface of samples, subjected to different breakdown duration, was analyzed. An example of the state of the surface of two electrodes undergone different breakdown durations is presented in Figure 3.

These results show that with increasing time of galvanostatic breaking down of anodic oxide films, the number of points on the electrode surface affected by the breakdowns increases. From the obtained AFM-images values of certain parameters, which characterize the roughness of the surface, were estimated:  $S_a$  (average roughness value) is the average sum of the module of distances of all points from the measured surface, in direction, perpendicular to the conditional plane;  $S_m$  (mean roughness value) is also defined by the same average sum, but here the positive or negative values of the vectors are taken into account;  $S_v$  (valley depth) notes the distance between the conditional plane and the lowest point of the measured surface;  $S_p$  (peak height) is the distance between the highest point of the measured surface and the conditional plane;  $S_y$  (peak valley height) is the distance between the highest ( $S_p$ ) and the lowest ( $S_v$ ) points of the measured surface.

These parameters as a function of anodizing time (breakdown of the film) are presented in Figure 4. Data are averaged from six independent measurements.

The values of parameters, characterizing the roughness of the surface, show a logical change of the electrode surface with increasing number of electric breakdowns.

**3.2. Breakdowns at Different Current Densities.** Several authors [8, 13] have convincingly showed that the value of the breakdown voltage depends very slightly on the current density. It was of interest to examine, however, how current density affects the frequency and amplitude of oscillations in the formation voltage ( $U_f$ ), and the surface morphology of samples. For this purpose, electrodes were anodized with different current densities ( $0.2\text{--}5 \text{ mA cm}^{-2}$ ), so that the same charge density is conducted ( $2.5 \text{ C cm}^{-2}$ ). Kinetic  $U_f(t)$ -curves of anodic anodization with two different current densities are presented in Figure 5.

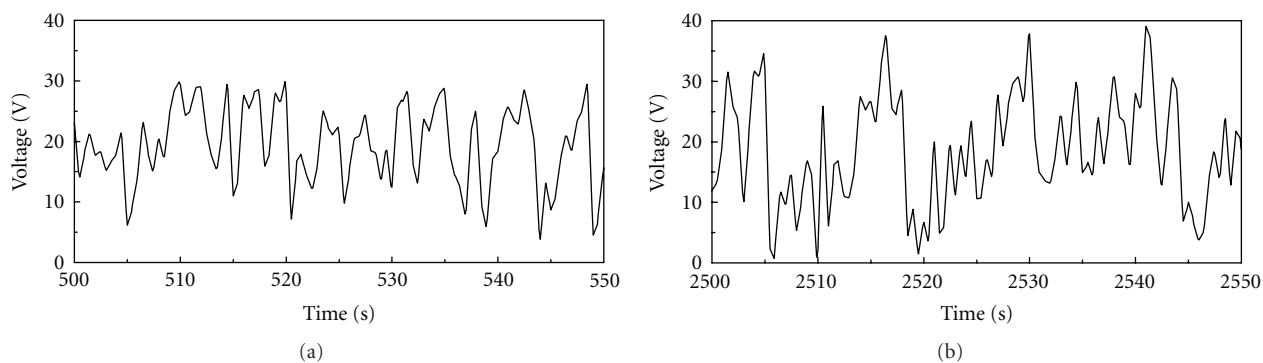


FIGURE 2: Fragments (50 seconds) of a kinetic curve (Figure 1) at different moments of anodizing (during breakdown).

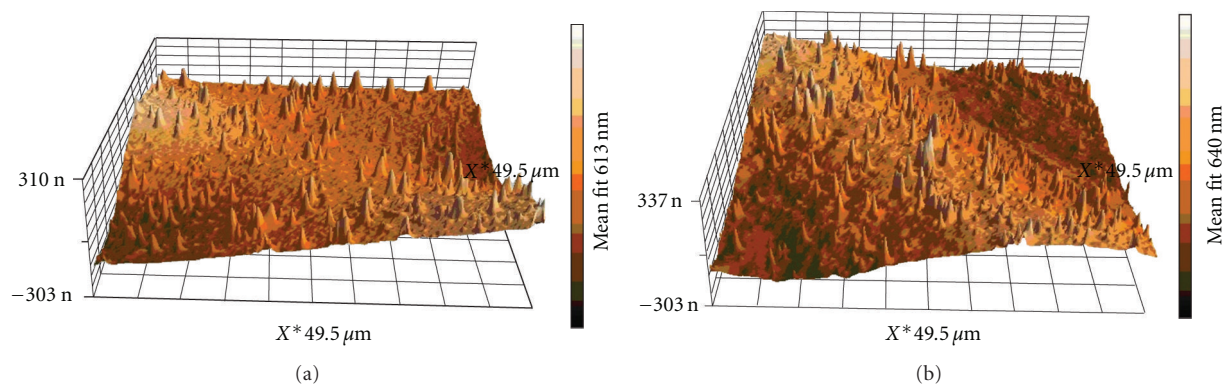


FIGURE 3: AFM images of the surface of a sample anodized at a current density of  $1 \text{ mA cm}^{-2}$  for 0.5 ks (a) and for 2.5 ks (b).

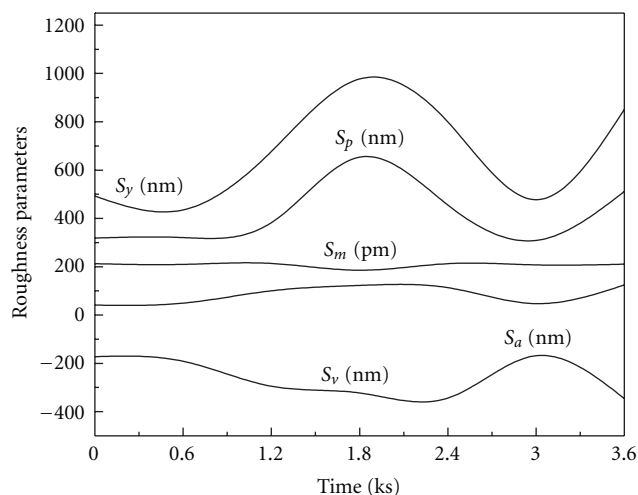


FIGURE 4: Roughness parameters as a function of anodization time.

Fragments of kinetic curves taken at different current densities (at interval of 50 s), are presented in Figure 6.

It has also appeared that the frequency of oscillations in the formation voltage are insensitive to variation of current density. A tendency to reduce the oscillations amplitude

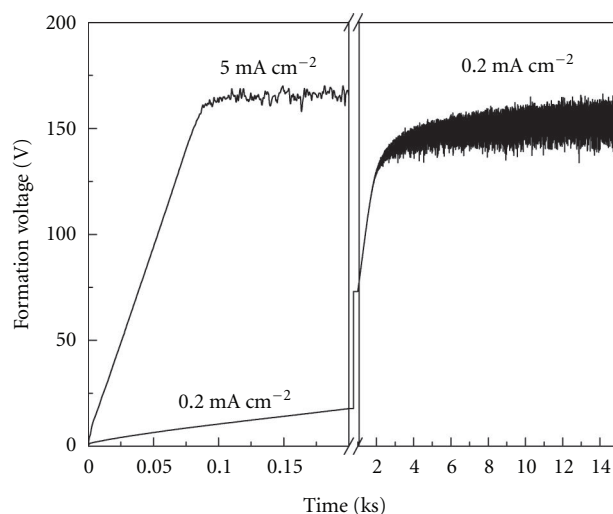


FIGURE 5: Kinetic curves of galvanostatic anodizing in 1 M AS/DMF with two current densities ( $20^\circ\text{C}$ ).

with increasing current densities ( $J$ ) is observed, whereas the number of breakdowns remains constant. This result could be explained assuming that breakdowns at higher  $J$

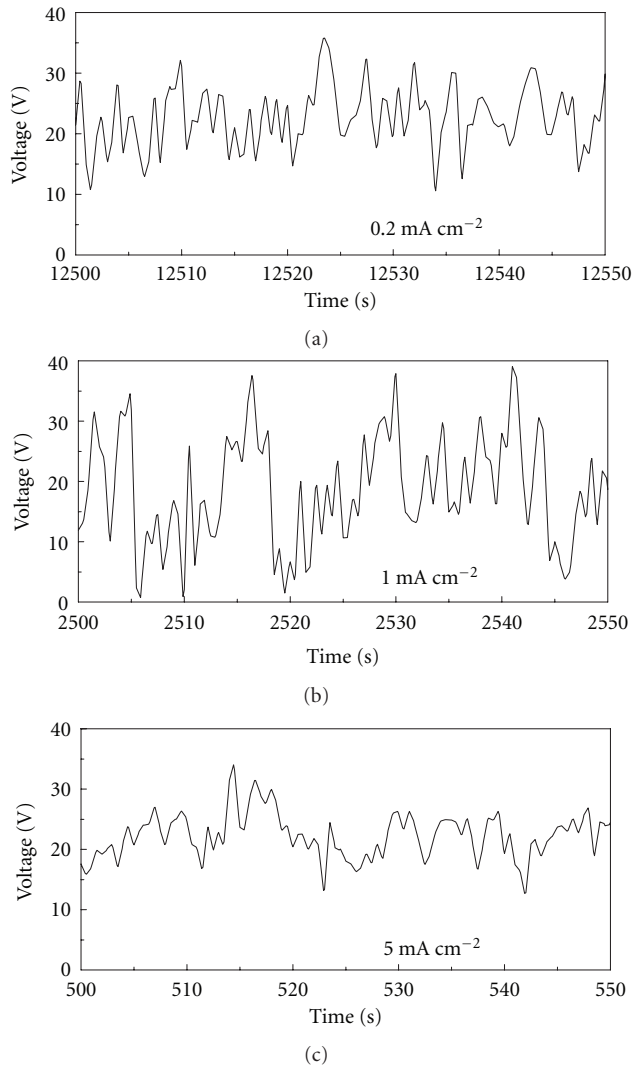


FIGURE 6: Frequency and amplitude of oscillations of  $U_f$  during anodization at different current densities, taken after  $2.5 \text{ C cm}^{-2}$  charge density passed.

gouge wider craters. This would also explain the observed [8] increase in brightness and size of sparks with increasing  $J$ .

In support of these views on Figure 7 a comparison of the surfaces of two electrodes after prolonged anodizing at two different current densities is presented, but at the same value of charge density passed ( $Q_f = \text{const}$ ).

It is of interest to compare the roughness parameters on samples anodized at different current densities, but with the same charge density passed ( $Q_f = \text{const}$ ). The data obtained (at  $2.5 \text{ C cm}^{-2}$ ) did not show any systematic dependence of these parameters on current density. This fact could be explained by the mechanism associated with the occurrence of breakdowns. Microscopically barrier anodic films are not uniform in topography, so that the probability of reaching a breakdown condition is not equal throughout the electrode surface. The first breakdown will occur in one of the film inhomogeneities, for which the breakdown condition is fulfilled first, as this will determine the first spark voltage ( $U_{FS}$ ). The film on the remaining surface

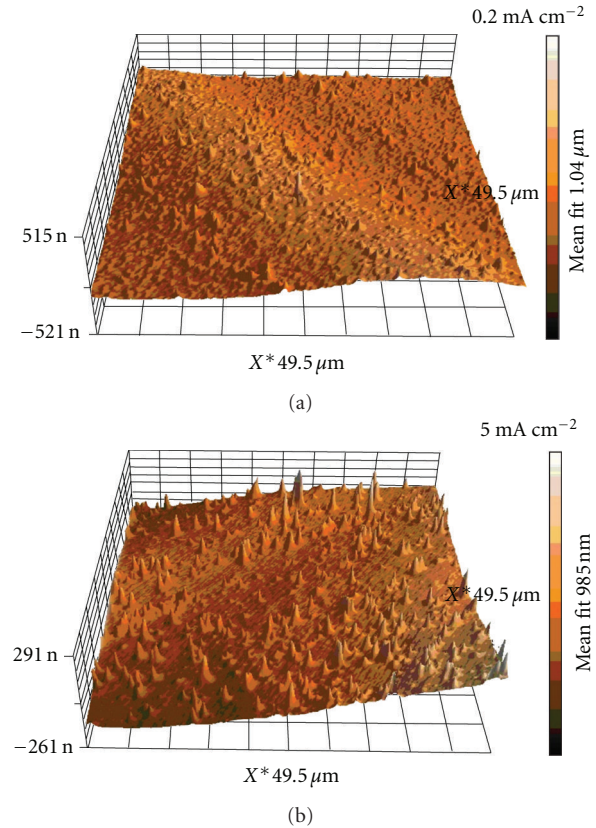


FIGURE 7: AFM images of the surface of samples anodized at current densities ( $0.2$  and  $5 \text{ mA cm}^{-2}$ ) after  $2.5 \text{ C cm}^{-2}$  charge density passed.

continues to grow, leading to rupture and removal on all inhomogeneities one after another. This explains the observed [10] increase of  $U_f$  after  $U_{FS}$  during breakdowns. Although, after reaching  $U_B$  the breakdown condition is statistically satisfied for the whole electrode surface, the breakdowns occur consistently. Breakdowns always occur at any point of the electrode surface. This is due to local variations in thickness and fluctuations in the concentration of the electrolyte on the interface and, therefore, in the injection on primary electrons.

#### 4. Conclusion

With increasing anodizing time and number of breakdowns, respectively, the surface roughness of formed oxide also increases. It is noted that with longer anodization (breakdowns) the amplitude on oscillations in the formation voltage tends to increase, without change in their frequency. Oscillations in voltage (the number on breakdowns) are also insensitive to the current density. The increase of current density only slightly decreases the amplitude of these oscillations. The results indicate that the number of breakdowns, respectively the surface modification of the oxide, depend more on the charge density passed ( $Q_f$ ), rather than on the current density.

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