Advances in Natural Science: Theory & Applications

Volume 2 No. 1 2013, 23-30
ISSN: 1715-7862 (printed version); ISSN: 1715-7870 (online version)
url: http://www.ansta.eu
doi: http://dx.doi.org/10.12732/ijpam.v2i1.3

ansta.eu

ELECTRICAL BREAKDOWNS DURING FORMATION OF ANODIC OXIDE FILMS ON ALUMINUM

Sashka Petkova[1 §], Christian Girginov[2], Todor Petkov[3]

[1]Department of Mathematics
University of Chemical Technology and Metallurgy
8 St. Kliment Ohridski blvd., 1756, Sofia, BULGARIA
[2]Department of Physical Chemistry
University of Chemical Technology and Metallurgy
8 St. Kliment Ohridski blvd., 1756, Sofia, BULGARIA

Abstract: The formation voltage oscillations have been analyzed during isothermal and galvanostatic anodizing of aluminum in two different in nature contact electrolytes. Special attention has been paid to the two main events during breakdowns: local breakdown of the film and its regeneration as a result of the increased current density at the breakdown site. The fluctuations in the formation voltage have been interpreted in terms of these aspects of electrical breakdowns. A Poisson distribution of the probability density both at the occurrence of electrical breakdowns and during the regeneration of Al_2O_3-films has been established. The Poisson's distribution of breakdown and regeneration voltage differences has been calculated. The small difference in these values obtained for two very different contact electrolytes, however, seems difficult to explain in the context of the strong influence of the electronic currents in the (+)Al/Al_2O_3/electrolyte system on the nature of the electrolyte.

Key Words: aluminum oxide, galvanostatic anodization, breakdown phenomena, breakdown voltage, probability density

1. Introduction

The breakdown events are an important feature of the process of formation of anodic oxide films on valve metals. They limit the maximum thickness of the obtained oxide films. On the other hand, these phenomena are quite different compared to breakdowns

Received: March 11, 2013

[§]Correspondence author

in "dry" dielectrics. Breakdowns in (+)valve metal/anode oxide/electrolyte system have a peculiar mechanism and the classical concepts of breakdowns in dielectrics cannot be applied. Breakdowns in these systems can be studied independently by specific methods and can be used to found theories for their explanation. The formation of barrier oxide films on valve metals is usually carried out under galvanostatic and isothermal conditions in non-dissolving electrolytes. The anodizing kinetics under these conditions is characterized by constant electric field strength (E), film growth rate and also immutability of the film's specific properties. The increase of formation voltage (U_{f}) with time (t) is limited by the occurrence of electrical breakdowns. Upon reaching the "breakdown voltage" (U_{B}), breakdowns follow each other and U_{f} practically ceases to increase. Determination of U_{B} is carried out in different ways: by oscillations in U_{f} [1], registration of high-frequency fluctuations of the anodizing current circuit [2], by the sound effect accompanying breakdowns [3], by tracking galvanoluminescence brightness [4] and others. Occurrence of electrical breakdowns has been explained by injection of electrons from the electrolyte to the anodic oxide and their multiplication [5-7] in the oxide bulk. On the other hand, since the electronic current strongly depends on the nature and concentration of the contact electrolyte [8-10] it is expected that breakdown phenomena should be influenced by electrolyte contact. The breakdowns are stochastic in nature and occur for a very short time. In this sense it is of interest to determine the probability density of the individual breakdown phenomenon, and the regeneration of the film during anodic polarization in two different in nature contact electrolytes.

2. Experimental

The formation and breakdowns of barrier films on aluminum has been studied in many different in nature and concentration electrolytes including aqueous and non-aqueous electrolytes. Data for the breakdown phenomena were obtained during galvanostatic anodizing of Al in an aqueous borate electrolyte (ABE, pH-6) [4] and in 1 M ammonium salicylate in dimethylformamide (AS/DMF) [13]. In order to obtain more detailed information on the stochastic nature of the breakdowns, experiments were conducted in these electrolytes under the same experimental conditions (10^{-3} A cm^{-2}, 293 K). The film formation was carried out in a two-electrode cell with a platinum mesh serving as a counter electrode, using a high voltage galvanostat (600 V, 0.5 A). The dependence of formation voltage (U_{f}) on time (t) was registered using a precision multimeter (Mastech MS 8050) and a PC-based data acquisition system.

3. Results and Discussion

3.1. Breakdown Voltage Registered by Oscillations of the Formation Voltage

Under galvanostatic ($J = \mathrm{const}$) and isothermal ($T = \mathrm{const}$) anodizing conditions, the kinetic $U_{\mathrm{f}}(t)$-curves represent a linear increase of the formation voltage (U_{f}) with time

(t). The increase in U_{f}, respectively of anodic film thickness (D), is limited by the occurrence of electrical breakdowns. The breakdowns begin when U_{f} reaches the value of "first spark" (U_{FS}). At this point the increase of U_{f} slows down and some sparks begin to appear occasionally on the electrode surface. Finally U_{f} reaches "breakdown voltage" (U_{B}), where breakdowns follow each other in the form of instantaneous point discharges, sparks or as individual travelers chains of sparks and increase of U_{f} practically ceases. During each breakdown, the formation voltage drops sharply and then increases quickly as the film is regenerated as a result of the greater current density at the breakdown site.

The observed breakdown events [4] are explained by models suggesting an avalanche mechanism of these phenomena during anodizing [5-7]. According to those views breakdowns result from electron injection from the electrolyte to the oxide and their further multiplication in the film bulk. The breakdown occurs when at any point of the surface the film reaches a thickness sufficient for the increase of the electronic current (J_{e}) to a critical value, specific for the oxide and electrolyte contact. Microscopically barrier anodic films have irregular topography and often contain inclusions built in the film. For this reason, the first breakdowns are expected to occur in one of the film heterogeneities. In this sense, the breakdown has an occasional nature, and the crater [11] formed in the oxide film is effaced through the rapid formation of new anodic film. As a result the oxide surface becomes significantly rougher [12].

Figure 1 shows kinetic $U_f(t)$ curves of galvanostatic anodization of aluminum in ABE, (pH-6) [4] and 1 M AS/DMF [13]. These kinetic relationships give an idea of the voltage oscillations and the influence of the contact electrolyte type on breakdown characteristics.

In the present experiments particular attention has been paid to the two main breakdown events:

i) Local film breakdown (characterized by a sharp drop of the formation voltage U_{f});

ii) Film regeneration due to the high current density at the breakdown point (fast-growth of U_{f}).

3.2. Distribution of the Formation Voltage Oscillations

In order to analyze the distribution of the formation voltage oscillations, one time interval $[t_{FS}, T]$ of the experiment can be examined, which is the time limited by the appearance of the first spark (t_{FS}) to its end (T). For this interval the following indications may be introduced:

$$t_{FS} < t'_1 \leq t_1 < t''_1 \leq t'_2 \leq t_2 < t''_2 \leq \ldots \leq t'_N \leq t_N < t''_N \leq T,$$

where:

- N is the number of peaks in the $U_f(t)$–kinetic curves
- t'_i $(i = 1, 2, \ldots, N)$ corresponds to the beginning of the appearance of the i-th breakdown (i –th crater in the oxide film begins to form)

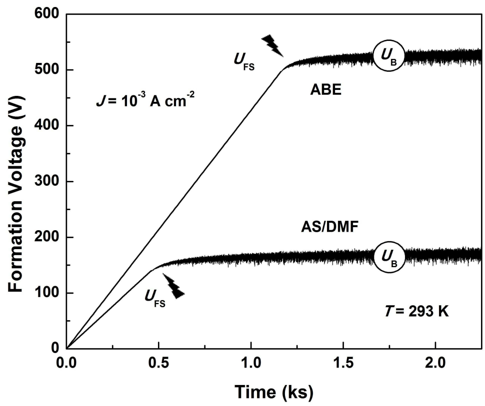

Figure 1: Kinetic$U_f(t)$ curves of aluminum anodization in two electrolyte solutions (ABE and AS/DMF) are presented. The "first spark voltage" (U_{FS}) is denoted by broken arrows

- $t_i\,(i = 1, 2, \ldots, N)$ the time, when the respective i-th crater has already been formed, which corresponds to a lower peak in the kinetic curve
- $t''_i\,(i = 1, 2, \ldots, N)$ corresponds to the moment of a crater being filled (the oxide film has regenerated)

In the present examination, as a random variable (X') can accept the variation (ΔU) of the formation voltage U_f in the intervals $[t'_i, t_i]\,(i = 1, 2, \ldots, N)$, which correspond to the descending voltage oscillations, resulting in the occurrence of electric breakdowns.

The values for $x'_i, (i = 1, 2, \ldots, 18)$ of the random variable X' can be averaged by weight in the interval $(n-1, n]$, $n = 1, 2, \ldots, 18, (18, \infty)$, and are calculated with the formula:

$$x'_n = \frac{N_1^{(n)}\Delta U_1^{(n)} + N_2^{(n)}\Delta U_2^{(n)} + \cdots + N_k^{(n)}\Delta U_k^{(n)}}{N_1^{(n)} + N_2^{(n)} + \cdots + N_k^{(n)}}, \tag{1}$$

where:

- k is the number of different values of ΔU in the interval $(n-1, n]$;
- $\Delta U_1^{(n)}, \Delta U_2^{(n)}, ..., \Delta U_k^{(n)} \in (n-1, n]$;
- $N_1^{(n)}, N_2^{(n)}, ..., N_k^{(n)}$ are the absolute frequencies of $\Delta U_1^{(n)}$, $\Delta U_2^{(n)}$,..., $\Delta U_k^{(n)}$;
- $N = \sum\limits_{n=1}^{L}\sum\limits_{i=1}^{k} N_i^{(n)}$

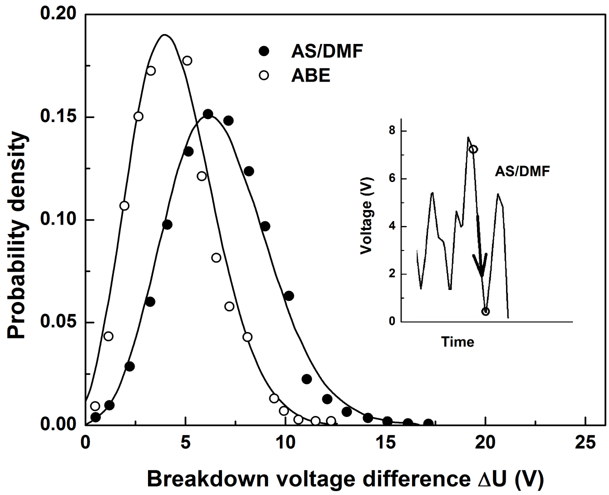

Figure 2: Breakdown probability density for (ΔU) in ABE and AS/DMF. The points represent experimental data and the curves drawn - Poisson's distribution parameters (4.50 and 6.66 respectively for the two electrolytes).

3.3. Distribution of the Formation Voltage Oscillations in the Event of Electrical Breakdowns

It was of interest to define the type of the random variable X' distribution (which in the considered problem is the variation (ΔU)of the formation voltage (U_{f}) during the occurrence of electrical breakdowns). A hypothesis could be made, that the variation of (ΔU)at breakdown occurrence has a Poisson's character. In order to verify this hypothesis χ^2-Pierson criterion, at significance level 0.05, was applied. The conducted calculations on experimental data indicated a value for $\chi^2_{observed} = 15.77$. This value is lower than $\chi^2_{critical} = 26.30$, which allows the assumption of this hypothesis [14].

The probability density during breakdowns (decrease in formation voltage) at anodizing in the two investigated electrolytes is presented in Fig. 2.

3.4. Distribution of the Formation Voltage Oscillations during Regeneration of the Anodic Film

The same procedure can be employed to define the probability density of the variation (ΔU)of formation voltage (U_{f}) during regeneration (growth) of the anodic film, in the craters formed by breakdowns.

In this case the random variable (X'') is the variation of U_{f}, but in the interval $[t_i, t''_i]\,(i = 1, 2, \ldots, N)$. In these intervals the regeneration (growth) of the film occurs.

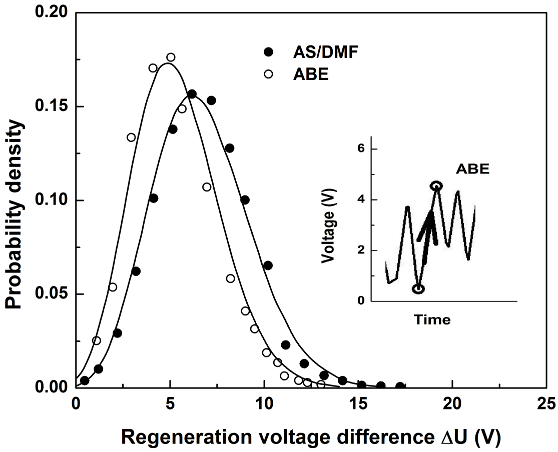

Figure 3: Regeneration probability density for (ΔU) during breakdowns in ABE and AS/DMF. Points denote experimental data, while the curves illustrate Poisson's distribution parameters (5.41 and 6.61 for the two electrolytes, respectively).

Parameter	Contact electrolyte	Parameter of Poisson's distribution
Breakdown difference voltage [volt]	1 M AS/DMF ABE (pH 6)	6.66 4.50
Regeneration difference voltage [volt]	1 M AS/DMF ABE	6.61 5.41
Number of current pulses [number s^{-1}]	0.1 M ammonium tartarate + Tartaric acid (pH 6)	6.86 [6]

Table 1: Values of probability density

The results for the two investigated electrolytes are presented in Figure 3.

The values of Poisson's distribution parameters are presented in Table 1. The results show that the contact electrolyte does not significantly affect the distribution character of the formation voltage variation both in case of breakdowns and during regeneration of the film during breakdown phenomena.

This result seems quite surprising, given the strong dependence of the electronic conductivity of (+)valve metal/anodic oxide/electrolyte systems on the nature and concentration of the contact electrolyte. One possible explanation for this result could be the different thickness (for different electrolytes) where the electronic current (J_{e}) reaches a critical value, causing an electron avalanche.

It is worth noting that other authors have also commented on the probability of breakdowns. For example, Kadary and Klein [6] have investigated and registered the breakdown voltage in anodization of aluminum by highfrequency current oscillations. The results are interpreted by the stochastic succession of avalanche breakdown model [5]. As a result the authors have found a dependence of the probability density on the alteration distribution of the number of current pulses also finding a Poisson distribution (Table 1). Furthermore the reproducibility of the breakdown voltage value has been statistically tested [13]. A high reproducibility of the value of U_{B} (from 216 independent experiments) has been established - (6%) deviation from the mean value.

4. Conclusions

The results obtained are in accordance with the characteristics of the breakdown voltage estimated from other authors by other methods. The results support the mechanism for dielectric breakdown which is due to electronic avalanche, accelerated under the influence of the electric field applied. The formation voltage oscillations in case of electrical breakdowns in galvanostatic and isothermal regime of aluminum anodizing have been analyzed. The obtained results indicate that the contact electrolyte does not affect significantly the character of formation voltage distribution during breakdowns. This has been found during the local breaking of the oxide, as well as during its regeneration at the breakdown site. This result seems in some sense unexpected, due to the definitely established dependence of electronic conductivity on the nature and concentration of the contact electrolyte. A Poisson distribution of the probability density has been established during the occurrence of electrical breakdown, as well as during the regeneration of Al_2O_3-films. The Poisson's parameters for both breakdown voltage difference and the regeneration voltage difference distribution have been calculated respectively. The results are in accordance with breakdown voltage characteristics identified by other authors in other methods. The results support the mechanism for dielectric breakdown which is due to the electronic avalanche which is accelerated under the influence of the electric field applied.

Acknowledgments

The authors are grateful for the financial support of European Social Fund, Human Resources Development Programme, under the contract BG 051PO001-3.3.06-0014.

References

[1] A. Guntherschulze, H. Betz, Electrokondenzatoren (II edn), Herbert Cram, Berlin (1952).

[2] V. N. Orlov, L. L Odynets, T. I. Ryungenen, Sparkling at the anodic oxidation of tantalum with impurities Electrokhymia 9 (1973) 818-821

[3] F. J. Burger, J. C. Wu, Dielectric breakdown in electrolyte capacitors, J. Electrochem. Soc. 118 (1971) 2039-2042

[4] S. Ikonopisov, A. Girginov, M. Machkova, Electric breaking down of barrier anodic films during their formation, Electrochim. Acta 24 (1979) 451-456.

[5] V. Kadary, N. Klein, Electrical Breakdown: I. During the Anodic Growth of Tantalum Pentoxide, J. Electrochem. Soc. 127 (1980) 139-151

[6] N. Klein, V. Moskovici, V. Kadary, Electrical Breakdown: II. During the Anodic Growth of Aluminum Oxide, J. Electrochem. Soc. 127 (1980) 152-155

[7] S. Ikonopisov, Theory of electrical breakdown during formation of barrier anodic films Electrochim. Acta 22 (1977) 1077-1082

[8] S. G. Christov, Electronic currents in anodic polarization of oxide-covered valve metals, J Electroanal Chem 105 (1979) 275-282

[9] A. Girginov, V. Trifonova, A test of the anodic electron current on oxide-covered valve metals, J. Electroanal. Chem. 107 (1980) 105-114

[10] Ch. Girginov, S. Petkova, A. Zahariev, Electronic conductivity in the (+)metal/anodic oxide/electrolyte system, Current topics in Electrochemistry 15 (2010) 43-47

[11] K. Shimizu, G. E. Thompson, G. C. Wood, The electrical breakdown during anodizing of high purity aluminium in borate solutions Thin Solid Films 92 (1982) 231-241

[12] Ch. Girginov, S. Kozhukharov, Surface of alumina films after prolonged breakdowns in galvanostatic anodization, International Journal of Electrochemistry Volume 2011, Article ID 126726, 5 pages, doi:10.4061/2011/126726

[13] A. Girginov, S. Ikonpisov, The analysis methods indicating electrolytical breakdown during anodic oxidation of aluminum, Compt. rend. Acad. bulg. Sci. 28 (1975) 257-260.

[14] H. Nickel, R. Conrad, S. Voelkel, W. Leupold, G. Herfurth, Mathematik fuer Ingenieur- und Fachschulen, Band 1,2, VEB Fachbuchverlag, Leipzig (1979).