An Approach to the Investigation and Assessment of the Electric Field Non-Uniformity

Peter Dineff[1], Raina Tzeneva[2]

Abstract – **The experimental-and-theoretical approach to studying the effect of the field geometrical structure, which acts through its transition from uniform field to non-uniform one as a result of varying the ratio of the active anode and cathode areas, upon the anodic aluminum dissolution in solutions of sodium chloride is presented in a finished form, said ratio being assumed to be a measure for the non-conformity with Faraday laws. Two non-uniformity factors of the electric field are used: α – the "length" geometrical factor, and β – the "surface" geometrical factor. The general factor is determined by the product of the two factors: $G = \alpha\beta$. The distribution of the current density in the experimentally investigated cases of anodic dissolution is visualized by appropriate mathematical modeling of the electric field.**

Keywords – **Anode dissolution, electric field geometry or topology, electrolysis, general non-uniformity factor, length geometrical factor, non-uniformity, surface geometrical factor.**

I. INTRODUCTION

The scientific literature does not indicate any generally accepted mechanism of aluminum anodic dissolution in electric field of various degree of non-uniformity which could be not only of theoretical importance, but also of great practical value for applying effectively the aluminum as anode material in electrocoagulation, electroflotation, electro-M process, etc. [1, 2].

The objective of the present theoretical and experimental investigations is to study the effect of the electric field non-uniformity on the galvanostatic anodic dissolution of technically pure aluminum in a comparatively wide range of variation of the quantity of electricity and the degree of non-uniformity.

Electric field parameters characterizing the change in the geometrical (topological) field structure and helping the comparison of the non-uniformity degrees of different electric fields, e. g. the degree of field non-uniformity β, the electrode polarity, and the relative length of the average currant tube α, have been defined [1, 2].

II. THEORETICAL INVESTIGATION

There are two ways to change the electric field of conductivity structure:

[1]Peter Dineff is with the Department of Electric Apparatuses, Faculty of Electric Engineering, Technical University of Sofia, Blvd. Kliment Ohridski 8, 1000 Sofia, Bulgaria, E-mail: dineff_pd@abv.bg

[2]Raina T. Tzeneva is with the Department of Electric Apparatuses, Faculty of Electric Engineering, Blvd. Kliment Ohridski 8, 1000 Sofia, Bulgaria, E-mail: tzeneva@tu-sofia.bg.

$ varying the ratio between the electrode – anode and cathode, active areas S_a and S_c, or changing the degree of non-uniformity $\beta \geq 1$ ($\beta = 1$ for uniform electric field) [1]:

$$\beta = S_g^o \, S_g^{-1} = S \, S_g^{-1} = S \left(S_a \, S_c \right)^{-1/2} \quad , \quad (1)$$

where S is anode S_a^o and cathode S_c^o active area for uniform electric field: $S = S_g^o = S_a^o = S_c^o = \left(S_a^o \, S_c^o \right)^{1/2}$, and S_g^o - the geometrical mean of anode and cathode areas; $S_g = \left(S_a \, S_c \right)^{1/2}$ - the geometrical mean of anode and cathode areas for non-uniform electric field, S_a and S_c - the anode and cathode active areas; electrodes polarity may be straight (SP) - $S = S_a$ or reverse (RP) – $S = S_c$;

$ varying the apparent relative length of the average current tube $\alpha \geq 1$ ($\alpha = 1$ for uniform electric field):

$$\alpha = l \, d^{-1} , \quad (2)$$

where d is the distance between the two electrodes or the minimum possible length of the current vector tube: $l = d$ and $\alpha = 1$ for uniform electric field.

For a non-uniform electric field of conductivity the electric resistance R_{NU} of electrolysis cells may be expressed by the resistance R_U for a uniform field:

$$R_{NU} = \rho l S_g^{-1} = \rho \alpha d S^{-1} = \rho d S^{-1} \alpha \beta = R_U \alpha \beta \quad (3)$$

$$G = R_{NU} \, R_U^{-1} = \alpha \, \beta , \quad (4)$$

where G is the general degree of non-uniformity.

The degree of non-uniformity β can be an independent factor of the electrolysis which is modified by varying the ratio between areas S_a and S_c, and the polarity of electrodes: SP - $S = S_a$ or RP - $S = S_c$, while keeping $S_g = const$.

The apparent length α follows the changes of the voltage U across the electrolysis cell in a galvanostatic regime, $I = const$, of anodic dissolution of aluminum:

$$I = U \left(\rho \, \lambda \, \alpha \, \beta \right)^{-1} = U \left(\rho \, \lambda \, G \right)^{-1} = const ; \quad (5)$$

$$U \, \alpha^{-1} = const \; (\rho = const, \lambda = const, \beta = const ; \quad (6)$$

where $\lambda = d\, S_g^{-1}$ is the geometric factor of the electric resistance of electrolysis cell.

For the same time of electrolysis t_e the quantity of electricity Q transferred through the solution remains constant, too, or $Q = I\, t_e = const$, in the galvanostatic regime of electrolysis.

In the galvanostatic regime of electrolysis the basic relationships representing the influence of non-uniformity upon anodic dissolution of aluminum may be presented in the following way:

$$M_a = \eta_a\, M_F = \frac{A\, \eta_a}{F\, z}\, \frac{t_e}{\rho}\, \frac{U}{\lambda\, \alpha\, \beta} = m_a\, \frac{t_e}{\rho}\, \frac{U}{\lambda\, G}\; ; \quad (7)$$

$$w = \frac{W}{M_a} = \frac{Q\, U}{M_a} = \frac{F\, z}{A\, \eta_a}\, \frac{\rho}{t_e}\, \lambda\, \alpha\, \beta\, Q\; ; \quad (8)$$

$$w = \frac{l}{m_a\, t_e}\, \rho\, \lambda G Q\, ; \quad (9)$$

$$R = \rho\, \lambda\, \alpha\, \beta = \rho\, \lambda\, G\; ; \quad (10)$$

$$N_e = \frac{z}{\eta_a}\, , \quad (11)$$

where M_a is the mass of anode dissolved aluminum, g; η_a - the current efficiency; $F = 96\,487$ is Faraday's number representing the quantity of electrons, C/mol; $z = 3$ – the normal oxidation level of aluminum; A – the atom weigh of aluminum, g/mol; w - the specific energy consumption per unit of dissolved aluminum mass, (W.s)/g; W – the energy consumption, W.s; R – the resistance of the electrolysis cell, Ω; N_e - the effective oxidation level.

III. GENERAL FORMULATION OF INVESTIGATIONS

The dissolution of plane-parallel electrodes made of aluminum 99.5 with main additions: 0.26 Fe, 0.14 Si, 0.10 Cu, and 0.001 Mg (mf%), has been studied [4, 5].

The electrolysis has been performed under galvanostatic conditions of direct current at room temperature (20 ^{0}C) in a 0.052 M solution of chemically pure sodium chloride (NaCl) in distilled water. The volume of the electrolysis cell is 1 dm^3. The electrolysis time t_e is t_e = 900 s (15 min).

The quantity of electricity Q has been varied at five levels: 144, 432, 720, 1008, and 1440 C. The electrodes active area S is S = 16 cm^2, and the current has been determined as 0.16, 0.48, 0.80, 1.12, and 1.60 A, respectively.

The distance between the electrodes remains unchanged: d = 15 mm. The geometrical structure of the electric field has been changed at three levels of the non-uniformity degree β, namely $\beta = 1$, $\sqrt{2}$, and 2. The electrodes under test are made with the following dimensions: (40 x 40 x 10) mm, (40 x 20 x 10) mm, and (20 x 20 x 10) mm, respectively. The back and side walls of electrodes are electrically insulated by

a coating of epoxy resin defining precisely the size of the active electrodes' area.

The mass of dissolved aluminum M_a has been determined gravimetrically, after appropriate washing and drying, in five parallel experiments [4, 5].

Additional investigations have been carried out with the task of modelling and visualizing with the aid of modern software products the **3-D** spatial distribution of the current density of $\vec{J}$ and the geometrical structure change for various values of the non-uniformity degree β. The electric field $\vec{J}$ in the electrolysis cell has been modeled spatially by using the method of boundary elements.

Pictures of the distribution of current density $\vec{J}$ for the three experimentally investigated cases of non-uniformity are shown in Figs. 1, 2, and 3.
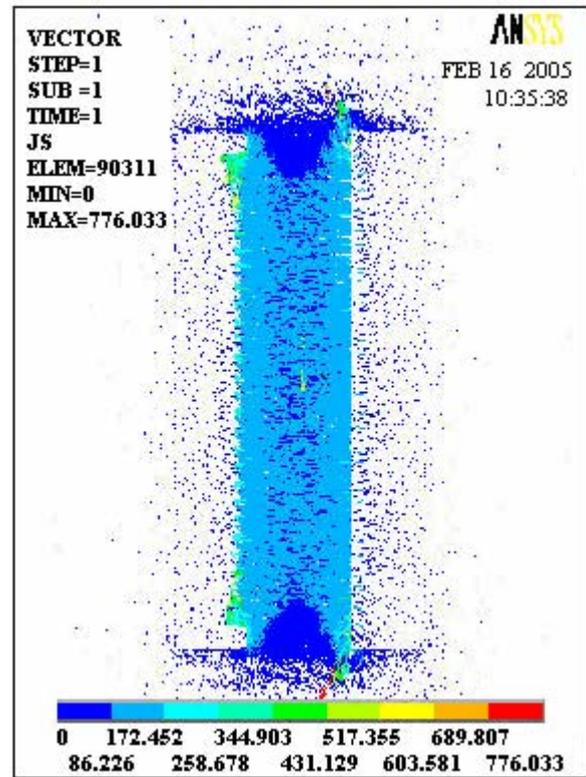

Fig. 1. Sectional view of the geometrical structure of the electric field of an electrolysis cell, which is represented by the distribution of the vectors of current density $\vec{J}$ for plane-parallel configuration of two identical aluminum electrodes of active area S = 16 cm^2 (β = 1) and distance d = 15 mm between them. The electrodes are electrically insulated over the back wall as well as over all side ones. The geometrical mean of the current density is $\vec{J}_g$ = 625 A/m^2.

The presented **3-D** visualization of the electric field corresponds most exactly to the real structure of the electric field created. The **2-D** distributions presented in [4] are a rather rough approximation as the electric insulation of the surrounding walls as well as the back one of the electrodes creates a very characteristic structure of the electric field that cannot be modeled by products for 2-D analysis as *Quickfield* or *FEMM*.

In the **3-D** modeling the edge effect is expressed by suction of the field inward between the electrodes, Figs. 1, 2, and 3, while the **2-D** plane-parallel mathematical models show the edge effect by outward swelling. In the plane-parallel **2-D** model it is impossible to insulate electrically the two surrounding walls of electrode, which are situated in parallel to the plane of modeling.
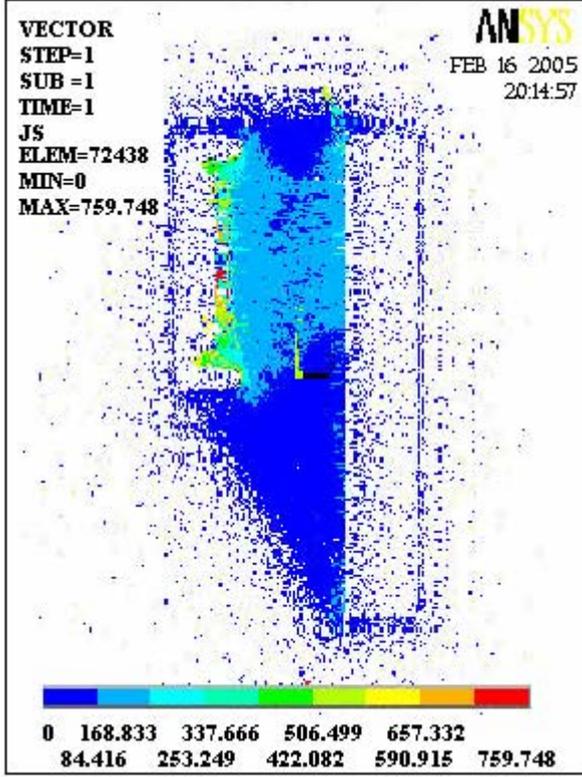

Fig. 2. Sectional view of the geometrical structure of the electric field of an electrolysis cell, which is represented by the distribution of the vectors of current density $\vec{J}$ plane-parallel configuration of two aluminum electrodes of active areas $S = 8$ cm^2 and 16 cm^2, respectively, ($\beta = \sqrt{2}$) and distance $d = 15$ mm between them.

IV. RESULTS AND DISCUSSION

The mass of aluminum dissolved at the anode, M_a, has been determined experimentally, and then all the remaining characteristics of the anodic dissolution are calculated in accordance with equation 10-14.

All calculations are performed for specific electric resistance of the electrically conductive media $\rho = 1.352$ Ωm and geometrical factor of the resistance, $\lambda = 9.375$ m^{-1}.

The regression relationships obtained show a relatively weak dependence of the current efficiency η_a upon the quantity of electricity Q,:

$$\eta_a = 121.60 + \frac{542.92}{Q}, \ r = 0.9986 \tag{12}$$

The current efficiency η_a decreases with increasing the quantity of electricity Q in the interval studied $Q \in [144 - 1440]C$, changing relatively weakly: from 1.25 to 1.22, or within the range of 2.5 %. The current efficiency is higher than one, which indicates the presence of a process going in parallel to the Faraday anodic dissolution, namely corrosion of aluminum [3, 4].

The effective oxidation level N_e may be also represented by the regression equation obtained – equation 12, and equation 11, $Q \in [144 - 1440]C$:

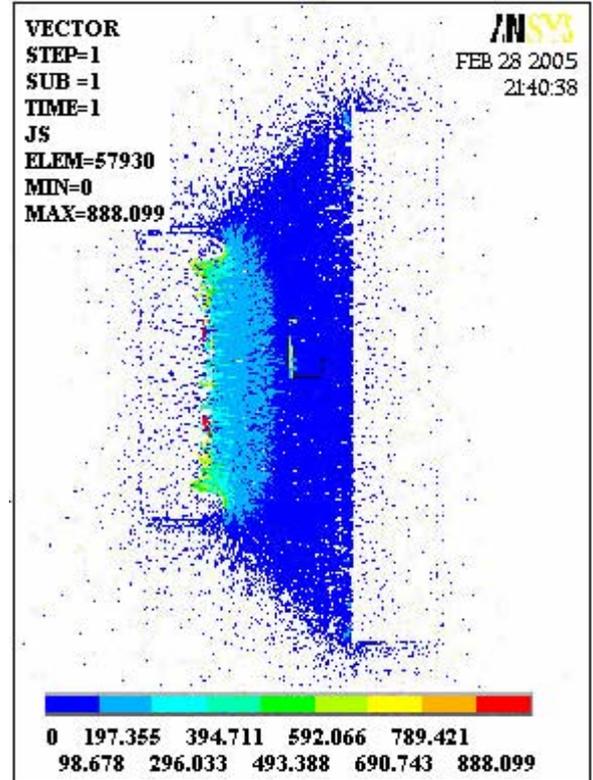$$N_e = \frac{Q}{40.53 \ Q + 180.97}, \ r = 0.9986 . \tag{13}$$

Fig. 3. Sectional view of the geometrical structure of the electric field of an electrolysis cell, represented by the distribution of the vectors of current density $\vec{J}$, for plane-parallel configuration of two aluminum electrodes of active areas $S = 4$ cm^2 and 16 cm^2 ($\beta = 2$) and distance $d = 15$ mm between them.

The experimentally determined effective oxidation level N_e is lower than the normal oxidation level of aluminum $z = 3$, and changes within a comparatively narrow range from 2.39 to 2.46.

According to the known hypothesis for the stepwise mechanism of the anodic oxidation of aluminum at varying the effective oxidation level in the region $2 < N_e < 3$, two of the oxidation stages are realized inevitably with the participation of the anode (in accordance with Faraday), while about 50 % of the aluminum ions taking part in the third act of oxidation do not get into contact with the anode.

The influence of the general degree of non-uniformity G or of the geometric factor of electrolysis cell $\lambda\alpha\beta$ on the mass of anodically dissolved aluminum M_a for straight (SP) and reverse (RP) polarities of the electrodes is shown graphically in Fig. 4.

The observed relative shortening of the average current tube may be explained with the tightening action exerted by the proper magnetic field of the current.
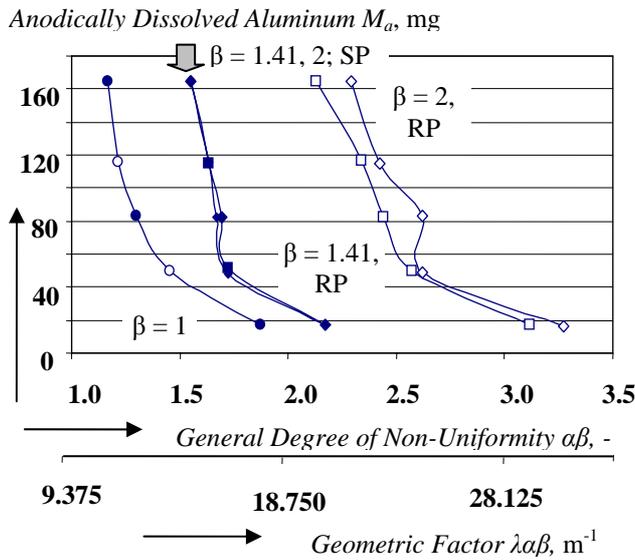
Anodically Dissolved Aluminum M_a, mg

Fig. 4. Dependence of the mass of anodically dissolved aluminum M_a on the general degree of non-uniformity $G = \alpha\beta$, the general geometric factor $\lambda\alpha\beta$, and the degree of non-uniformity β at straight and reverse polarity of electrodes.

Analogous considerations are made for the specific energy consumption *w*, which is the quantity of electric energy used in anodic dissolution and corrosion, Fig. 5.

In all cases examined increasing the anodic dissolution rate, $M_a\left(t_e = 900\ s\right)$ becomes the cause of a fast increase in the electric energy consumption.
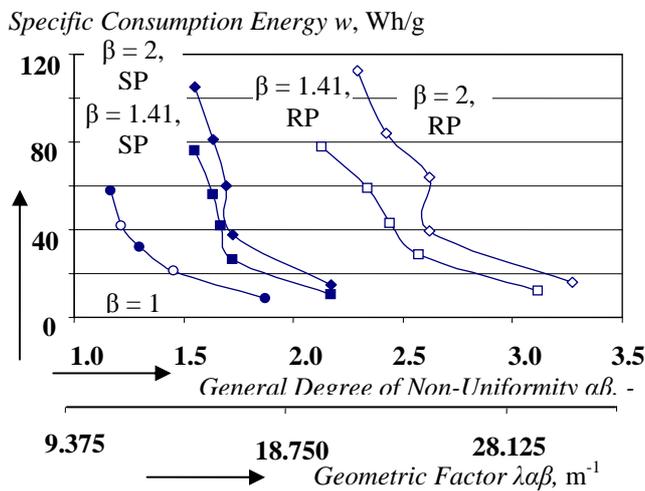
Specific Consumption Energy w, Wh/g

Fig. 5. Dependence of the specific energy consumption *w* on the general degree of non-uniformity $G = \alpha\beta$, the degree of non-uniformity β, and the general geometrical factor $\lambda\alpha\beta$ at straight and reverse polarity of electrodes.

The present investigation permits making an addition to the increase in the electric energy consumption at a higher degree of non-uniformity of the field, already established by us in [4]. The more non-uniform electric field leads to a more essential increase in the electric energy consumption at higher rates of anodic dissolution of aluminum.
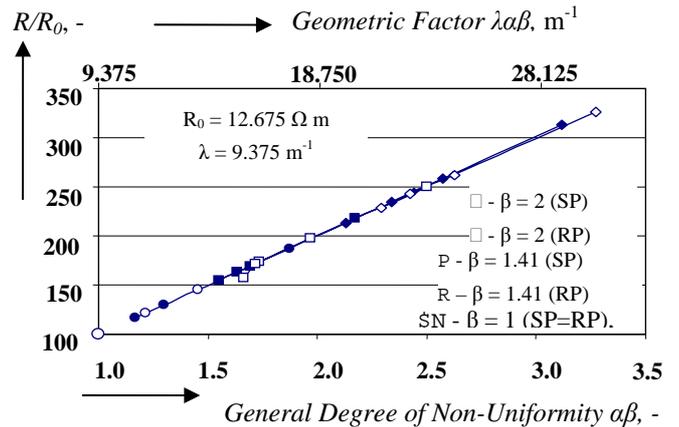

Fig. 6. Dependence of the relative electric resistance R/R_0 ($R_0 = 12.675\ \Omega m$) on the general degree of non-uniformity $G = \alpha\beta$, the degree of non-uniformity β, and the general geometric factor $\lambda\alpha\beta$ at straight and reverse polarity of electrodes.

The relative change in resistance R / R_O depends linearly on the change in the general degree of non-uniformity $G = \alpha\beta$, Fig. 6.

The assumed hypothesis of linearity of the electrically conductive medium is confirmed, because $R_0 = \rho\ \lambda$ should remain of constant value for the change in the general non-homogeneity of the electric field, *G*, in order to be manifested the linear relationship observed in Fig. 6.

Irrespective of the polarity of the electrode system – straight or reverse, all operating points are located on the straight line for a change in the quantity of electricity within the range $Q \in \left[144 - 1440\ \right]C$.

V. CONCLUSION

Changing the non-uniformity degree β exerts much weaker influence on the rate of anodic dissolution and on the specific consumption of electric energy than the increase in the quantity of electricity transferred through the electrolyte. The high rates of anodic dissolution and corrosion define the considerably increased consumption of electric energy in this case, which is practically independent of the non-uniformity of the electric field. The non-uniformity of the electric field contributes essentially to increasing the electric energy consumption at high rates of anodic dissolution.

The high rates of anodic dissolution and corrosion and the high values of the electric current, respectively, define the observed relative shortening of the elementary vector current tubes. An explanation of this fact may be connected with the influence of its own magnetic field that „tightens" the region of conductivity, or with the so called pinch-effect.

REFERENCES

[1] P. Dineff, E. Sabeva, *Indian Journal of Chemical Technology*, Vol. 11, July, pp. 486-494, 2004.
[2] P. Dineff, E. Sabeva and I. Dobrevsky, *Corrosion Science*, Vol. 36, No 4, pp. 717-732, 1994.