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Anodic oxide films on antimony formed in oxalic acid solutions

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Anodic oxide films on antimony were grown in aqueous solutions of oxalic acid in a large current density and acid concentration range. Under galvanostatic conditions, the common linear increase of the formation voltage with time proved to occur at current densities higher than 2 mA cm^{-2} and in electrolytes with oxalic acid concentrations lower than 0.01 M. Under these only conditions the relationship between the ionic current density and the field strength is described by *Güntherschulze* and *Betz* equation.

The electrical breaking down of anodic antimony oxide in the oxalic acid electrolytes was studied. The experimental data obtained for the breakdown voltages are well described by *Burger* and *Wu* equation. The amplitude and the frequency of voltage oscillations during electrical breaking down were found practically not to depend on current density.

The results are compared with those obtained for anodic oxidation of antimony in other aqueous solutions. Under specified conditions, the oxalic acid electrolyte proved to be suitable for the formation of anodic oxide films on antimony.

Key words: anodic antimony oxide, galvanostatic anodization, breakdown voltage, oxalic acid

INTRODUCTION

Apart from the assumed effect of its formation in lead–acid batteries, antimony oxide has found applications as electro catalyst, photoconductor, for thin film capacitors and in preparing electro chromic devices [1]. Barrier-type anodic oxide films on antimony have been grown in a number of aqueous solutions of acids, bases and salts [2-11], as well as in non-aqueous electrolytes [12, 13]. In all cases, however, a strong influence of nature and concentration of the forming electrolyte on the kinetics of anodizing has been established. The anodizing of antimony often exhibits a specific kinetics, such as appearance of induction periods, *S*-shaped curves and maxima in the kinetic dependencies [3-6, 10]. It was therefore of interest to search for electrolytes ensuring a linear potential growth during galvanostatic anodizing of antimony in a wide range of concentrations and current densities.

In the present study, data for the formation kinetics and the breakdown phenomena of antimony oxide films in aqueous solutions of $(COOH)_2$ at various current densities were obtained.

EXPERIMENTAL

Specimens of high purity (99,999%) antimony were cut out of polycrystalline Sb with a working area of 2.5 cm^2. The electrodes were mechanically polished with sandpaper R 4000 (d = 5 μm). The anodizing was carried out under galvanostatic conditions at a temperature of 293 K. The current densities (J) varied from 2 mA cm^{-2} to 20 mA cm^{-2}. Various $(COOH)_2$ solutions in the range from 0.01 M to 0.1 M were used as forming electrolytes. The electrolytes were not stirred in order to avoid the influence of hydrodynamic effects.

The formation of the films was carried out in a two-electrode cell with a platinum mesh serving as a counter electrode, using a high voltage generator of constant current (600 V, 0.5 A). Kinetic curves, i.e. dependences of the formation voltage (U_f) on time (t) were registered with a precision multi meter (Mastech MS 8050) and a PC-based data acquisition system.

RESULTS AND DISSCUSSION

Kinetics of galvanostatic anodization

The formation of barrier anodic films on valve metals at galvanostatic and isothermal conditions is known to be associated with a linear increase of the formation voltage (U_f) with time (t), or respectively with the density of electric charge passed (Q). It turned out that the concentration of the oxalic acid and the current density used had a strong influence on the kinetics of the process. Examples of kinetic $U_f(t)$-curves (respectively $U_f(Q)$-dependencies) obtained in solutions with different concentrations at a constant current density of 2 mA cm^{-2} are presented in Fig.1.

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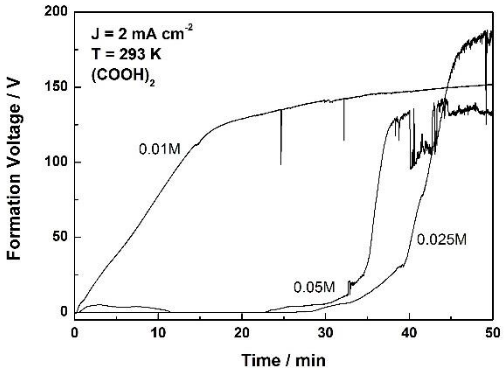

Fig. 1. Kinetic curves of galvanostatic anodization of antimony in oxalic acid solutions with different concentrations

The kinetic curves proved to have different shapes depending on the concentration of the oxalic acid. As it was shown earlier [14], a linear relationship between formation voltage (U_f) and time (t) was observed only at the lowest concentration (0.01 M). That is why the corresponding electrolyte was chosen for subsequent experiments.

It was of interest to trace the influence of current density (J) on the anodization kinetics. Figure 2 presents kinetic curves obtained at different current densities. The slopes ($\partial U_f/\partial Q$) of these curves are also calculated.

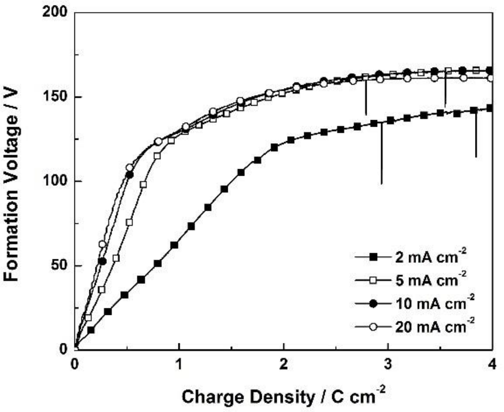

Fig. 2. Kinetic curves of antimony anodization in 0.01 M $(COOH)_2$ at different current densities

During galvanostatic anodization, the ionic current (J_i) is known to depend on the intensity of the electric field (E) in the oxide. This $J_i(E)_T$-dependence is described in a first approximation, known as the high field approximation, by Güntherschulze and Betz equation [15],

$$J_i = A_G \exp\left(B_G E\right)_T \qquad (1)$$

At constant temperature, the constants A_G and B_G are independent of the field intensity. The current (J) flowing through the system metal/oxide film/electrolyte is assumed to be completely ionic, i.e. $J = J_i$. It has been shown [12] that the high field approximation describes the anodization of antimony in a number of aqueous electrolytes as well. The validity of eqn. (1) has been further confirmed for the anodizing kinetics in a phosphate buffer [16], the anodic antimony oxide being determined as Sb_2O_3.

As a matter of fact, eqn. (1) describes well the anodizing kinetics of antimony even after the appearance of induction periods [13]. Unfortunately, there are differing opinions about the composition of the anodic antimony oxide and, moreover, no reliable methods for determining the film thickness. Hence, it seems impossible to calculate the electric field intensity (E). Based on Faraday's law, this intensity can be expressed:

$$E = \frac{zF\rho}{M}\left(\frac{\partial U_f}{\partial Q}\right)_{J,T} \qquad (2)$$

Here, F is the Faraday constant, M is the molecular mass and ρ is the density of the film, z is the number of electrons involved in the electrochemical process, and ($\partial U_f/\partial Q$) is the slope of the kinetic curve. The fact that the growth rate of formation voltage U_f with charge density $(Q)_{J,T}$ remains constant during the first anodizing stage, could be an indication that film growth dominates over film dissolution and a barrier type film is formed. In this case, the ionic current is controlled only by the film properties and $(\partial U_f/\partial Q)_{J,T}$ should depend on the current density. The Güntherschulze and Betz equation can be used to describe the anodizing kinetics on replacing the field intensity (E) by its proportional magnitude $(\partial U_f/\partial Q)_{J,T}$. An assessment of the validity of eqn. (1) was carried out by replacing the field intensity in eqn. (1) by the proportional magnitude $(\partial U_f/\partial Q)_{J,T}$ from eqn. (2):

$$J_i = A_G \exp\left[B_G^*(\partial U_f/\partial Q)_T\right], \qquad (3)$$

The notation B_G^* marks here the expression $B_G^* = B_G zF\rho/M$.

Figure 3 presents the plot of $(\partial U_f/\partial Q)_{J,T}$ vs. ln$J$. The obtained linear dependence shows that eqn. (3) adequately describes the anodizing kinetics of antimony in 0.01 M $(COOH)_2$.

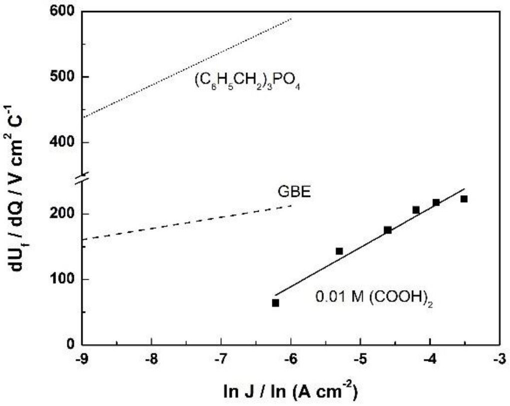

Fig. 3. $(\partial U_f/\partial Q)_{J,T}$ / ln*J* - dependence for galvanostatic anodization of antimony in 0.01 M $(COOH)_2$. Similar relationships for two other electrolytes are presented for comparison.

Values for the constants A_G and B_G^* were determined from the data in Fig. 3. These values were then compared (Table 1) with those estimated for anodization of antimony in a glycol-borate electrolyte (GBE) [12] and in a phosphate ester $(C_5H_6CH_2O)_3PO_4$ [13].

Table 1 Values of the constants A_G and B_G^* in equation (3)

Electrolyte	A_G (A cm^{-2})	B_G^* (C V^{-1} cm^{-2})
0.01 M $(COOH)_2$	0.56×10^{-8}	0.017
GBE [12]	1.25×10^{-8}	0.058
$(C_6H_5CH_2O)_3PO_4$ B_G^* [13]	2.30×10^{-8}	0.020

It is worth noting that the anodization in $(C_5H_6CH_2O)_3PO_4$, which occurs with the appearance of a pronounced induction period, is also well described by eqn. (3) [13]. It was of interest to study the dependence of $(\partial U_f/\partial Q)_{J,T}$ on the concentration of $(COOH)_2$ during anodization at a constant current density. An example of such dependence during anodizing with $J = 10^{-2}$ A cm^{-2} is presented in Figure 4. It turned out that the dependence was linear only at lower concentrations (under 0.02 M). A similar picture is observed [17] during anodization of antimony in sulfuric acid solutions.

Breakdown phenomena

The breakdown phenomena are important anodizing characteristics. It is well known that the increase in anodic film thickness, respectively the anodizing voltage, is limited by the occurrence of electrical breakdowns. The first evidence for a limiting voltage attained during anodization has been furnished in the pioneer work of Güntherschulze and Betz [15].

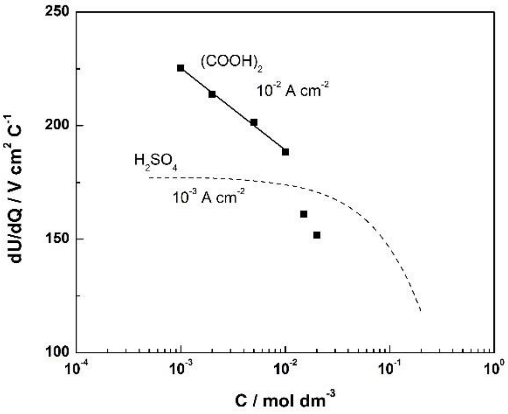

Fig. 4. $(\partial U_f/\partial Q)_{J,T}$ / log*C* - dependence for anodization of antimony in $(COOH)_2$ solutions. For comparison, a similar dependence in H_2SO_4 solutions is presented [17].

Numerical values for breakdown voltages of antimony oxide in some acid, base and salt solutions have been calculated by Ammar and Saad [3, 9]. The dependence of the breakdown voltage (U_B) on the electrolyte resistivity (ρ) for anodic films on different valve metals is well described by the empirical equation of Burger and Wu [18]:

$$U_B = a_B + b_B \log \rho \tag{4}$$

The only question remaining controversial is whether the constants a_B and b_B depend on the electrolyte composition. To clarify this, the breakdown voltage of Sb was studied in oxalic acid solutions with different concentrations (or specific resistances ρ, respectively), as shown in Fig. 5. Current density and temperature were held constant.

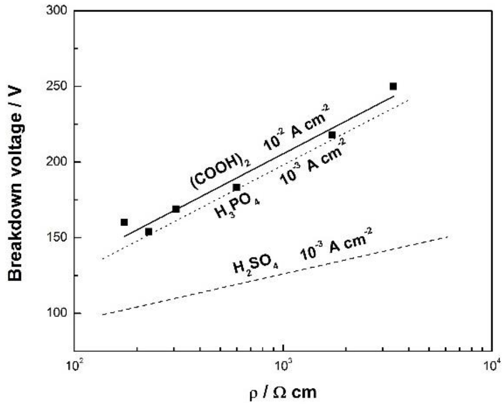

Fig. 5. Breakdown voltages are shown as a function of the specific resistance of the oxalic acid electrolyte. The results are compared with those obtained in two other solutions.

The anodizing process was conducted in galvanostatic regime with a current density of 10^{-2} A cm^{-2} at a constant temperature (293 K). In all cases, after reaching a specific value of U_f, voltage oscillations which are typical for the electric breakdown could be observed (Fig.1). The oscillations began at different values of U_f depending on the type and concentration of the contact electrolyte. Next, the voltage increased slowly, with continuous oscillations and after a certain time (or charge density passed) remained practically constant. The value of U_f, after a charge of 3 Ccm^{-2} passed since the first appearance of oscillations [17], was adopted to be the breakdown voltage (U_B). The data obtained for U_B (Fig. 6) allowed the calculation of the constants in eqn. (4). This equation proved to describe well the experimental data obtained during anodization of antimony in oxalic acid solutions. The values of the constants a_B and b_B are presented in Table 2. For comparison, values for the same constants obtained in solutions of other two acids, H_3PO_4 [12] and H_2SO_4 [17], are also presented.

Table 2 Values of the constants in the *Burger* and *Wu* equation

Electrolyte	Current density	a_B (V)	b_B (V)
$(COOH)_2$	10^{-2} A cm^{-2}	-10.4 ± 1.8	72 ± 5
H_3PO_4 [12]	10^{-3} A cm^{-2}	-18.0 ± 2.3	72 ± 8
H_2SO_4 [17]	10^{-3} A cm^{-2}	58.5 ± 4.2	24 ± 3

The studies on breaking down during anodization of antimony in aqueous oxalic acid solutions showed that breakdowns obeyed the common regularities typical for valve metals. On the other hand, the constants a_B and b_B for antimony oxide in Burger and Wu equation [18] depended on the nature of the forming electrolyte as the other oxides on valve metals. The amplitude and frequency of the voltage oscillations during breaking down were analyzed. Fragments of the oscillations are presented in Fig. 6.

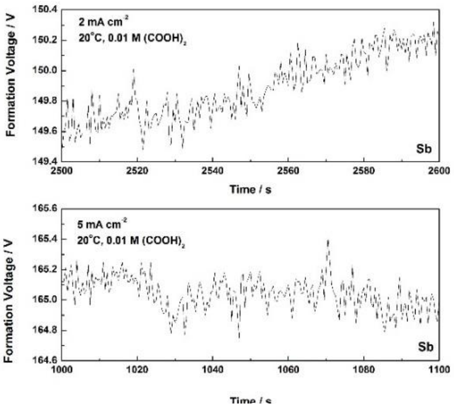

Fig. 6. Fragments of the kinetic curves during breaking down for anodization with two current densities

The results show that both the frequency and the amplitude of voltage oscillations during breaking down are insensitive to the applied current density. A similar result has been obtained with oxide films on other typical valve metals.

CONCLUSIONS

Oxalic acid solutions are suitable for the formation of anodic oxide films on antimony. The common kinetics of linear increase of the formation voltage with time in galvanostatic conditions were observed only at current densities greater than 2 mA.cm^{-2} and electrolytes with concentrations lower than 0.01 M $(COOH)_2$. The kinetics of formation is subject to known relationships between current density and field intensity (*Güntherschulze* and *Betz* equation). Breaking down is discussed on the base of *Burger* and *Wu* equation which describes well the experimental data. Furthermore, the amplitude and frequency of formation voltage oscillations during electric breakdowns is found to be practically independent of current density.

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МЕХАНИЗЪМ НА АНОДНО ОКИСЛЕНИЕ НА АЛУМИНИЕВИ СПЛАВИ В СУЛФАТНО-ФЛУОРИДЕН ЕЛЕКТРОЛИТ

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(Резюме)

Изследвана е кинетиката на образуване на анодни оксидни филми във водни разтвори на оксалова киселина. Процесът е изучен при широко вариране на концентрацията и плътността на тока. Установено е, че обичайната кинетика с линейно нарастване на формиращото напрежение с времето (в галваностатични условия) се наблюдава при анодиране с плътности на тока над 2 mA cm^{-2} в електролити с концентрация по-ниска от 0.01 M $(COOH)_2$. При тези условия е в сила уравнението на Гюнтершулце и Бец, което описва зависимостта на йонния ток от силата на приложеното електрично поле. Получените експериментални данни за пробивните напрежения по време на анодирането на антимона се описват добре с емпиричното уравнение на Бургер и Ву. Стойностите на константите в уравнението са съпоставени с тези, получени при анодирането на антимон във водни разтвори на други киселини. Установено е също така, че амплитудата и честотата на осцилациите на напрежението по време на пробивите не се повлияват значително от плътността на тока. При определени условия водните разтвори на оксаловата киселина са подходящи за формирането на анодни оксидни филми върху антимон.