

DETERMINATION OF THE PARAMETERS OF THE ELECTRONIC CURRENT DURING TENSIOSTATIC ANODIZATION OF BISMUTH

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ABSTRACT

In the present work, the electronic current density flowing through anodic oxide films is estimated from the total current vs. time dependence in tensiostatic anodization experiment using a numerical procedure. The parameters, characterising its field dependence, are compared to previously obtained values for galvanostatically formed films, measured at low field strengths in the oxide. The good correspondence between the two sets of electronic current values gives credibility to the proposed procedure and demonstrates a new possibility to account for the electronic conduction in anodic films during their formation.

Keywords: valve metal, tensiostatic anodization, anodic oxide, ionic conduction, electronic conduction, numerical calculation.

INTRODUCTION

The total current density (j), measured in systems metal/anodic oxide film/electrolyte consists of three components: $j = j_i + j_e + j_{dis}$. The ionic current density (j_i), which results from the migration of ionic point defects under the influence of the electric field, leads to the growth of the anodic film. The electronic current (j_e) through the oxide film does not influence its thickness and is due to the occurrence of reactions of electron transfer at the film/solution interface, such as oxygen evolution. The dissolution current (j_{dis}) can attain significant values when the films are produced in electrolytes which are aggressive to the oxide film. Usually the formation of anodic oxide films and their subsequent polarisation are carried out in non-dissolving electrolytes. In this case, $j_{dis} = 0$, so that: $j = j_i + j_e$. These two components of the current depend on the field strength (E) and the temperature (T).

Theoretical background

Ionic current

Ionic conduction through anodic oxides is usually studied at high current densities (i.e. at high field strength). Under these conditions the electronic component of the total current can be neglected ($j = j_i$). Different equations have been proposed for the $J_i(E, T)$ -dependence. The applicability of three of them (the equations of Gunterschultze-Betz [1], Tafel-Frenkel and Young [2]) has been verified for anodization of various valve metals. These three equations have been theoretically interpreted [3].

The dependence $j_i(E)_T$, according to the *Tafel-Frenkel* equation is:

$$j_i = A_i \exp \left(- \frac{B_i - \alpha_i E}{k_B T} \right), \quad (1)$$

where A_i , B_i and α_i are constants depending on the nature of the metal and oxide, as well as the temperature.

Electronic current

The electronic conductivity is studied usually during anodic polarization of already formed oxide films at potentials lower than the formation voltage, i.e. at comparatively low field strengths. In these cases an empirical equation for the $j_e(E)_T$ dependence has been reported:

$$j_e = \alpha_e \exp\left(\beta_e E^{1/2}\right) \quad (2)$$

where α_e and β_e are constants depending on the nature of the metal, the contact electrolyte and the temperature. Such a dependence has been experimentally found for different metals: Al [4], Ta [5,6], Nb [7,8], Bi [9]. Different models [10] have been proposed explaining the mechanisms of the electronic currents (Schottky emission, Poole-Frenkel effect). Only the model of Christov [11] explained dependence of j_e on the nature and concentration of the contact electrolyte. In this model the electrolyte was considered as a semiconductor and the redox couples in it were assumed to play the role of electron donors.

Galvanostatic anodization

The anodic oxidation of valve metals is usually carried out in galvanostatic ($j = \text{const}$) and isothermic ($T = \text{const}$) conditions. The anodic oxidation in this regime is characterised with a constant rate of oxide growth, and the specific properties of the film do not change during growth. It is usually assumed that the potential difference is consumed as a drop in the film bulk, called formation voltage (U_f), which grows quasi-linearly with time, i.e. with the charge density passed through the system ($Q = j \cdot t$). The increase of U_f is limited by the occurrence of electrical breakdown of the oxide. During anodic film growth the electric field strength defined as $E = U_f / D$, where D is the film thickness, remains constant ($E = \text{const}$).

Tensiostatic anodization

Tensiostatic anodization is carried out by applying a constant voltage U_v in the electrolytic cell. This voltage is usually reached by a prior galvanostatic stage (with a comparatively high current density), during which an anodic film with a thickness D_0 is formed. The process of tensiostatic anodization is a non-station-

ary process, because the flowing ionic current causes the increase of the thickness of the oxide:

$$D(t) = D_0 + \frac{\mu \lambda(t)}{zF\rho\sigma} \int_{t_0}^t j_i(\tau) d\tau \quad (3)$$

where m is the molar mass of the oxide, z is the number of transferred electrons per oxide molecule, F is Faraday's number, r is the oxide density, s is the roughness factor of the surface, $l(t)$ is the current efficiency of film formation and t is an integration variable. As a result of the increase of thickness the field strength, defined in this case as $E = U_v / D$, as well as the ionic and electronic current densities continuously decrease with time. In the initial stages, the current is predominantly ionic ($j \sim j_i$), but the relative importance of the electronic current increases gradually. It can be assumed that in the final stage the current will be practically electronic ($j \sim j_e$), thus its values will depend on the nature and concentration of the electrolyte. Such a dependence has been theoretically predicted [11] and experimentally proven for the (+)Bi /Bi/Bi₂O₃/electrolyte system [9]. Thus the prolonged tensiostatic anodization offers another possibility to estimate the electronic currents in the (+)metal/anodic oxide /electrolyte systems.

Numerical calculations

In order to estimate the electronic current from equations (1) to (3), in accordance with the above theoretical considerations, it is assumed that for times of anodization up to 1 ks,

$$\lambda(t) = 1, \quad t \in [t_0, t_1], \quad t_1 = 10^3 \text{ s}, \text{ as } j_e \ll j_i.$$

Using the substitution

$$y(t) = \int_{t_0}^t j_i(\tau) d\tau, \quad t \in [t_0, t_1] \quad (4)$$

it follows that

$$\frac{dy(t)}{dt} = j_i(t), \quad t \in [t_0, t_1], \quad y(t_0) = 0.$$

By combining (3) and (4), we obtain

$$D(t) = D(t_0) + \frac{\mu}{zF\rho\sigma} y(t), \quad t \in [t_0, t_1],$$

and using (1), it follows that

$$\frac{dy(t)}{dt} = A_i \exp\left(-\frac{B_i}{k_B T}\right) \exp\left(\frac{\alpha_i U}{k_B T} \frac{1}{D(t_0) + \frac{\mu}{zF\rho\sigma} y(t)}\right), \quad t \in [t_0, t_1] \quad (5)$$

$$E(t) = \frac{U}{D(t_0) + \frac{\mu}{zF\rho\sigma} y(t)}, \quad t \in [t_0, t_1]$$

When $t = t_0$

$$\frac{dy(t_0)}{dt} = A_i \exp\left(\frac{D(t_0)\alpha_i U - B_i}{k_B T D(t_0)}\right) \quad (6)$$

The constant A_i in equation (1) is determined so that the value of the ionic current density is equal to the measured value at $t=t_0$, $A_i = 5.73 \times 10^6 \text{ A cm}^{-2}$. By introducing

$$\begin{aligned} r &= \exp\left(-\frac{B_i}{k_B T}\right), \\ a &= \exp\left(\frac{\alpha_i zF\rho\sigma U}{\mu k_B T}\right), \\ r_0 &= \frac{D(t_0)zF\rho\sigma}{\mu} \end{aligned} \quad (7)$$

an initial problem for ordinary differential equations is obtained from equations (5) and (7):

$$\begin{aligned} \frac{dy(t)}{dt} &= A_i r a^{\frac{1}{r_0 + y(t)}}, \quad t \in (t_0, t_1] \\ y(t_0) &= 0 \end{aligned} \quad (8)$$

which allows only for a numerical solution.

For the times of anodization, longer than 1 ks we calculated the values of the electronic current density as the difference between the measured values of the total current density and the calculated values of the ionic current density, assuming once more that.

In analogy to the treatment above

$$\begin{aligned} y(t) &= \int_{t_1}^t j_i(\tau) d\tau, \quad t \in [t_1, t_2], \\ r_1 &= \frac{D(t_1)zF\rho\sigma}{\mu} \end{aligned}$$

the following initial problem for ordinary differential equations is obtained:

$$\begin{aligned} \frac{dy(t)}{dt} &= A_i r a^{\frac{1}{r_1 + y(t)}}, \quad t \in (t_1, t_2] \\ y(t_1) &= 0 \end{aligned} \quad (9)$$

Using the condition of continuity of the first derivative of the solutions of (8) and (9), for $A_i = 1.33 \times 10^6 \text{ A cm}^{-2}$, which agrees by order of magnitude with the value estimated above.

RESULTS AND DISCUSSION

Fig. 1 depicts the measured and calculated total current densities during tensiostatic anodization of Bi in glycol-borate electrolyte (GBE) at $U_v = 36 \text{ V}$, $T = 293 \text{ K}$. The very good agreement between the two sets of values demonstrates the validity of the proposed calculation procedure.

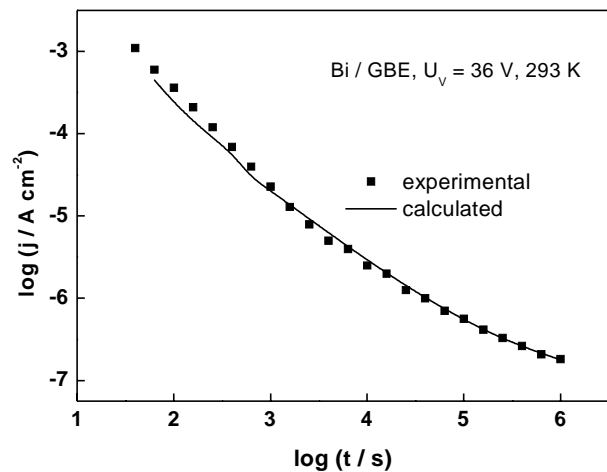


Fig. 1. Experimental (points) and calculated (solid lines) total current densities during the tensiostatic anodization of Bi in GBE at $U_v = 36 \text{ V}$, $T = 293 \text{ K}$.

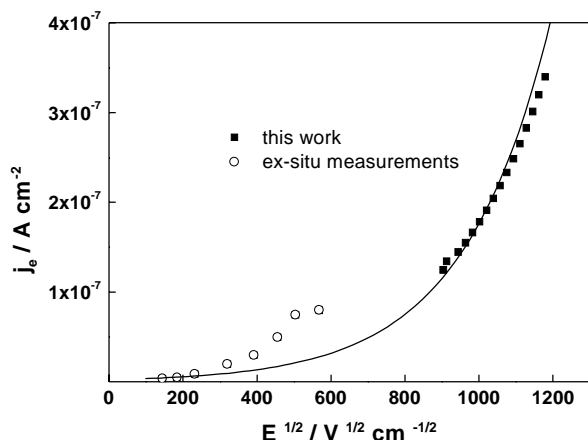


Fig. 2. Dependence of the electronic current on field strength according to equation (2): full symbols – this work, open symbols – ex-situ measurements [9], line – NLLS fit.

Fig. 2 compares the dependence of the electronic current density on the field strength, as obtained from the present numerical treatment of the tensiostatic anodization data, with previous measurements for galvanostatically formed films at low field strength [9]. It is evident that despite the quite different conditions of the measurements, the two sets of data can be interpreted to a first approximation by equation (2), shown as a solid line. The parameters of the electronic current, determined by the approximation of the data obtained in this work by using the non-linear least squares method, $\alpha_e = 4.68 \times 10^{-9} \text{ A cm}^{-2}$ and $\beta_e = 3.64 \times 10^{-3} \text{ V}^{-1/2} \text{ cm}^{1/2}$, agree within order of magnitude with the results obtained in [9].

CONCLUSIONS

In this work, a numerical procedure for estimation of the contribution of the electronic current to the

total current during tensiostatic anodization of Bi in GBE has been advanced. The validity of the procedure has been demonstrated by comparing the numerical calculations with a set of experimental data. The parameters characterising the field dependence of the electronic current, calculated from these experiments, have been found to be in fair agreement with previous independent estimates stemming from measurements of galvanostatically obtained films at low field strengths. As a next step in this investigation, the effect of film formation parameters, as well as electrolyte nature, on the parameters characterising the field dependence of the electronic current will be assessed.

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