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SHORT COMMUNICATION

On the duplex layer nature of anodic Al_2O_3 films

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1. Introduction

Since the discovery of the double layer structure of anodic oxide films, several methods have been envisaged to observe the duplex nature of these films. Radiotracer techniques [1], internal reflectance spectroscopy [2], capacitance measurements [3], ellipsometry [4], etc., have been commonly used to study the composition and the structure of each layer. This short communication reports a method to detect the presence of the different layers in the Al_2O_3 anodic films based on the reanodization curves after chemical dissolution. It is known that the reanodization of a previously formed oxide constitutes an excellent method of measuring the oxide thickness [5]. The results obtained by this method are also compared to those obtained by capacitance measurements which are currently used to characterize the structural properties of anodic films.

2. Experimental details

Aluminium foil samples ($10 \times 10\,mm^2$) were anodized at room temperature in a $NH_4H_2PO_4$–$(NH_4)_2HPO_4$ solution in deionized water by standard methods at a constant current density of $1.0\,mA\,cm^{-2}$. The concentration of $NH_4H_2PO_4$ in the anodizing solution was always half of the concentration of $(NH_4)_2HPO_4$ and varied between 0.0033 and 0.66 M. The samples were previously degreased and electropolished in a 25% perchloric acid solution in ethanol at 4° C by applying 20 V d.c. for 6 min.

After anodization at 120 V under the above conditions, the samples were subjected to successive 10-min chemical dissolution steps. The dissolution process was carried out in a 2 M H_2SO_4 solution in water at 60° C. Subsequently, the samples were washed in deionized water and dried in air and then reanodized in the previous anodizing solution at a constant current density of $0.1\,mA\,cm^{-2}$. Before the reanodization, capacitance measurements were made in the anodizing electrolyte at 100 Hz by means of a HP LCR meter, model 4274A.

3. Results and discussion

Fig. 1 shows the reanodization curves of a sample subjected to the above 10-min dissolution steps. The reanodization voltage increases almost linearly with time, reaching a stationary value after few seconds. The rapid increase of the voltage and the slight overshoot observed at the beginning of the reanodization process indicates that the oxide covering the sample is compact and homogeneous. According to the work of Hunter and Fowle, the final reanodization voltage is proportional to the thickness of the remaining oxide [5].

The variation of the final reanodization voltage as a function of the dissolution time, for samples anodized in electrolytes with different solute concentrations, is represented in Fig. 2.

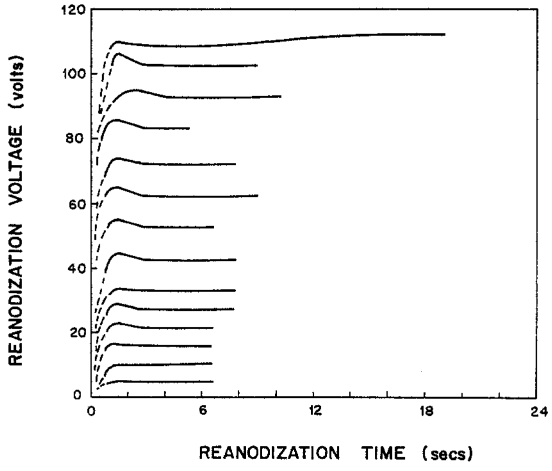

Fig. 1. Reanodization voltage–time curves for a sample dissolved in successive time intervals of 10 min.

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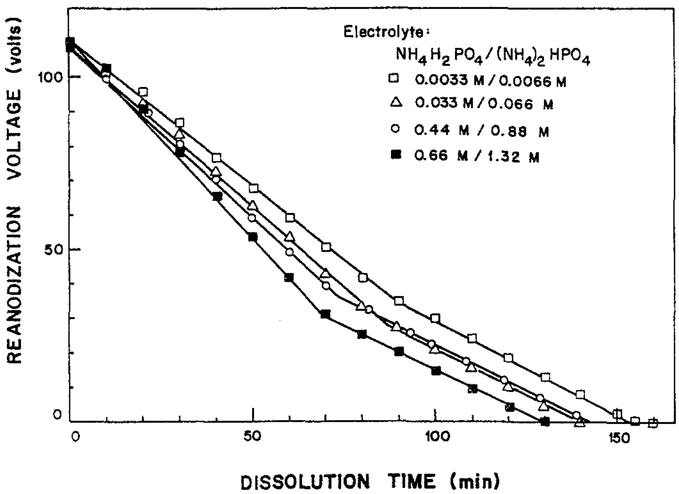

Fig. 2. Final reanodization voltage for the $NH_4H_2PO_4$–$(NH_4)_2HPO_4$ electrolyte with different concentrations as a function of the dissolution time.

Taking the reanodization voltage as a measure of the oxide thickness, the curves of Fig. 2 indicate an increase of the dissolution rate in the outer layers of the film as the anodizing electrolyte concentration increases. This effect has been generally attributed to the incorporation of electrolyte species into the outer layer of the oxide during the anodization process [1–4]. At certain definite points, the curves of Fig. 2 change the slope to a lower constant value which corresponds to the purer inner layer of the Al_2O_3 films. For all samples the change in the slope occurs at practically the same voltage, which suggests that the thickness of the inner layer is independent of the concentration of the electrolyte. For the samples studied in this work, this thickness amounts to about one-third of the total thickness. Inverse capacitance measurements also display a similar behaviour as observed in Fig. 3.

If v_1 and v_2 represent the rate of chemical dissolution of the inner and outer layers, respectively, the equations governing the variation of the reanodization voltage in each part of the curves of Fig. 2 are given by

$$V = V_0 - E_2 v_2 t \quad \text{(outer layer)}$$

and

$$V = V_1 - E_1 v_1 t \quad \text{(inner layer)}$$

where V_0 is the initial reanodization voltage and

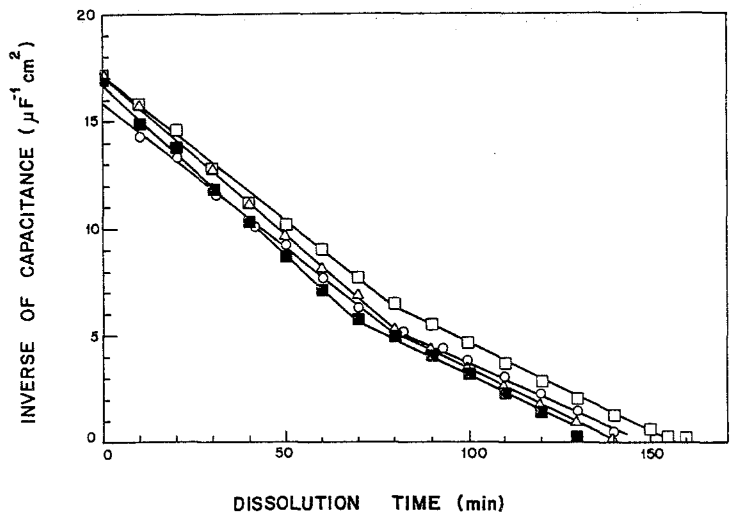

Fig. 3. Inverse of the parallel capacitance as a function of the dissolution time for the same electrolytes as Fig. 2 (electrolyte concentrations labelled as in Fig. 2).

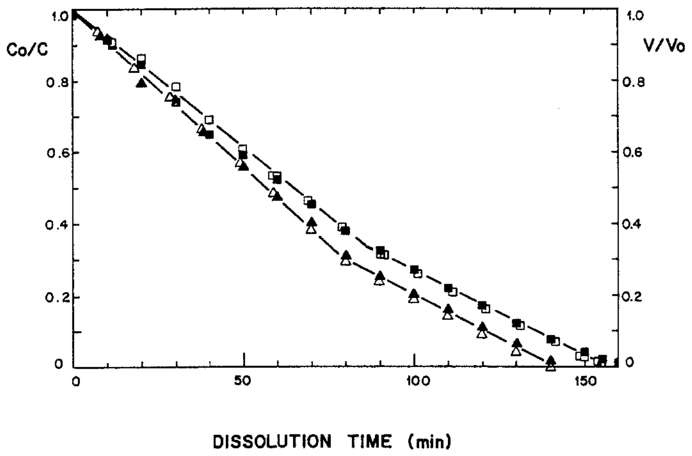

Fig. 4. Variation of the relative values of V/V_0 (open symbols) and C_0/C (solid symbols) as a function of the dissolution time for a sample anodized in the 0.0033 M/0.0066 M (□) and 0.33 M/0.66 M(Δ) $NH_4H_2PO_4$-$(NH_4)_2HPO_4$ electrolytes.

V_1 is the value of the voltage at which the curves of Fig. 2 change slope, the time t in the second equation being measured from this point. E_1 and E_2 in these equations represent the electric field in each layer during the reanodization process. The good linearity of both parts of the curves of Fig. 2 indicates that both E_1 and E_2 maintain the same value after the successive removal of the layers. Thus, the values of the electric field in each layer of the oxide seem to be determined by the metal–oxide and oxide–electrolyte interfaces, instead of the bulk of the oxide [4].

It is also worth noting that the relative variation of both the reanodization voltage, V/V_0, and the inverse of the capacitance, C_0/C (where C_0 is initial capacitance), are practically coincident, as can be observed in Fig. 4 for the case of the diluted electrolytes. As can be easily demonstrated by a simple calculation, this fact implies that the product of the permittivity of each layer and the electric field in the layer is constant, i.e.

$$\varepsilon_1 E_1 = \varepsilon_2 E_2 = \bar{\varepsilon}\bar{E}$$

where $\bar{\varepsilon}$ is the mean permittivity of the Al_2O_3 anodic films and $\bar{E}$ is the mean electric field during reanodization.

The above equation has also been observed to hold in tantalum oxide in experiments at different current densities [4]. In fact, this equation gives a direct explanation for the constancy of the product $C_0 V_0$, as has been shown for different anodic oxides regardless of the anodizing conditions [6].

As a conclusion, this paper proves the feasibility of the reanodization technique as a method for the study of the duplex nature of the anodic films. For the electrolyte investigated in this work, the thickness of the inner layer is practically independent of the concentration of the electrolyte. In addition, the reanodization electric field in each layer seems to be controlled by the corresponding electrolyte–oxide and oxide–metal interfaces. This technique, combined with the absolute measurement of the oxide thickness which is currently being carried out, can be used to determine the absolute values of both the reanodization electric fields, E_1 and E_2, and the permittivities, ε_1 and ε_2, of the layers in the anodic oxides.

References

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