

THE ANODIC OXIDATION OF ALUMINIUM

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Abstract

This note deals with the determination of (a) the geometrical structure of porous Al_2O_3 layers, obtained by anodic oxidation of aluminium in oxalic acid, (b) the growth mechanism of these layers and (c) the transport number f_+ of the Al^{3+} ions during anodic oxidation.

An extensive study has been made of the geometrical structure and growth mechanism of porous Al_2O_3 layers obtained by anodic oxidation in oxalic acid ("anodizing"). For this purpose a number of relatively simple experimental techniques were used; a detailed report of the results in the form of three papers will be published in the near future. Also, a method was developed to determine the transport number f_+ of the Al^{3+} ions during subsequent anodic oxidation in, for example, boric acid ("forming"). The technique of anodizing and subsequent forming has been used earlier by Dekker and Van Geel ¹⁾. They observed that during the forming of the porous layer the pores are filled *); this implies that at least part of the ionic current during forming is carried by the Al^{3+} ions. However, the conclusion of Dekker and Van Geel that the porosity equals the ratio of the two slopes observed in the voltage-time diagram of the forming process with constant current density is incorrect; in fact, they assume implicitly that the ionic current is carried exclusively by the Al^{3+} ions, whereas our results show that the major part of the current is carried by O^{2-} ions.

In order to determine the porosity α_a of the anodized layers we measured their weight and determined their thickness by means of the Tolansky method. Furthermore a "duo circuit" was used in which anodized and a virgin plate with the same surface area were formed in parallel with a constant total current. The ratio β of the two branch currents through the anodized and virgin plate is related to α_a and f_+ according to

$$f_+ = \frac{\alpha_a}{1 - \alpha_a} \frac{1 - \beta}{\beta}. \quad (1)$$

The experiments show that β is equal to the ratio of the two slopes in the voltage-time curve observed during the forming of a single anodized layer at constant current density. From the experimental values obtained for α_a and β we found $f_+ = 0.24 \pm 0.02$. It was found that the field strength used during the

*) During the preparation of our paper we noted that the pore-filling process has been confirmed by C. G. Dunn ²⁾.

forming and the temperature of the electrolyte had no measurable influence on the magnitude of f_+ ; a dependence on the forming electrolyte was observed, however. Once the value of f_+ for a given electrolyte is known, expression (1) permits a convenient and rapid determination of the porosity α_a by measuring β .

If the anodizing process is carried out in two stages with different current densities, a superposition of two porous layers is obtained. Using the technique of Dekker and Van Geel it was found that the oxide last formed resides at the metal side. It is also possible to choose the anodizing conditions such that during the second stage the wall between the pores become vanishingly thin; in that case the porous layer generated during the first stage separates itself from the metal base.

From an experiment in which the porous layer was dissolved stepwise in a mixture of chromic and phosphoric acid, and weighed after each step, it was possible to determine the number of pores per unit area as well as the mean pore diameter. The results showed that the pore diameter and the size of the cell associated with a pore³⁾ depend linearly on the anodizing voltage. In contrast to this, Keller, Hunter and Robinson³⁾ concluded that the pore diameter is independent of the anodizing voltage. However, their opinion that the thickness of the cell wall is equal to the thickness of the barrier layer is reasonably consistent with our results.

When the above-mentioned information concerning the gross geometrical features of the porous layer is combined with an analysis of the dV/dt versus time diagram during the anodizing process, it appears possible to draw some important conclusions about the growth mechanism of the porous layer (V = anodizing voltage). One of these conclusions is that the transport number for the aluminium ions during anodizing is $f_+ \approx 0.3$.

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