SHORT COMMUNICATION

Electron-beam-induced crystallization of anodic barrier films on aluminium: influence of incorporated anions

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1. Introduction

Observations, using the transmission electron microscope, of electron-beam-induced crystallization of ultramicrotomed sections of anodic barrier films formed on aluminium in ammonium pentaborate solutions have shown that the films consist of two well-defined layers having markedly different susceptibilities to the induced crystallization from noncrystalline to γ-Al_2O_3 [1]. Next to the metal there is an inner layer where crystallization proceeds more freely than an outer layer originally adjacent to the electrolyte. The proportion of the outer layer of lower susceptibility to the induced crystallization to the total film was estimated to be 0.41, which agrees quite well with the cationic transport numbers reported by Takahashi and Nagayama [2], Brown and Mackintosh [3], and recently by Shimizu *et al.* [4], for films formed under similar conditions. It is, then, apparent that the outer layer of lower susceptibility to the induced crystallization represents the film material grown at the oxide–electrolyte interface via outward migration of aluminium and the inner layer represents the film material grown at the metal–oxide interface via inward migration of oxygen.

In view of the observations [5–8] that the outer layer grown at the oxide–electrolyte interface via outward migration of aluminium contains an appreciable amount of anion species from the electrolyte, and also of the observation [9, 10] that the incorporated anion species, phosphate in particular, are known to have tendencies to lower the ionic conductivity of the film, the lower susceptibility of the outer layer to the induced crystallization was ascribed tentatively to the presence of borate species [1]. In this communication further confirmatory evidence is presented which was obtained by the observation of the induced crystallization of the films consisting of multilayers of different levels of anion incorporation. Such films were prepared by sequential anodizing of aluminium in ammonium pentaborate solutions of different concentrations at the same current density and temperature.

2. Experimental details

Superpure aluminium foils with dimensions of 50 x 5 x 0.1 mm were electropolished in a perchloric acid–ethanol bath, rinsed first in absolute ethanol and thoroughly in distilled water, and dried in a cold air stream. The electropolished specimens were first anodized at 298 K in 0.3 M ammonium pentaborate solution up to 200 V with a constant current density of $50\,A\,m^{-2}$, and then in 0.03 M ammonium pentaborate solution up to 400 V with the same current density and temperature.

Ultramicrotomed sections of the aluminium substrate and the anodic film, about 25 nm thick, were prepared in the now usual manner using a Du Pont Sorvall MT 5000 ultramicrotome [11] and were examined and crystallized in a Philips 301 transmission electron microscope operated at 100 kV. As reported earlier [1], crystallization was induced even under the normal operation conditions of the microscope. It was not necessary to remove the condenser aperture to increase the electron beam flux; this was reported by Aladjem *et al.* [12] to be essential to induce the

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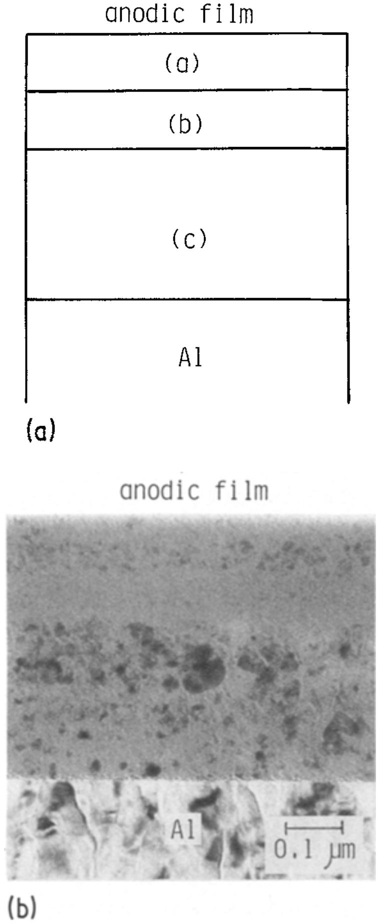

Fig. 1 (a) Supposed structure of a barrier film formed by two-step anodizing. (b) Transmission electron micrograph of the ultramicrotomed section of the film formed by sequential anodizing of aluminium under the conditions shown in the text. The micrograph was taken after the film section had been exposed to the electron beam for about 13 min in the electron microscope.

crystallization of stripped films of comparable thickness.

3. Results and discussion

The films formed by two step anodizing under the conditions described above are supposed to consist of three distinct layers of different levels of borate incorporation as schematically shown in Fig. 1a. Here the cationic transport number was assumed to be 0.4. The innermost layer, labelled (c), formed in each anodization via inward migration of oxygen at the metal–oxide interface is composed of relatively pure oxide, and the two outer layers contain borate species in different concentrations. Since greater incorporation is expected at higher electrolyte concentration, the amount of incorporated borate species is expected to be greater in the middle layer (b) than in the outermost layer (a).

The overall process of the induced crystallization can be described qualitatively as follows. Upon initial observation in the transmission electron microscope, the film appears relatively featureless and uniform in thickness. No layered regions, indicative of the innermost anion-free nor outer layers of different levels of anion incorporation, are readily apparent. The film thickness is estimated to be about 480 nm, which represents a nanometer-to-volt ratio of about 1.2. On prolonged exposure to the electron beam in the transmission electron microscope a few very small crystals, which are evident as regions that are diffracting at that particular orientation to the electron beam, first appear in the innermost layer (c) after an induction period which can be shortened simply by increasing the electron flux density to the film. After about 8 min exposure, these crystals grow and, at the same time, more crystals appear rapidly in the innermost layer (c). After about 10 min exposure, the growing crystals impinge upon one another and the innermost layer (c) becomes entirely crystalline with the development of a relatively sharp demarcation line between the crystallized innermost layer (c) and the middle layer (b) which, at this moment, is still noncrystalline and featureless. On further exposure to the electron beam small crystals start to appear in the outermost layer (a) and the number of crystals increases rapidly. Fig. 1b shows the transmission electron micrograph of the ultramicrotomed section of the film after about 13 min exposure to the electron beam, where the number of crystals in the outermost layer (a) is large enough to reveal the difference in the susceptibility to the induced crystallization between the outermost layer (a) and the middle layer (b). It is interesting to note that at this point only a few crystals are apparent in the middle layer (b) where borate incorporation is supposed to be the greatest. Eventually after about 18 min exposure, numerous small crystals appear even in the middle layer (b) and the entire film becomes crystalline.

The overall process of the crystallization, described above, follows the pattern predicted exactly from the supposed structure of the film shown schematically in Fig. 1a. The layer of likely greater borate incorporation crystallizes less rapidly.

Incorporation of borate species into the films formed on aluminium in ammonium pentaborate solutions has been reported by several workers [13–15]. Using a technique based on sputter etching combined with detecting photons from sputter excited atoms, Shehata *et al.* [13] have found that the films contain borate species only in an outer layer of the film adjacent to the electrolyte, with no borate species detected from an inner layer next to the metal. The ratio of the outer layer doped with borate species to the total film thickness has been reported to be 0.45 ± 0.1. Essentially similar results have been obtained by Thompson using SIMS [14]. More recently, Skeldon *et al.* [15] have investigated the boron distribution profiles using $^{11}B(p, \alpha)^{8}Be$ nuclear reaction combined with chemical sectioning of the films in sulphuric acid solution. In agreement with previous results borate species are found to be incorporated only in the outer layer of the film whose ratio to the total film thickness is 0.44 ± 0.07.

Unfortunately, the dependence of the amount of incorporated borate species on the electrolyte concentration has yet to be determined. However, for films formed in neutral phosphate solutions, the incorporation has been shown by Randall *et al.* [5] to be greater at higher electrolyte concentration. Although the mechanism of anion incorporation into barrier anodic films is still largely uncertain, there is no reason to suppose why the mechanism of borate incorporation should be different from that of phosphate incorporation. Accordingly the present result may be taken as strong evidence supporting the view that the lower susceptibility of the outer layer to the induced crystallization is due to the presence of the incorporated borate species.

The chemical state of the incorporated borate species and their influence on the atomic migration during the induced crystallization and also during the film formation are now under investigation and the results will be published in due course.

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