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Effect of Electrolyte Species on Crystallinity and Dielectric Properties of Anodic Oxide Films Formed on Aluminum

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The effect of electrolyte species as well as electrolytes combination during multistep anodization on crystallinity and dielectric properties of anodic barrier films formed on aluminum after hydration treatment was investigated. The *CV* value, i.e., capacitance *C* multiplied by withstand voltage *V* of the film, which is proportional to permittivity, increased with increasing crystallinity of anodic film in the following order: salicylate < adipate < succinate < tartrate < phosphate < citrate < borate. Among them, the films formed in phosphate and borate showed favorable dielectric properties such as relatively high *CV* value and low leakage current.

Keywords: *Aluminum, Anodic oxide film, Dielectric property, Crystallinity.*

1. Introduction

Anodic films formed on aluminum and its alloys are widely used in decorative finishes, adhesive bonding, and electronic components, and in protection against corrosion and wear. Among them, crystalline anodic barrier films, which are formed on aluminum substrate by multistep anodization including hydration process, first anodization, heat treatment and second anodization, are industrially used as a dielectric film of aluminum electrolytic capacitors for high voltage [1-4]. Because of the increasing demands for their utilization as high voltage power supplies and inverter applications, improvement of dielectric property of anodic oxide film should be an urgent requirement.

With the above background, we have studied the dielectric properties of crystalline anodic barrier films formed on aluminum by multistep anodizing with focusing on the effects of each processing stage and electrolytes species. Recently, we reported that the dielectric properties such as a capacitance, a withstand voltage and a leakage current of crystalline anodic films were strongly affected by the anion incorporation behavior, especially the incorporation content of boron in the film [6]. The *CV* value of the film formed in phosphate and organic salts at first anodization was higher than that of the film formed in borate due to low incorporation content of boron in the films. The *CV* values, which is a product of capacitance (*C*) and withstand voltage (*V*) measured by electrochemical method, are proportional to the permittivity of film. In the case of the multistep anodization using a mixed solution of boric acid and sodium borate, and ammonium citrate as electrolytes, the *CV* value increased with decreasing boron content. These results suggest that the *CV* value is highly dependent on boron content [5, 6]. In this study, therefore, we investigated the effect of the crystallinity of anodic alumina films on dielectric properties by focusing on different electrolyte species including organic salts as well as their combination during multistep anodization.

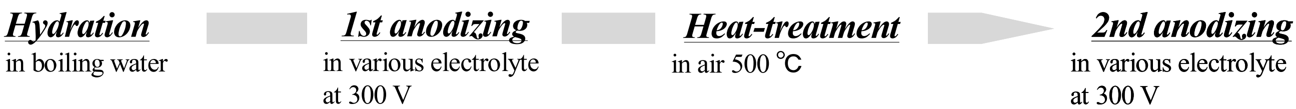

Fig. 1 Schematic of multistep anodization process.

2. Experimental

High-purity (99.99 %) aluminum sheets were cleaned by immersion in 5 wt % NaOH for 20 s, followed by a vigorous rinse in deionized water, 1min immersion in 30 vol % HNO_3 and a thorough rinse in a deionized water. After pretreatment, multistep anodization was carried out as illustrated in Fig. 1. Aluminum sheets were first immersed in a boiling water to form a hydrated oxide. After hydration treatment of aluminum, the first anodization was conducted at a constant current density of 0.5 mA cm^{-2} up to 300 V in a mixture of 1.6 mol dm^{-3} boric acid and 0.008 mol dm^{-3} sodium borate solution (B-borax) or 0.01 mol dm^{-3} various ammonium salt solution (i.e. borate, adipate, citrate, tartrate, succinate, salicylate, or phosphate) at 85 ^{o}C. Subsequent voltage holding was carried out for 45 min. After the first anodization, the specimens were heat-treated in air at 500 ^{o}C for 5 min. Finally, the second anodization was conducted in the same electrolyte to fill in the voids, which was induced by crystallization during heat treatment.

The dielectric properties of crystalline anodic oxide films were evaluated by measuring the capacitance, the leakage current and the withstand voltage. The capacitance of the anodic oxide film was measured at 120 Hz in 150 g dm^{-3} ammonium adipate at 20 ^{o}C using a LCR meter. The withstand voltage of each film was measured by electrochemical technique, i.e., a voltage jump at re-anodization of the anodized specimen. For this evaluation, the voltage-time curves were measured during re-anodization at 0.1 mA cm^{-2} in a mixed solution of 1.6 mol dm^{-3} boric acid and 0.008 mol dm^{-3} sodium borate at 85 ^{o}C, where the voltage jump is suggested to be proportional to the film thickness. The leakage current was measured by applying 225 V, i.e., 75 % of the formation voltage in a mixed solution of 0.5 mol dm^{-3} boric acid and 0.05 mol dm^{-3} sodium borate at 20 ^{o}C. The crystallinity of films was evaluated by X-ray diffraction analysis (XRD).

3. Results and Discussion

Figure 2 shows a cross sectional SEM image of anodic oxide film formed by multistep anodization in 0.01 mol dm^{-3} ammonium borate. The film was composed of two layers having different film structure. Namely, the outer layer was composed of platelet-like hydrated oxide and the inner layer was composed of granular crystalline oxide, respectively. Similar film structure was also found in all other films despite the difference of electrolyte species.

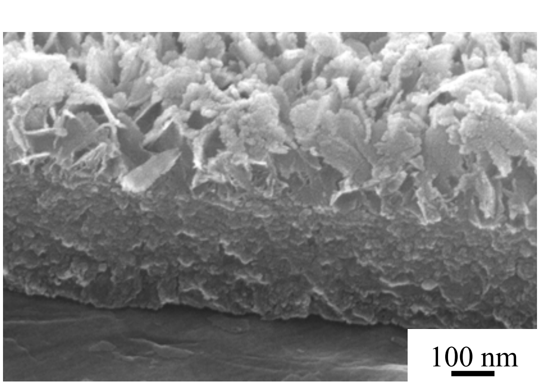

Fig. 2 Cross sectional SEM image of the film formed in ammonium borate.

The difference in *CV* value between the films formed by multistep anodization in different electrolyte is shown in Fig. 3. Although the capacitance varied with electrolyte species, the oxide films formed in borate and citrate showed relatively high values. On the other hand, the withstand voltages of the films formed in inorganic electrolytes were higher than that of films formed in organic electrolytes. As a result, the *CV* value of the film formed by multistep anodization increased in the following order: salicylate < adipate < b-borax < succinate < tartrate < phosphate < citrate < borate.

For the evaluation of the crystallinity of anodic oxide films formed by multistep anodization, the structure of the specimens was analyzed by XRD, as shown in Fig. 4. In XRD patterns, two peaks at 46° and 67° were ascribed to γ-Al_2O_3. Intensity of both peaks of γ-Al_2O_3, that is, the crystallinity of alumina was affected by electrolyte species used for the anodization. Among them, the crystallinity of the film formed in borate was higher than that of the films formed in other organic electrolytes with the exception of citrate. The crystallinity of the films increased in the following order: salicylate < adipate < succinate < tartrate < phosphate < citrate < borate < b-borax. This order of the crystallinity is nearly the same to that of the *CV* value shown in Fig. 3. From these results, it is deduced that the changes in the dielectric properties of crystalline anodic alumina films with the change in electrolyte species and electrolytes combination during multistep anodization are primarily correlated with the difference in the crystallinity of each film.

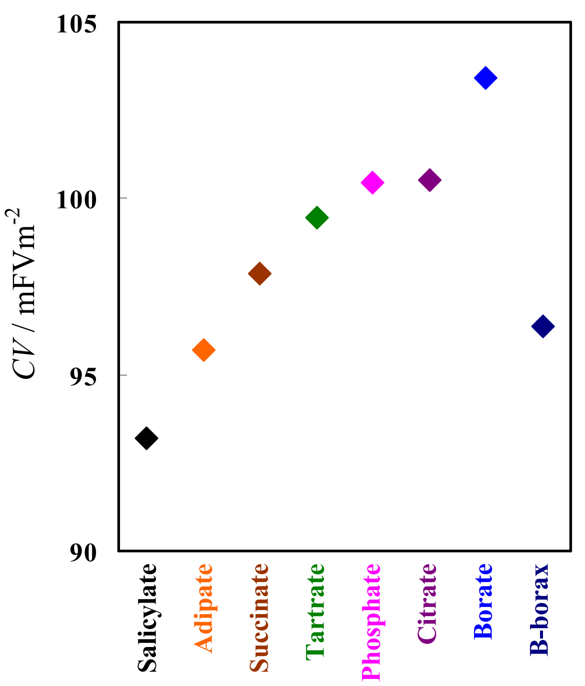

Fig. 3 *CV* value (product of capacitance and withstand voltage) of the anodic films formed by multistep anodization for various electrolytes.

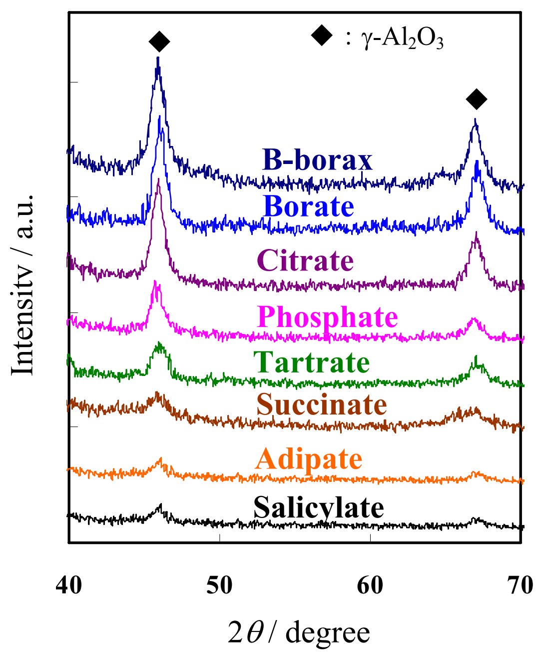

Fig. 4 X-ray diffraction spectra of crystalline anodic films formed in different electrolyte by multistep anodization.

Figure 5 shows the leakage current of crystalline films formed by multistep anodization. The leakage current of the films formed in salicylate, phosphate, and borate was lower than that of the films formed in other organic electrolytes and inorganic electrolytes. The leakage current increased in the following order: salicylate < phosphate < borate < adipate, tartrate, citrate, succinate < b-borax. The dielectric properties of the crystalline films were primarily caused by the different incorporation behavior of electrolyte species. These results indicate that the films formed in phosphate and borate were suitable dielectric films for aluminum electrolytic capacitors owing to relatively high *CV* value and low leakage current.

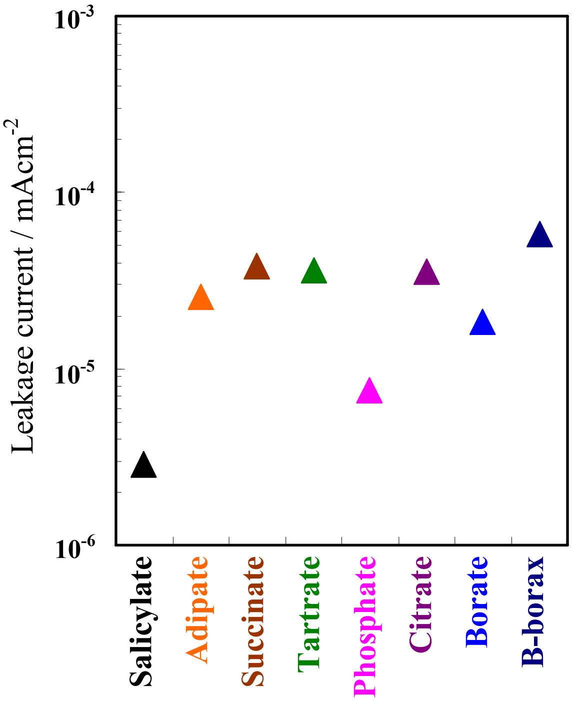

Fig. 5 Leakage current determined 15 min after applying 225 V on anodized specimens. Anodic films were formed by multi-step anodization in various electrolytes.

4. Conclusions

The effect of electrolyte species as well as electrolytes combination during multistep anodization on the crystallinity and dielectric properties of anodic films formed on aluminum was investigated. The dielectric properties of the film formed by multistep anodization were strongly affected by the electrolyte species used. The *CV* value increased with increasing the crystallinity of anodic film. In this study, the films formed in phosphate and borate showed good dielectric properties such as relatively high *CV* value and low leakage current. From these results, it is concluded that the changes in the dielectric properties of the crystalline anodic films with the changes in electrolyte species including organic salts as well as their combination during multistep anodization are primarily caused by the different incorporation behavior of electrolyte species.

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