Dielectric Properties of Anodic Films on Superpurity Aluminium from a Glycol-Borate Non-aqueous Electrolyte

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Dielectric properties, viz, capacitance, loss factor, leakage current of anodic films on super-purity aluminium from non-aqueous glycol-borate electrolyte have been measured and compared with those reported earlier. A study of drift of capacity and dissipation factor with time and temperature has been observed. The current efficiency for these films has been found to be 100%. Effect of various halide ions on the dielectric growth behaviour of these films has been studied. These ions inhibit the growth in the following decreasing order: chloride > bromide > iodide > fluorid.

The chemical composition, formation technique, thickness and some other parameters of anodic oxide films, and the nature of electrolyte used are some of the major factors which affect dielectric strength, loss factor, capacity, leakage current, long term stability under voltage and temperature stresses and the electrical behaviour of thin film capacitors. The present paper is an extension of our earlier study on the dielectric behaviour of anodic films on superpurity aluminium formed from aqueous electrolytes. A non-aqueous electrolyte, viz. ethylene glycol-ammonium hydrogen borate, has been employed to have a comparative study of growth characteristics and the dielectric behaviour of the oxide films obtained in both aqueous and non-aqueous electrolytes.

Stresses in oxide films can cause rupture which results in a reduced efficiency in anodic oxidation. The presence of small amounts of fluoride ions in the ammonium borate anodizing electrolyte has been observed to have a profound effect upon the nature and magnitude of internal stresses developed during the growth of anodic zirconium oxide films. Presently we have studied the effect of halide ions incorporation on the dielectric properties of such electrolytic capacitors using superpurity aluminium. In order to ensure that the applied current has been used completely in the growth of oxide dielectric, current efficiency measurements, employing weight gain method have been presented.

Materials and Methods

The method of surface preparation of aluminium specimens, experimental set-up and the procedure for anodic polarization have been reported elsewhere. Heating effects, if any, produced at the anode were avoided by constant stirring which also helped in maintaining a constant temperature. The dielectric measurements were made using an electrolytic capacitor bridge (BPL Pvt Ltd, India).

The electrolyte consisted of 30% by weight ammonium hydrogen borate solution in ethylene glycol. The electrolyte concentration chosen was nearly the stoichiometric proportion for the reaction (1) in which \( H_2O \) molecules play an important role during anodization. Therefore, negligible amount of ethylene glycol exists in solution. Even otherwise, vapour pressure of pure ethylene glycol at 0.14 torr and 25° is too low to affect the results in any way. Hence, the most probable reaction taking place at the anode could be represented by Eq. (2).

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\begin{align*}
\text{Na}^+ + \text{H}^+ + \text{HO-B} + \text{BOH} & \rightarrow \text{CH}_2\text{OH} \\
\text{H}_2\text{C} & \begin{array}{c} \text{O} \\
\text{C} & \text{O} \\
\text{O} & \text{C} \\
\text{H} & \text{OH} \\
\text{H} & \text{CH}_2 \\
\text{OH} & \end{array} \\
\text{H}_2\text{O} & + \text{B} \\
\text{CH}_2\text{OH} & \\
\end{align*}
\]

\[
\text{Eq. (1)}
\]

\[
\begin{align*}
\text{2Al}^+ + \text{3H}_2\text{O} & \text{(in glycol-borate electrolyte)} \\
& \rightarrow \text{Al}_2\text{O}_3 + \text{3H}_2 \uparrow \\
& \text{Eq. (2)}
\end{align*}
\]

All measurements were made at current density 1-0 mA/cm² and 16-5°. Halide ions in the concentration range of 0-001-100-0 ppm were used to study their effect on the growth behaviour of anodic films. The estimation of current efficiency for oxide growth was done using weight gain method. The weight of oxygen uptake during oxide growth was measured using a microbalance. It was observed that the results of weight gain for each sample (at least ten) were reproducible within ±0.5%.
Results and Discussion

Anodic film formation characteristics in the present case differ significantly as compared to those in aqueous electrolytes\(^1\). A linear plot of voltage of formation vs charge passed was obtained in the case of glycol-borate system (Fig. 1) whereas in the case of aqueous electrolytes\(^2\) a quadratic variation of the voltage of formation with time of anodization was observed. The breakdown voltage was found to be a function of current density in contrast to a constant breakdown voltage 74.5 V observed for molten alkali nitrates\(^3\), and its magnitude was observed to be lower than that of aqueous electrolyte film (citric acid). When the anodic polarization was continued beyond the breakdown voltage, very slow oxide growth rate was observed after a sharp decline in voltage of formation. The growth rates of anodic films before and after breakdown differed significantly. A slower growth rate observed in the latter case implied that a major portion of the current was involved in corrosion reaction and only a small quantity of ionic current was utilized in barrier oxide layer growth. That the potential difference across the oxide film after dielectric breakdown did not approach zero suggested the presence of a passive layer at the base of the cracks supporting some of the field. The fact that broken down anodic film continued to grow in an electrolyte with characteristically higher breakdown voltage, known for other metals, has been confirmed for aluminium\(^4\), as well. The leakage current, being negligibly small in the beginning, vanished completely after 2V of film formation till the breakdown voltage occurred. This showed that the current was ionic in character with 100% current efficiency. A small leakage current in the beginning might be attributed to surface conditions of the specimen and the pre-history of the film.

Dielectric measurements were made at various current densities. Fig. 2 presents the plot of tan \(\delta\) vs charge passed at different current densities. In general, there was a decrease of tan \(\delta\) with increase in thickness. At the breakdown voltage, the loss factor increased to very high values as also the leakage current. Similar observations have been reported\(^9,10\) with tantalum, niobium and zirconium. Hoar et al.\(^11\) ascribed the decrease in tan \(\delta\) to the fissure depth distribution. Very much larger losses were observed for some very leaky films.

**Drift in capacity and tan \(\delta\) with time and temperature** — The effect of time on the magnitude of capacitance and tan \(\delta\) was studied for the films of given thickness formed at a given temperature. A negligible drift was observed for these parameters (Fig. 3). This suggests that there was no structural change or oxide dissolution on standing. In other words, the dielectric constant and the oxide film structure remained unchanged. The variation in temperature, keeping film thickness and time constant, brought about an increase in the value of capacity and a decrease in tan \(\delta\) with temperature (Fig. 4). The decrease in the tan \(\delta\) values with temperature suggests that the losses are chiefly due to a part of the film which has undergone a change. This confirms the experiments of Lilienfeld et al.\(^12\) with aluminium and could be due to (i) variation in stoichiometry; or (ii) amorphous-crystalline transition; or (iii) dissolution of the oxide film. The possibilities (i) and (ii) seem to be the most likely ones as tan \(\delta\) values for higher film thicknesses tend to zero.

**Effect of halide ions on oxide growth and dielectric properties of anodic films** — The rate of formation of anodic films in the glycol-borate electrolyte remained unaffected by the addition of various
halide ions—a phenomena earlier observed by Nigam and Kapoor and Archibald et al. However, formation characteristics and dielectric properties of the anodic film grown in presence of fluoride ions differed significantly from those grown in the presence of halide ions, other than fluoride ions. The values of capacitance, tan δ and leakage current were lower for films grown in the presence of fluoride ions than those grown not only in the presence of different halide ions but even in pure glycol-borate electrolyte. This observation accounts for higher insulating properties and dielectric strength for films grown in the presence of fluoride ions. This can be substantiated by the fact that the ionic radii of fluoride and oxide ions are approximately equal. Fluoride ions enter the outer layers of the oxide film and replace easily the oxide ions and help in oxide growth, contrary to the inhibiting effect of other halide ions.

In the presence of halide ions, the leakage current remained zero till the breakdown occurred. We have also obtained data for the leakage current at different formation voltages in the presence of 0.01 ppm halide ions and in the presence of different concentrations of iodide ions. For brevity the data are not included in this paper. With increase in the concentration of halide ions, tan δ values increased. This is probably due to the adsorption on the anodic film of halide ions which cause imperfections in the film. At very high concentration of halide ions, the film formation was totally inhibited and the metal surface was observed to have pits. The addition of these aggressive halide ions to a metal/electrolyte system, probably, caused local distortion on the passive metal oxide layers and an ultimate dielectric breakdown. Pit formation may be attributed to the metal dissolution at the active sites of metal surface. The local activation of the passive layers by halide ions has been suggested to be due to (i) penetration of halide ions through pores in the oxide; (ii) formation of thin film by adsorption and absorption of halide ions; (iii) the
replacement of some oxide ions by halide ions in the film (same radii); and (iv) peptization of the thin oxide film by strong negative charge. The addition of these ions to the electrolyte considerably enhanced the imperfections in the oxide film. The imperfections, i.e. pores, fissures or microfissures, or cracks generally increased with increase of ionic radius and concentration of halide ions in the electrolyte. These imperfections in the oxide film caused stress and there was a localized corrosion in areas which got disrupted due to these stresses.

Estimation of current efficiency in glycol-borate electrolyte — The estimation of current efficiency during oxide growth on superpurity aluminium in glycol-borate electrolyte was done by a weight gain method. The samples used in this investigation were of 40.0 cm² area and the polarization was carried at current density 1.0 mA/cm². The estimated values of current efficiency (Table 1) at all temperatures (0°-60°) of the anodic growth, is found to be unity (or 100%). This suggests that the oxide growth in such electrolytes is purely associated with ionic current. In other words, there is no oxygen evolution during oxide growth. This appears to be a significant finding as far as the presently studied dielectric films are concerned. The current efficiency, \( \eta > 100\% \) has been reported by Cheseldine\(^7\) who ascribed this to incorporation of electrolyte in oxide films. Whereas, in the present case slight variation of \( \eta \) from unity may be due to errors in weighing and pre-history of the film.

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References