Anodic Oxide Films & Related Properties on Superpurity Aluminium

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The differences in the formation characteristics of anodic oxide films formed on super-purity aluminium and Hindalco aluminium samples used earlier [*Indian J. Chem.*, 9 (1971), 578] are reported. The properties of anodic oxide films on superpurity aluminium, such as, dielectric losses, leakage current, capacity drift with time and temperature, and effect of chloride ion concentration on the growth behaviour of anodic oxide films are presented. A preliminary report of X-ray diffraction patterns of such films has also been presented.

IN our earlier communication[1], the conditions, particularly concentration limits and current density limits, have been standardized for the formation of films on aluminium in aqueous electrolytes. Aluminium specimens used earlier, besides containing 99·5% Al, had $Si+Fe+Cu = 0·45\%$ and $Ti+V = 0·008\%$. The senior author could procure superpurity aluminium due to the courtesy of Prof. T. P. Hoar (Cambridge, England) and on his suggestion, the characteristics of formation of anodic oxide films in aqueous electroytes were reinvestigated with this superpurity aluminium and the results are reported in this paper. Such investigations were undertaken also because it has been reported[2,3] that impurities in a metal considerably affect the leakage current of electrolytic capacitors and the properties of the oxide film. The effect of chloride ions on the growth of the film and drift of capacity with time and temperature of such electrolytic capacitors have been reported. A preliminary report of X-rays for such films has also been presented.

Materials and Methods

Aluminium samples (2 cm² area) with a short tag were cut from superpurity aluminium using a die. The method of preparing surfaces of the samples, experimental set-up and the procedure for anodization was the same as reported earlier[1,4]. The major difference here was that a Honeywell variable chart speed recorder was employed for recording the voltage of formation during the growth of films. An electrolytic capacitor bridge (British Physical Laboratories Pvt Ltd) was used for direct measurements of the leakage current, capacity and tan δ for the films. The Honeywell recorder with very fast and variable chart speed was found very suitable for the formation of films at high current densities.

The aqueous electrolytes used for the formation of films were tartaric, citric, oxalic and phosphoric acids. The effect of chloride ions on the formation of anodic oxide films has been studied in tartaric acid only. All measurements were carried out at 20°.

In order to study the capacity drift of the film with time and temperature, two different experi-

ments were performed. Anodic oxide films of various thicknesses were formed on aluminium at c.d. 2 mamp/cm² at 20° in 0·1N tartaric acid electrolyte. In the first experiment, dissipation factor and leakage current were measured in aqueous electrolytes and the specimens, then, were placed in molten salt electrolyte ($LiNO_3+KNO_3+NaNO_3$) at 220°. In the second experiment, the drift in capacity and tan δ were measured when the samples were placed in aqueous and molten salt electrolytes respectively.

Results and Discussion

(a) *Formation characteristics of anodic oxide films and related behaviour* — The characteristics in respect of concentration limits and current density limits of formation of films on superpurity aluminium were found identical to those reported[1] with Hindalco aluminium. The breakdown voltage for the films was found different for superpurity aluminium — higher, under identical conditions, than that of Hindalco aluminium.

The plot of reciprocal capacitance of the film against charge passed is found linear in each electrolyte used (Fig. 1), indicating that the film was uniformly formed with constant field. The leakage current in each case of film formation was found very small in magnitude or zero after a given thickness of 5 to 10 V film was reached. This observation, therefore, showed that the current was ionic in character with 100% current efficiency, and that no electronic current was present. The plot of tan δ versus charge passed is presented in Fig. 2 for different electrolytes in which anodic oxide was formed on superpurity aluminium. As expected, tan δ decreased with increase of thickness of film in tartaric, oxalic and phosphoric acids. In the case of citric acid, a slight increase in tan δ was observed after 60 V of film formation. These results are in agreement with the experiments with Zr of Young[5] who ascribed such behaviour to the presence of microfissures. Wanklyn and Silvester[6] have suggested that the losses with tan δ constant might be due to a distribution of fissure depths. If fissures were responsible, one would expect a decrease of tan δ on anodic polarization (healing of fissures) and an increase on standing, the latter
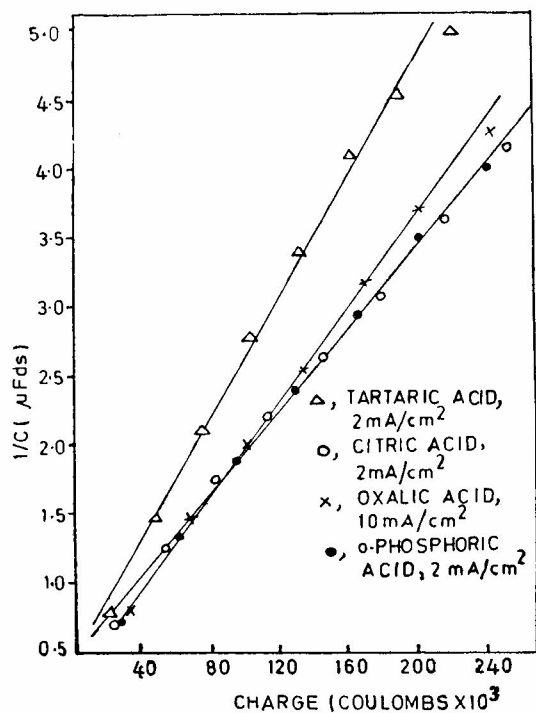
Fig. 1 — $1/C$ versus the charge passed during the growth of films in various aqueous electrolytes

effect being observed only with distinctly leaky films. With some very leaky films on aluminium, very much larger losses were observed. This appears to be similar to the behaviour reported by Wanklyn and Silvester[6] for corrosion films and might indeed be due to a distribution of cracks. The microfissures, if small, could leave the capacitance unaffected. During the film growth, ion movement must occur via the existing film suggesting that the imperfections were probably "pools" of electrolyte enclosed in cavity of oxide film, most of which are not in direct contact with the bulk of the solution. This fact is substantiated by tan δ measurements in tartaric acid in the presence of chloride ions during the anodic growth of film. In the presence of chloride ions, the imperfections in the film were considerably enhanced and a behaviour similar to that of citric acid in the absence of chloride ions was observed. The leakage current was found zero or very low initially in all the cases, and decreased to practically zero value when the film voltage reached 20 V. This is probably due to the healing of fissures or their "choking" with oxygen or closure by the condenser pressure.

(b) *Effect of chloride ions on anodic polarization of superpurity aluminium in aqueous electrolytes* — It has recently been suggested[7-10] that the breakdown of the film and the properties of the film change either due to the penetration of small chloride ions through the oxide film pores, the displacement of the (very thin) film by adsorption of chloride ion, the migration of chloride ions inwards through the oxide lattice, or the peptization of thin oxide film by a strong negative charge[11] caused by adsorbed anions[12]. We, therefore, attempted to study the anodic formation of film on aluminium in the

presence of chloride ions in the electrolytes used above.

It was observed that the rate of formation of thin film was unaffected by the addition of chloride ions in electrolyte solution. The magnitude of capacitance for films in the presence of chloride ions was found higher for a 10 V film and acquired the same value for a 20 V film as that in the absence of chloride ions. Tan δ values at low concenrations of chloride ions (0·01 ppm) in tartaric acid were found greater for the same thickness of the film than those in the absence of chloride ions in solution. On further addition of chloride ions, the value of tan δ, on initial anodization, decreased but after about 40 V of film formation, it increased (Fig. 3). This is due to the adsorption of chloride ions on the anodic oxide film, which caused imperfections in the film. This is supported by the fact that when concentration of chloride ions was 3 ml of 1000 ppm in 250 ml 0·1N tartaric acid, the film could not be formed beyond 2·5 V. Thus chloride ions has an inhibiting effect on the growth of the oxide film. Furthermore, at this concentration of chloride ions, the 2·5 V film was observed to have white patches and pits on its surface.

(c) *Preliminary X-ray report of the anodic oxide films formed in aqueous and molten salt electrolytes* — X-ray diffraction patterns were obtained for 19 film samples formed on aluminium both in aqueous electrolytes (9 samples) and molten salt electrolytes (LiNO$_3$+KNO$_3$+NaNO$_3$, 10 samples) at 237-331 The films were stripped from the substrate, mounted over a hole 1/8 inch in diameter in a small piece of platinum and diffraction patterns were taken using CuK$_\alpha$ radiations. Thn X-ray diffraction gave
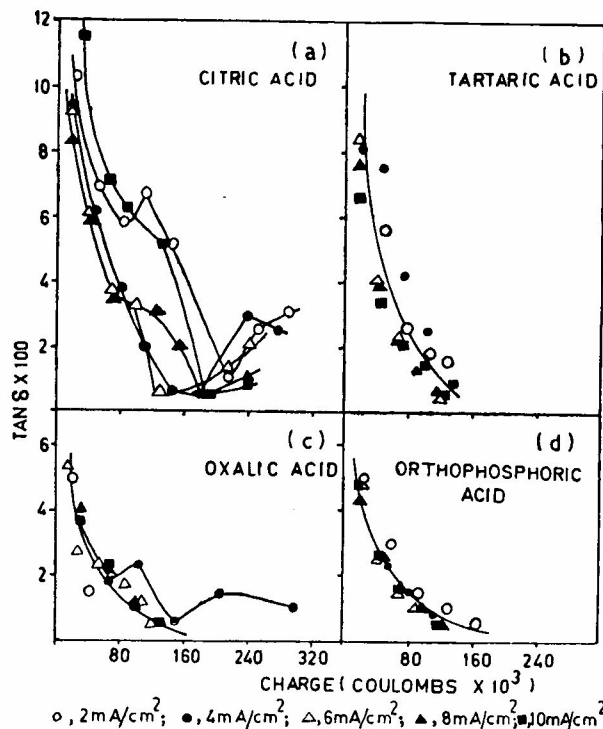

Fig. 2 — Variation in tan δ with the charge passed during the growth of film at different current densities in various aqueous electrolytes
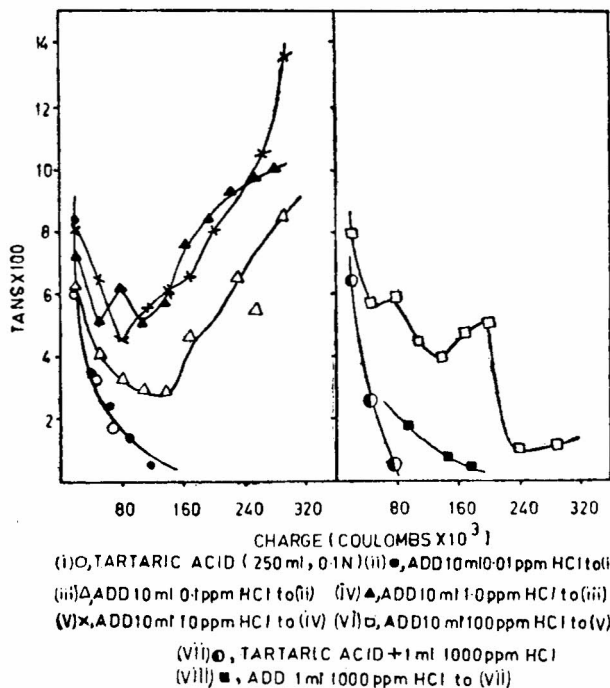
Fig. 3 — Variation in tan δ with the charge passed during the growth of anodic oxide films on aluminium in the presence of chloride ions in tartaric acid electrolyte at 20°
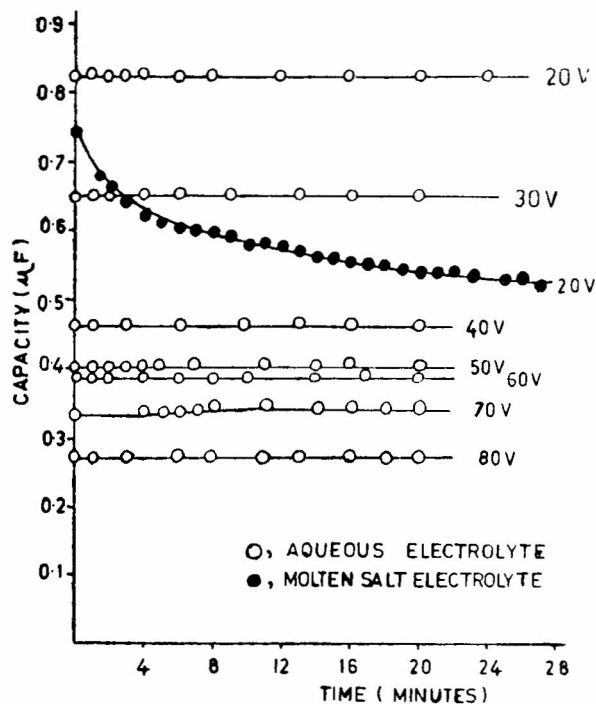
(i)O,TARTARIC ACID (250 ml , 0·1 N)(ii)●,ADD 10 ml 0·01 ppm HCl to(i)
(iii)△,ADD 10 ml 0·1 ppm HCl to(ii) (iv)▲,ADD 10 ml 1·0 ppm HCl to (iii)
(V)×,ADD 10 ml 10 ppm HCl to (iV) (Vi)□,ADD 10 ml 100 ppm HCl to(V).
(Vii)⦶, TARTARIC ACID + 1 ml 1000 ppm HCl
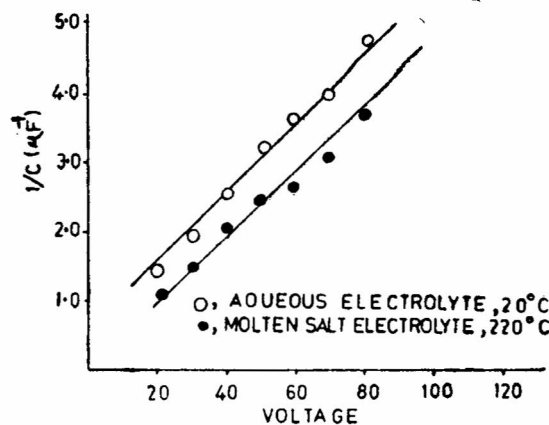(Viii) ■ , ADD 1 ml 1000 ppm HCl to (Vii)

Fig. 5 — Variation of reciprocal capacitance with voltage of formation for the film formed in aqueous electrolyte and subsequently placed in molten salt electrolyte ($LiNO_3 + KNO_3 + NaNO_3$) at 220°
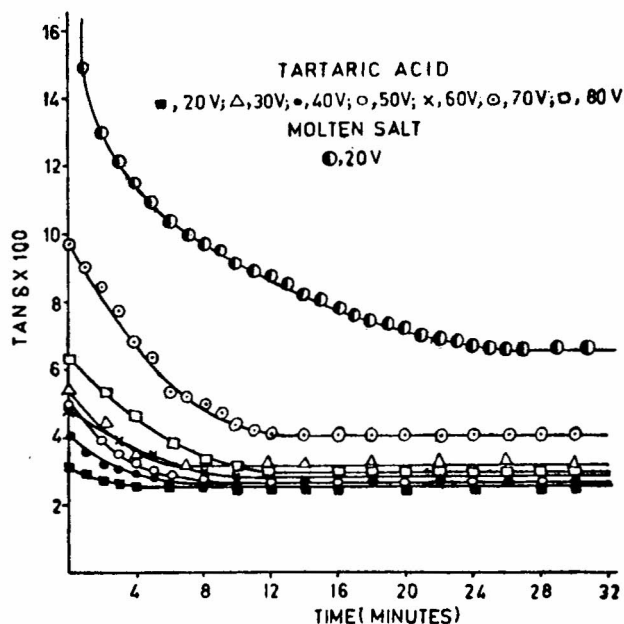

Fig. 4 — Capacity drift with time for the film formed in aqueous and molten salt electrolytes for different thicknesses

Fig. 6 — Variation in tan δ with time for the films formed in aqueous and molten salt electrolytes

patterns indicative of a few large crystallites of aluminium. These patterns gave no indication of amorphosity. The films formed on superpurity aluminium were found to be crystalline in nature.

(d) *Capacity drift with time and temperature* — The drift in capacitance with time for anodic oxide films formed in aqueous electrolytes was found negligible

(Fig. 4) whereas for a film formed in molten salt electrolyte at 220° at a c.d. 5 mamp/cm², a drift in capacity was observed. The capacitance first decreased up to 25 min, thereafter it became constant. This could be either due to the change in the structure of the film at elevated temperatures or due to the contribution of thermal oxidation. The second factor is not the contributing factor at all since when the film was further anodized at the same current density, the voltage of formation reached immediately to the previous value corresponding to the pre-existing thickness of film. The change in structure of the film, i.e. from amorphosity to crystallinity is, therefore, most likely. The film first formed is amorphous in nature and, later on, with the passage of time, changes to crystalline form. This is substantiated from the preliminary X-ray report of anodic oxide films which showed crystalline structure.

If an anodic film is formed in an aqueous electrolyte to any given voltage of formation or thickness and is placed in molten salt electrolyte at elevated temperatures, the capacity of the film increases (Fig. 5). The reciprocal capacitance vs voltage of formation plot for such a process is found linear and roughly parallel and thus the increase in capacitance with temperature is very nearly the same. Fig. 6 showed that the corresponding drift in tan δ for films formed in molten salt with time is larger than those formed in aqueous electrolytes. This observation is quite consistent with tan δ values reported in this paper.

The results can thus be summarized in the following manner. The impurities of the order present in Hindalco aluminium do not affect the formation characteristics of the anodic oxide film as compared with the superpurity aluminium. The information about the electrolytic capacitors with respect to dielectric losses, dissipation factor and drift in capacity will be helpful in the study of electrical and related properties of the film, and ionic conduction mechanism, which will be reported later.

Acknowledgement

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