

Annealing of Anodic Oxide Films on Superpurity Aluminium & Mechanism of Ion Transport Through Such Films

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Annealing of anodic oxide films on superpurity aluminium formed in different electrolytes and of different thicknesses at various temperatures (from 300° to 500°) has been studied. The mobility of metal ion during the growth of anodic oxide films has been established. A pore-widening-concurrent pore-shortening dissolution mechanism proposed by Diggle *et al.* [*J. electrochem. Soc.*, 116 (1969), 1347] based on a truncated pore model fits our data for the dissolution of anodic oxide films on superpurity aluminium.

THE properties of the anodic oxide films undergo change upon annealing. Okubo¹ performed the salt-spray tests for annealed ($\leq 600^\circ$) anodic oxide films on aluminium and showed that their corrosion resistance had increased. The resistance to electrical breakdown and friction-wear did not change on annealing the oxide films for 2 hr at 300°, but the oxide porosity increased with increase in annealing temperature². Similarly, the ionic conductivity is found to decrease with annealing. Contradicting views exist on the mobility of ions during anodic film formation on metals. Davies *et al.*³ studied Al, Ta, Nb, W, Zr and Hf anodic films and showed both cation and anion movements during oxide film growth. Vermilyea⁴ observed that at least the majority of the current carriers in anodic oxide films are metal ions. Fromhold and Kruger⁵ observed both cation and anion movements. In the absence of any firm evidence with regard to the mobility of ions during anodic growth, we thought it desirable to study the mechanism of anodic growth in greater detail employing "sandwich experiment"⁶ and Vermilyea etching experiment⁴ and using superpurity aluminium samples. Annealing effects on anodic oxide films on superpurity aluminium have been studied as data available in the case of aluminium are unreliable and superpurity aluminium was not used for such a study.

Materials and Methods

Annealing of anodic oxide films on superpurity aluminium— Superpurity aluminium specimens (area 2 cm²) having a small tag were taken and surfaces prepared in the manner described elsewhere⁷. They were, then, anodically polarized at 2 mA/cm² and films of 30, 50 and 80 V formed in 0.1N tartaric acid at 25°, and of 40 V formed in molten salt electrolyte⁷ at three different temperatures, viz. 220°, 270° and 330°. The dielectric measurements for the aqueous-formed films were made with Electrolytic Capacitor Bridge (British Physical Laboratories). For molten-salt films, the specimen was taken out of the cell, cooled to room temperature, washed with cold distilled water and dried. The

capacities of these films were measured in 0.1N tartaric acid at 1 KHz by an Impedance Bridge (Toshniwal, Bombay) because of the limitations of the earlier bridge at low capacitances. During dielectric measurements, special care was taken to prevent the tag from dipping in the electrolyte.

The specimen was sealed in a pyrex tube which was evacuated (10^{-4} mm) by connecting it to a vacuum line. This sealed capsule was annealed at desired temperatures (accuracy $\pm 5^\circ$) for different intervals of time in a muffle furnace. After annealing, the specimen was taken out by breaking the capsule, and capacitance again measured by dipping it in 0.1N tartaric acid to the same depth as earlier. Annealing above 500° could not be carried out as the pyrex tube under vacuum softened at higher temperatures. For both types of films, annealing was carried out at 300°, 350°, 400°, 450° and 500° for 3, 5 and 8 hr at each temperature of annealing.

Results and Discussion

The plots of change in capacity after annealing vs annealing temperature (Fig. 1) show that with increase of annealing time, the increase in capacity was more and this effect was pronounced above 350°. This is in agreement with experiments of Vermilyea⁸. The overall increase in capacitance of aqueous-formed films was much lower than that of the molten-salt films. This is because of the higher porosity and the amorphous-crystalline transition of molten-salt films. Vermilyea⁹ has reported a slight sharpening of the X-ray diffraction pattern upon annealing, indicating that some ordering of the structure has occurred. In the case of aqueous-formed films, the increase in capacitance upon annealing is inversely proportional to the thickness of the film (Fig. 1A-C). The dissipation factor for these films shows a decrease with annealing. Young¹⁰ has also reported that heating at 450° caused a considerable reduction of dielectric losses but an increase in capacity. For molten-salt films (Fig. 1D-F), the temperature of formation of anodic films did not have any particular effect on the annealing

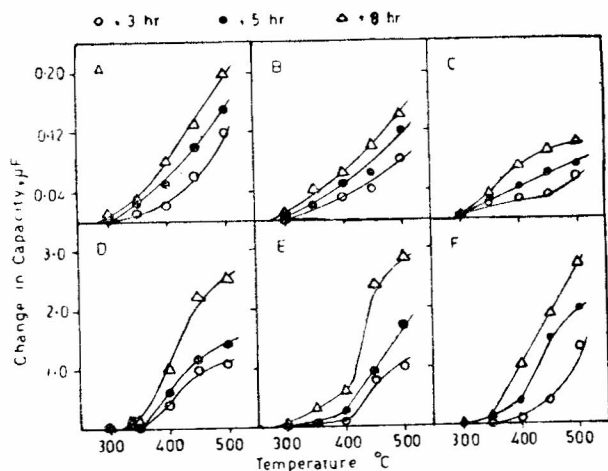


Fig. 1—Increase in capacity when the specimens with 30(A), 50(A) and 80(C) V films in 0.1N tartaric acid at room temperature, and with 40 V films formed from molten-salt electrolyte at 493° (D), 543° (E) and 603°K (F) are annealed at various temperatures for different periods

of the films except that the increase in capacity was not uniform with increase in annealing time. This can be attributed to the difference in specimen and to the not-very-accurate capacitance measurements. The interference colours of the specimens before and after annealing are not changed⁸. Some other changes inside the film might have taken place resulting in such a behaviour.

When anodized aluminium is heated in vacuum, air or oxygen, the capacitance increases at a rate which depends on the oxide thickness and the heating temperature. Using hydrogen, Vermilyea⁸ has reported 40 to 50% increase in capacitance at 500°. This can be due to short-circuiting of portions of the oxide film due to extraction of some of the oxygen from the oxide film by the metal. In vacuum, the capacitance continues to rise until it approaches a value which would be observed for unanodized aluminium. In other words, the entire oxide film becomes conducting, leaving the Al_2O_3 film oxygen-deficient. According to Dewald¹¹, this can be referred to as oxygen-vacancies. Two electrons must be associated with these oxygen vacancies in order to maintain charge neutrality. The vacancies can be thus considered as donor centres. These oxygen-deficient portions of the Al_2O_3 film could exhibit *n*-type semiconductivity. It is this conductivity which mostly affects the dielectric properties of the film. As compared to annealing *in vacuo* or in the presence of H_2 , annealing in air or ordinary nitrogen, when oxygen-deficiency reaches the oxide-air interface, renders oxygen to flow into the film, thereby maintaining a constant composition at this interface. Thus, an equilibrium is set up during heat-treatment in an oxygen-containing atmosphere. Oxygen enters the aluminium oxide, flows across it and enters the aluminium at the same rate. The oxide compositions at the metal-oxide and oxide-air interfaces remain fixed. This composition may be a function of the ambient oxygen pressure since evidence has been found¹² that the capacitance increase due to heat treatment is pressure-dependent. In the reducing atmosphere

or *in vacuo*, the film oxygen would not be replenished. Thus, it can be postulated that the capacity increase can be controlled to a desired extent by regulating the order of vacuum or oxygen pressure. Smith *et al.*¹² have shown that on reanodization of the heat-treated sample, its properties approach those of the unheated sample and the interference colour of the oxide film remains unchanged. The permanent increase in the dielectric constant of the oxide film is probably related to the increase in crystallinity after an annealing treatment as observed by Vermilyea⁹.

Ionic mobility: (a) Sandwich experiment— Superpurity aluminium specimens of sizes $1.5 \times 1.5 \times 0.025$ cm³ (specimen A) and $1.0 \times 1.0 \times 0.025$ cm³ (specimen B) having small tags were polished and prepared as earlier⁷. On both the specimens A and B, 20, 30 and 40 V films were formed respectively in 0.1N tartaric acid at 25° and c.d. 2 mA/cm². Dielectric measurements were made with the electrolytic capacitor Bridge (Table 1). Specimens A and B with the same voltages of formation were, then, paired and sandwiches made by the technique described earlier⁶. The dielectric measurement of the combined system was made with A and B in the impedance Bridge circuit respectively. On further anodization with A in the circuit, say up to 50 V, current supply was cut off. The capacitance and $\tan \delta$ were again measured for the combined system by taking contact with A and B respectively. These were found to be the same implying a complete sealing of A and B and no possibility of electrolyte creeping through the oxide (Table 2). This is supported by the fact that no leakage current was observed for the combined system. Specimens A and B were, then, separated by dissolving lacomite in acetone, and finally washing with distilled water. The capacitance and loss-tangent were measured for the outer and inner surfaces of B respectively by applying lacomite to the other side (Table 3). The capacitance of specimen A in each case remained

TABLE 1—CAPACITANCE AND $\tan \delta$ OF SPECIMENS A AND B BEFORE SEALING
(Leakage current, nil; colour of film, off-white)

Film voltage of specimen A (V)	Total charge mC	Capacitance μF	$\tan \delta \times 10^2$
20	59.8	1.74	9.0
30	92.0	1.29	6.5
40	118.4	0.95	5.6

TABLE 2—CAPACITANCE AND $\tan \delta$ OF SPECIMENS A AND B UPON REMAKING A 50 V FILM ON THE ASSEMBLY BY TAKING CONTACT WITH A AND SEPARATING

(Leakage current was nil)

Film voltage V	Specimen	Capacitance μF	$\tan \delta \times 10^2$
20	A	1.72	6.1
	B	0.94	5.4
30	A	1.30	3.5
	B	0.56	6.5
40	A	0.97	5.2
	B	0.45	3.5

TABLE 3 — CAPACITANCE AND TAN δ OF SPECIMEN B AFTER SEPARATION FROM A

Film voltage V	Capacitance, μF		Tan δ × 10 ³	
	Outer surface covered	Inner surface covered	Outer surface covered	Inner surface covered
20	0.78	0.24	8.0	2.0
30	0.49	0.22	6.2	1.5
40	0.37	0.145	3.2	—

unchanged in magnitude from the value determined when no sealing was done. This shows that the film on A was not affected at all by further anodization. This observation is substantiated by the fact that on further anodization of A after separation the formation voltage rose immediately and attained the voltage of the film pre-existing over it (Fig. 2).

During the sandwich experiment, the field in-between the specimens A and B was not affected in any way because (i) the anodization rate in the sandwich experiment is equivalent to the normal rate of anodization, and (ii) there is no effect of anodization in sandwich experiment on specimen A (Tables 1 and 2). Thus, there is no possibility of oxygen ion moving through the electrolyte to A to produce new layers inside the existing oxide layers. Instead, Al³⁺ ions produced in specimen A during anodization of the sandwich assembly are transferred to specimen B through a constant-field space and then to the solution to produce fresh layers on the outside of the existing oxide layers. Thus, only the metal ions are mobile during the anodic oxide growth. These results are in agreement with those of Amsel and Samuel¹³, Flint *et al.*¹⁴ and Young¹⁵.

Etching experiment — Four specimens of sizes 1 × 1 × 0.025 cm³, say alpha, beta, gamma and delta were prepared⁷. On specimen alpha, an anodic film of 40 V was formed in 0.1N tartaric acid at 25°. On beta, a 20 V film was formed in molten salt electrolyte at 200°. On specimens gamma and delta, so-called "duplex" films were formed. On gamma, a 30 V film, in tartaric acid first and then a 10 V film in molten salt electrolyte were formed, and vice versa for delta. All anodic polarizations were carried at c.d. 2 mA/cm².

Dissolution of the films has been studied in 5% sodium orthophosphate. Capacitance of the film has been measured as a function of time as etching proceeded. Fig. 3 shows plots of reciprocal capacitance vs time for all the specimens. It can be seen that in the case of specimen gamma, the thickness initially decreases with the rate of dissolution corresponding to that of molten salt film, and reverts to the aqueous-film rate later. Reverse is the case observed in the case of specimen delta. These results imply that at least the majority of current carriers were metal ions.

It is evident from Fig. 3 that the time required for dissolution is independent of initial porous film thickness. The dissolution rate decreases as etching proceeds. This can be explained in terms of a pore shortening-pore widening mechanism as proposed by Diggle *et al.*¹⁶, based on the truncated pore model of Paolini *et al.*¹⁷. There is a greater dissolu-

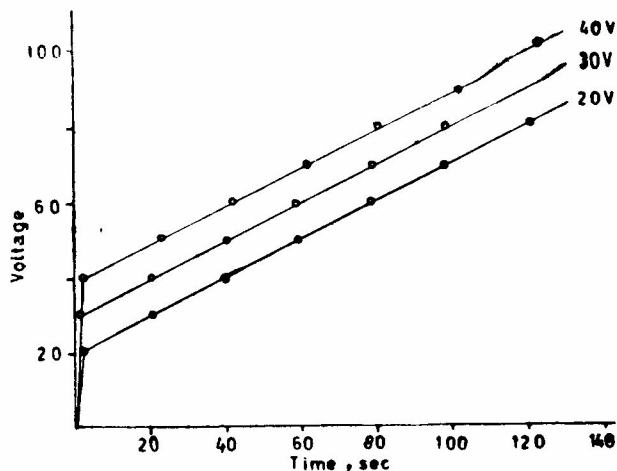


Fig. 2 — Plot of voltage of formation versus time for which current is passed when specimens A of different thicknesses are further anodized at 2 mA/cm²

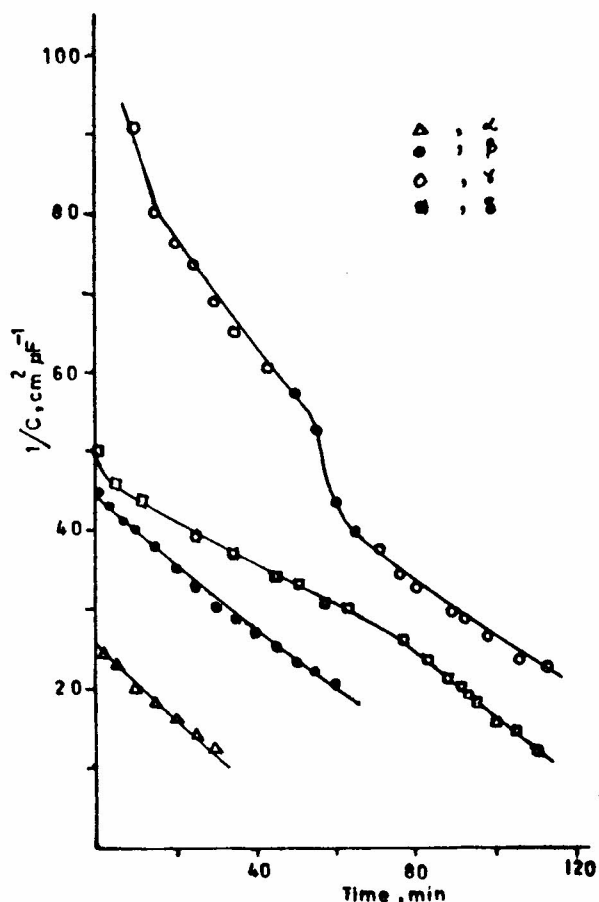


Fig. 3 — Variation of reciprocal capacitance (i.e. thickness of the film) with time during etching experiment

tion rate at the pore mouth due to ease with which the reaction products can diffuse away from the reaction site.

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