

Preparation and characterisation of alumina membranes by anodic oxidation of aluminium[†]

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Inorganic membranes of alumina have been prepared by anodic oxidation of aluminium. The kinetics of the growth of alumina layer in phosphoric acid has been studied at four different temperatures, viz., 20, 30, 40 and 50°C. The coating ratio, coating thickness, and weight of alumina formed at different time intervals, have been measured. The effect of formation current on the coating thickness has been elucidated. Separating the alumina layer from metal by specifically dissolving the later in bromine and methanol mixture, the surface structures of the oxide layer has been studied by scanning electron microscopy.

When aluminium is oxidised in certain acid electrolytes, like phosphoric acid, a porous oxide develops, which exhibits remarkably uniform array of cells, each containing a cylindrical pore of ultrafilter range¹. The ability to design porous films of pre-determined morphology, makes them practically well suited for use as ultrafilter membranes. Narrow pore size distribution, high pore density, and thickness are important attributes of the oxide film formed.

Materials and Methods

99.999% pure aluminium pieces procured from E Merck was used for anodization. A mixture of 34.5% volume of perchloric acid and 65.5% by volume of acetic anhydride was used for electropolishing. For the selective removal of oxide, a solution of phospho chromic acid prepared by dissolving 20 g of chromic anhydride and 35 mL of phosphoric acid in 1 L of water and for the selective removal of metal for obtaining the oxide layer, a solution of 2 mL of bromine in 100 mL of dry methanol was used². The amount of aluminium dissolved was determined spectrophotometrically using alizarin red-S at a max of 475 nm. the weight of oxide and the thickness of the layer formed were determined gravimetrically and the coating ratio were elucidated. The density of the

alumina formed was assumed to be 2.4 for finding out the thickness of the film formed³.

Experimental Procedure

A U-shaped glass tube with a jacket for circulating water externally was used as a cell for conducting the experiment (Fig. 1). An aluminium piece of 1 cm × 1 cm was used as anode with 0.5 cm of the piece immersed in the electrolyte giving rise to an area of 0.5 cm² for anodization. A graphite rod was used as cathode. The two electrodes were connected to a DC power supply. Different aluminium pieces of the same size were used for carrying out the experiments at different timings. The aluminium pieces were electropolished at 20°C employing a current density of 1 A/dm² at 20 V.

The pieces were weighed (w_1) and anodised in phosphoric acid at 325 V for 2 min at four different

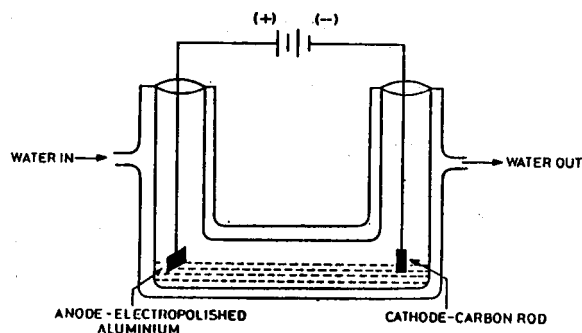


Fig. 1—Anodization set-up

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temperatures, 20, 30, 40 and 50°C. Different pieces were used for each experiment. One side of the piece not facing the cathode was covered with cello tape to avoid formation of oxide layer on that side. The aluminium pieces with the oxide coating were weighed (w_2). The aluminium oxide formed was selectively dissolved in phospho chromic acid and the pieces were re-weighed (w_3). From the above weights, the weight of oxide formed was calculated as ($w_2 - w_3$). The coating ratio defined as (weight of oxide formed)/(weight of aluminium lost) ($w_2 - w_3$)/($w_1 - w_3$) was calculated in each case³. The oxide layer was separated from the metal by bromine in methanol.

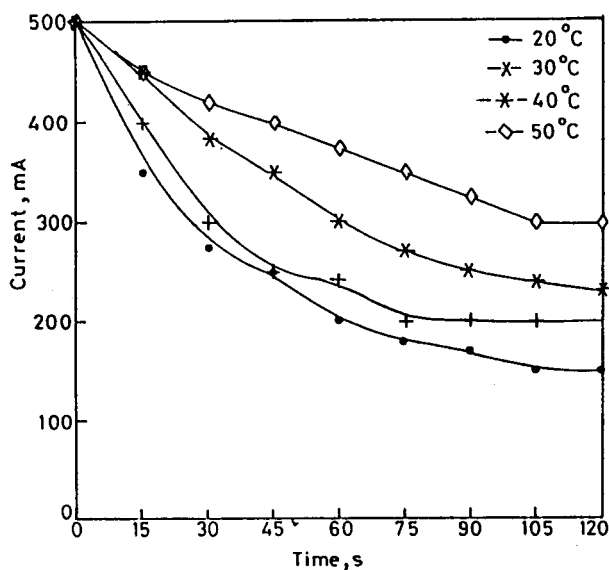


Fig. 2—Current-time characteristics at different temperatures

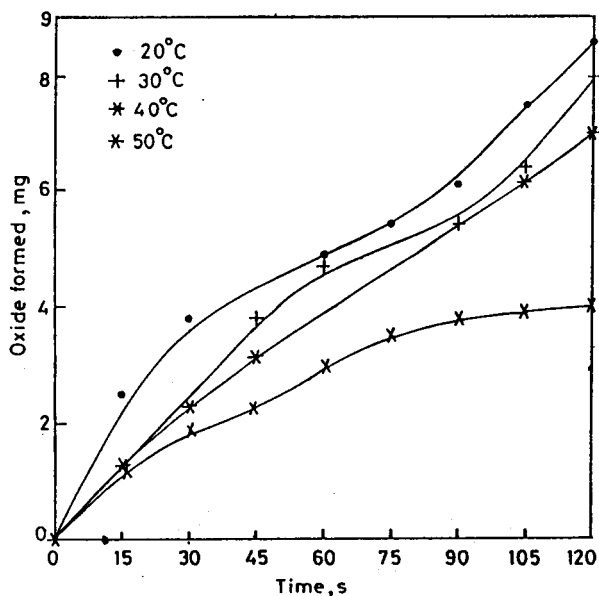


Fig. 3—Weight of oxide formed at different temperatures

Results and Discussion

In order to study the effect of current on the above parameters, the current was changed from 150 to 500 mA. To correlate the anodizing voltage, with the pore diameter, the anodization was carried out at different voltages of 150, 200, 250 and 325 V. The current-time characteristics in phosphoric acid was plotted for the four different temperature (Fig. 2).

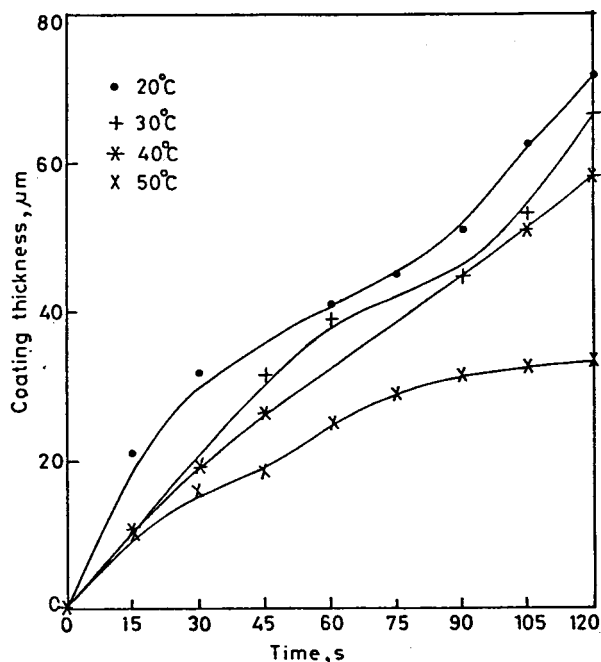


Fig. 4—Coating thickness at different temperatures

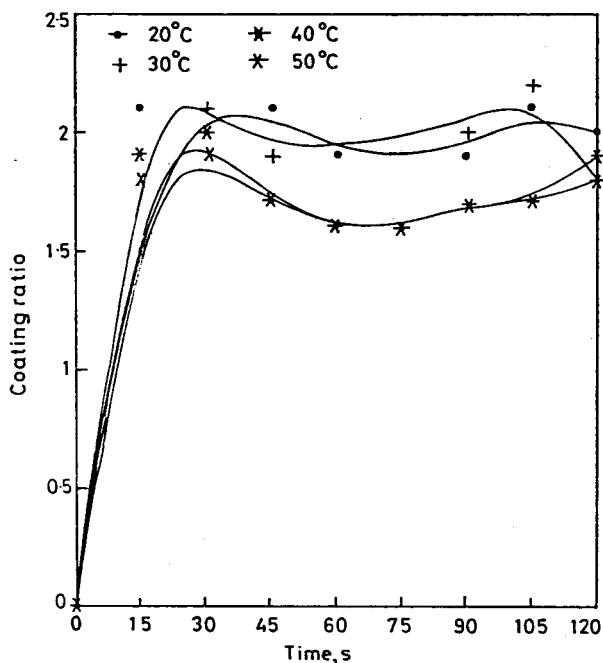


Fig. 5—Coating ratio at different temperatures

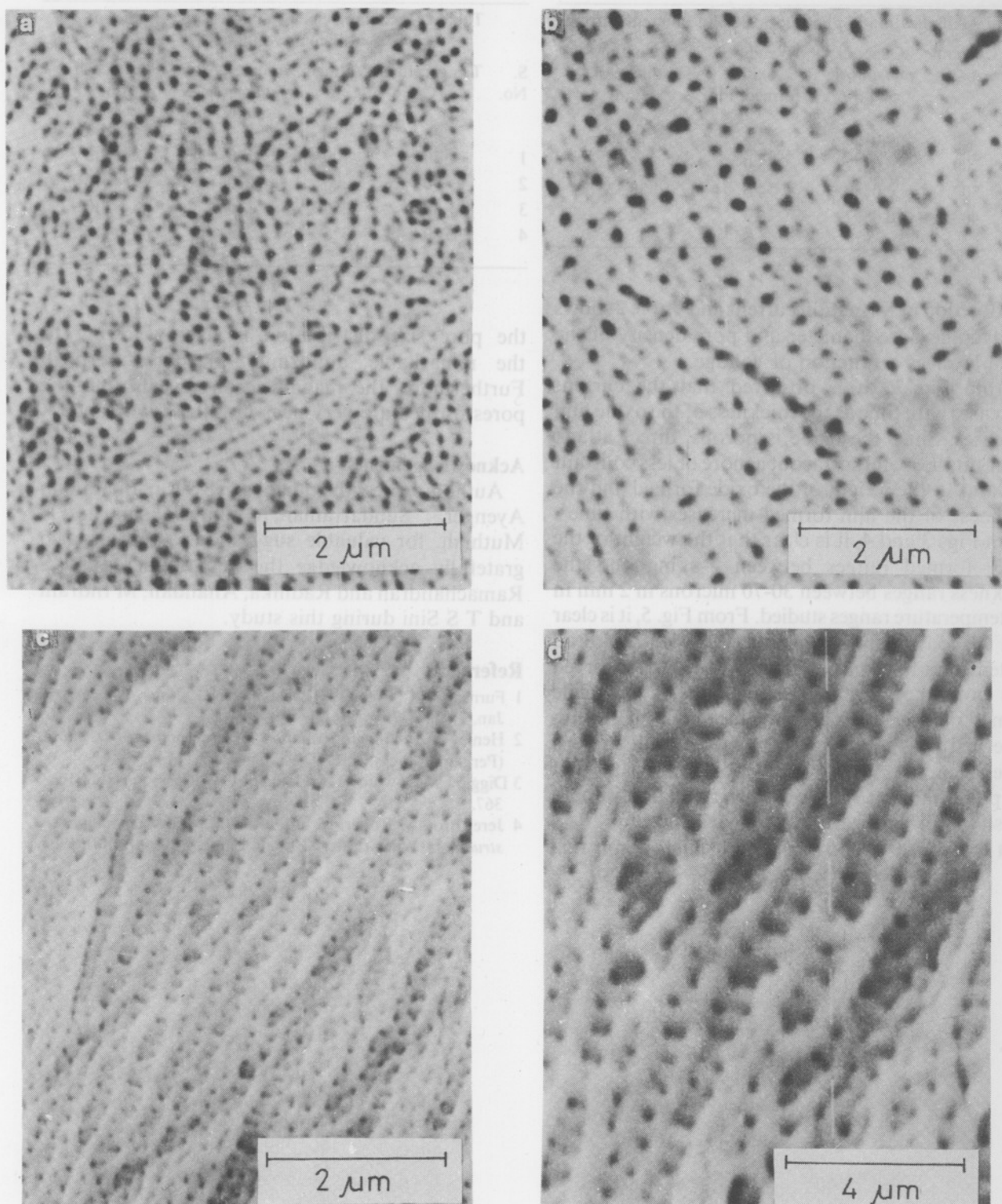


Fig. 6—Scanning electron micrographs showing anodized aluminium surface structure anodized in phosphoric acid at different voltages (a) 100 V, (b) 200 V, (c) 250 V and (d) 325 V

The weight of the oxide formed, the coating thickness, and the coating ratio are plotted as a function of time for the four different temperatures studied (Figs 3-5).

The scanning electron micrographs of the anodized films formed in phosphoric acid at different voltages is shown in Fig. 6.

Table 1 shows the thickness of oxide layer formed

Table 1—Anodization in phosphoric acid at different currents

S. No.	Current mA	Conc. of phosphoric acid, M	Weight of oxide formed, mg	Coating thickness (μm)
1	100	0.0100	2.3	19.16
2	200	0.0277	3.0	25.00
3	300	0.0550	4.6	38.33
4	400	0.0897	6.3	52.50

as a function of formation current and Table 2 shows the average pore diameter and pore density of the oxide layer as a function of voltage.

From Fig. 2, it is observed that the current decreases with time as the thickness of the oxide film increases. Since the oxide is porous, direct attack occurs at the metal surface at a more or less constant rate and so the weight of the oxide formed and the thickness of the film formed increases with time⁴. From Figs 3 and 4, it is clear that the weight of the oxide formed ranges between 4-8 mg and the thickness ranges between 30-70 microns in 2 min in the temperature ranges studied. From Fig. 5, it is clear that the coating ratio ranges between 1.8-2.1 for all the temperatures studied. From Table 1, it is observed that both the weight and thickness of the oxide formed increase with current since the thickness is governed by the charge deposited which in turn depends on the current while Table 2 indicates that the pore diameter increases with reduction in pore density with voltage.

It is evident from the electron micrograph that

Table 2—Scanning electron microscopic studies at different voltages

S. No.	Temperature °C	Voltage V	Average pore diameter nm	Pore density n/m^2
1	30	100	160	2.2×10^{13}
2	30	200	220	3.6×10^{12}
3	30	250	230	3.5×10^{12}
4	30	325	240	3.5×10^{12}

the pore size distribution is narrow owing to the remarkable uniformity in pores formed. Furthermore, the magnification reveals that the pores formed are very near to ultra filter range.

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