Characteristics of Anodic Film on Aluminium in Borate Bath

S. V. SOMAN, D. P. SALGAONKAR & S. K. MANJREKAR

Department of Chemistry, Institute of Science, Bombay 400032

The growth of anodic films over aluminium in an electrolyte containing sodium carbonate-sodium borate in dioxane-water mixtures of varying compositions has been studied. The activation energy and other relevant parameters have been calculated by a new method employing a simple anodizing assembly wherein the use of constant current device has been done away with.

THE type of anodic oxide film that can be produced on aluminium depends upon several factors, one of the important factors being the nature of the electrolyte[1]. The electrolytes in which the anodic oxide film is completely insoluble give rise to a barrier type of oxide film whereas electrolytes which have a slight dissolving action produce a porous type of film. The barrier and porous type of films are quite different in their overall physical appearance and other characteristic properties; however, these two types of films co-exist. A porous film is actually a porous extension of the thin compact barrier layer. But the overall complexity of the film increases as the formation voltage is increased.

In an electrolytic bath that has dissolving action on the anodic films the balance between the formation and the dissolution of the oxide film is complex[2]. The process is then strongly influenced by factors like the composition of solvent, concentration of electrolyte, anodizing temperature, impressed voltage current density and the period of anodization.

The present work deals with the anodic films obtained on an aluminium foil from borate-carbonate electrolytic bath (sodium borate + sodium carbonate) with dioxane-water mixtures as solvent. This mixture was used with a view to studying the effect of (a) lowering of water content in the anodizing electrolyte and (b) replacing water by poor ionizing solvent like dioxane.

Materials and Methods

An aluminium ribbon 40 mm wide and 30 μ in thickness and of 99·95% purity was used as an anode. The film was held firmly between two rectangular pieces of teflon from the centre of each a square piece of 25×25 mm was removed; thus 6·25 cm² area of the aluminium film was exposed for anodization. The cathodes were made of pair of graphite rods which could be fixed on either side of the anode at a desired distance. The direct current was obtained from dc power supply unit. This consisted of a stabilized stepdown transformer providing output voltages of 10, 20, 30, 40 and 50 V. With silicon rectifiers and smoothening condensers the unit gave a nearly ripple free direct current at varying voltages.

Immediately before the experiment the aluminium film was degreased with toluene. The surface was then chemically cleaned by dipping the film in 5% solution of NaOH at 80° for 15 sec. The film was then washed with water and dipped in an acid mixture containing 70% phosphoric, 25% sulphuric and 5% nitric acids. Finally it was flushed with plenty of distilled water to remove any adhering chemicals.

Other chemicals used were of BDH Analar quality and were used as such; dioxane, however, was distilled before use.

Current measurements — At the instant of application of the potential across the electrodes, a surge of current passes through the system, which falls and acquires a steady low value after about 20 to 200 sec depending upon the applied voltage. The extent of the current flowing through the system any time during the run being of interest was measured by introducing a high wattage nichrome wire exactly of one ohm resistance in series with the system (Fig. 1).

For any current passing through the system the potential that developed across this resistance was measured continuously with Carl-Zeiss strip chart millivolt recorder. From the time-millivolt graphs the current in the anodizing circuit and hence the resistance at any time could be determined. The results are given in Table 1.

Measurement of the field — A fairly accurate estimate of the variation in the field in the oxide
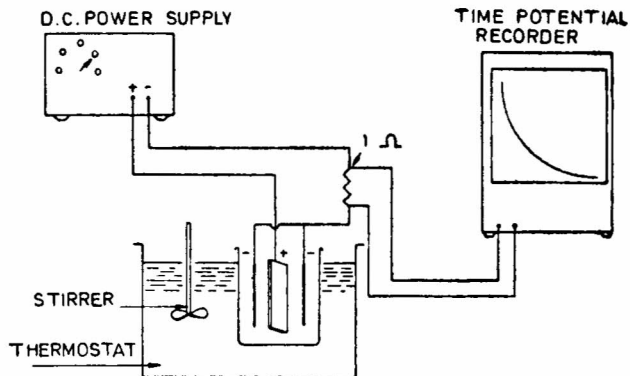

Fig. 1 — Circuit diagram for measuring current flows

film could also be made by measuring the changes in the resistance of the oxide film. For a substance like Al_2O_3 it can be assumed that the thickness of the film will be proportional to resistance, if the applied voltages are not high. Knowing the specific resistance of Al_2O_3 the thickness of the oxide film could be calculated. The value of the field can then be calculated by dividing the voltage by the thickness of the film. However, the actual value of the field being of no practical interest, a figure proportional to this actual value was obtained by dividing the voltage by the resistance of the film. It is this value which has been used as an index or a measure of the field in this investigation.

Results and Discussion

Using mildly alkaline carbonate-borate mixtures as the electrolyte and water-dioxane mixtures as solvent, anodization of aluminium foils was carried out under different experimental conditions. The relationship between the current and the field has been studied. The results have been grouped under following categories. Only the representative results have been presented in each case.

(i) *Effect of increase of voltage on field vs* ln*I plots*— In this group it has been observed that the field vs ln*I* plots were linear without any exception. The data are given in Table 2. It was further observed that with the increase in impressed voltage

the slopes of these plots increased. The slope values for impressed voltages of 10, 20, 30 and 40 V (dc) are 4·14, 4·44, 5·0 and 5·52 respectively.

Nigam and Arora[3] found that (1) the Tafel slope for a given electrolyte is dependent on the field strength and thickness of the oxide film, and (ii) the values of Tafel slope are different for different electrolytes. They attributed the difference in the values of Tafel slopes to thickness controlling parameters of oxide and to the density of the material.

According to Dewald[4] a modified form of his general equation (Eq. XIII) allows for a rise in the Tafel slopes with increasing current density when values of δ are near about 1. Since Dewalds theory involves inclusion of two extra parameters as compared to the Cabrera and Mott's theory[5] he suggests that further experimental verification would be highly desirable.

An explanation of increase in Tafel slope with increased applied voltage seems difficult at this stage.

(ii) *Effect of change in temperature* — This effect was studied by carrying out the anodization at three different temperatures, viz. 30°, 60°, and 100°. Since this caused a profound and a visible change in the appearance of the film, microphotographs of the surface were taken with a reflectance microscope. The variations in the field versus current relationship observed in these experiments are included in Table 3.

TABLE 1 — VARIATION OF RESISTANCE (VALUES IN OHM) OF THE ANODIC FILM WITH TIME

[Bath composition = 20% dioxane + 80% water; electrolyte = 15% Na_2CO_3 + 5% $Na_2B_4O_7$]

Time (sec)	30°		60°		100°	
	10 V (dc)	20 V (dc)	10 V (dc)	20 V (dc)	10 V (dc)	20 V (dc)
5	20·00	55·56	20·04	79·37	20·13	53·33
15	21·74	57·14	21·30	83·33	21·54	56·34
25	28·41	—	22·40	95·69	22·05	60·24
35	—	—	24·00	97·56	22·25	60·98
45	28·99	61·16	24·40	—	22·45	—
65	29·41	—	25·70	—	23·28	—
95	—	—	26·600	99·01	23·84	—
115	—	61·54	—	—	24·24	63·30
145	—	—	28·08	—	25·55	—
165	—	62·50	29·41	—	—	64·10
185	29·67	62·70	—	102·56	26·22	64·92
245	29·76	—	—	103·63	27·70	65·57
265	29·76	62·70	31·65	—	28·21	—

TABLE 3 — EFFECT OF TEMPERATURE ON FIELD VS ln*I* PLOTS

[Applied voltage (V) = 10 V dc; bath composition, 20% dioxane + 80% water; electrolyte, 15% Na_2CO_3 + 5% $Na_2B_4O_7$]

Temperature					
30°		60°		100°	
ln*I*	Field (V/R)	ln*I*	Field (V/R)	ln*I*	Field (V/R)
4·382	0·5000	4·331	0·499	4·597	0·6200
4·299	0·4599	4·263	0·446	4·484	0·5541
4·031	0·3520	4·190	0·410	4·461	0·5420
4·011	0·3449	4·095	0·376	4·421	0·5187
4·002	0·3420	3·989	0·340	4·389	0·5040
3·996	0·3400	3·932	0·316	4·357	0·4881
3·991	0·3380	3·762	0·246	4·277	0·4501
3·987	0·3370	3·611	0·230	4·231	0·4299
3·984	0·3360	3·527	0·210	4·190	0·4130

TABLE 2 — EFFECT OF INCREASE OF VOLTAGE

[Temp. 60°; bath composition, 20% dioxane + 80% H_2O; electrolyte, $Na_2B_4O_7$ + Na_2CO_3]

10 V dc		20 V dc		30 V dc		40 V dc	
ln*I*	Field (V/R)	ln*I*	Field/(V/R)	ln*I*	Field (V/R)	ln*I*	Field (V/R)
4·331	0·499	3·762	0·270	3·785	0·273	3·539	0·215
4·263	0·446	3·689	0·250	3·556	0·220	3·533	0·214
4·190	0·410	3·638	0·240	3·497	0·208	3·454	0·198
4·095	0·376	3·497	0·209	3·430	0·200	3·454	0·196
3·989	0·340	3·491	0·205	3·415	0·196	3·428	0·194
3·932	0·316	3·446	0·199	3·402	0·190	3·418	0·190
3·762	0·246	3·441	0·195	3·388	0·188	—	—
3·611	0·230	3·425	0·189	—	—	—	—
3·527	0·210	—	—	—	—	—	—

The surface microphotographs ($\times 800$) exhibited that with increase in the bath temperature the oxide grains become finer and provide a more uniform coverage for the metal surface.

(iii) *The change in the solvent composition* — The effect of the changes in the solvent composition on the structure of the surface oxide film was also studied using 0, 10, 20 and 30% dioxane-water mixtures as solvent. The increased concentration of dioxane in the solvent mixture did not influence the field versus $\ln I$ plots. However, the surface microphotographs clearly revealed that the fine grained and the smoothest films were formed in 20% dioxane-water mixtures.

The process of formation of oxide consists of two stages, viz. (i) the electrolytic formation of oxides and (ii) the hydration of the surface. Of these two, the formation of anodic oxide does not appear to be highly temperature sensitive, since changes in temperature brought about very small variations in the slopes of field versus $\ln I$ plots. The rate of hydration of the oxide, on the other hand, is known to be temperature dependent and quite fast at higher temperatures[6]. As the hydration process is simultaneous we get more hydrated oxide on the surface at higher temperatures than at lower ones.

Guntherschulze and Betz[7] have shown that under high field the ionic current density i could be written as

$$i = A \exp BE$$

where A and B are constants. Mott and Cabrera[5] while explaining the mechanism of ionic conduction proposed that the ionic current density could be written as

$$i = i_0 \exp \left[-(w - qaE)/kT\right]$$

where w = height of energy barrier over which the ion must pass in order to enter the oxide layer, i.e. activation energy, q = charge on the mobile ions, and a = activation half jump distance, i.e. the distance from the position of minimum to maximum potential energy, k = Boltzmann's constant and T = absolute temperature.

Both the expressions suggest an exponential correlation between the ionic current i and the field 'E'. This has been experimentally established by several workers[4,8,9], who obtained the linear plots of field E against $\ln I$. Further, the Tafel slope values, $dE/d\ln I$, were found to be constant for a given electrolyte but changed with the nature of the electrolyte[3].

Johansen et al.[10] have studied the anodic oxidation of several metals including aluminium in borate electrolytes at low current densities. They report that the films formed were 20 to 100 Å thick, i.e. were of such thickness that the Cabrera and Motts theory[5] would be expected to apply.

In the present investigation at a constant applied voltage the ionic current decreased with increase in resistance of the growing anodic film. This resistance (R) has been calculated at any instance as applied voltage-current I. It will also be seen that as R increases its numerical value will give the extent to which the applied potential will have to be raised in case we want the current to be

TABLE 4 — w-VALUES, $\ln I_0$ UNDER DIFFERENT UNPRESSED VOLTAGES

[Temp., 60°; bath composition, 20% dioxane + 80% water]

Applied voltage	Intercept (C)	Slope	$\ln I_0$	w (eV)
10 volts	2·79	4·14	4·478	0·483
20 volts	2·50	4·44	3·762	0·363
30 volts	2·45	5·00	3·685	0·355
40 volts	2·40	5·52	3·556	0·333

TABLE 5 — w-VALUES AND $\ln I_0$ AT DIFFERENT TEMPERATURES

[Applied voltage, 10 V (dc); bath composition, 20% dioxane + 80% water]

Temp. °C	Intercept (C)	Slope	$\ln I_0$	w (eV)
30	3·10	4·80	4·782	0·513
60	2·79	4·14	4·478	0·483
100	2·42	2·8	4·016	0·459

maintained at the initial level (i.e. constant current condition).

If the resistance R of the anodic film is a measure of the thickness of the film, the ratio V/R will be an index or a measure of the applied field and the plots V/R versus $\ln I$ will have the same significance as the Tafel's plots. And hence during anodization at constant voltage it will be reasonable to assume that the same relationship will exist between the V/R and I as is found between field and I under constant current conditions.

The validity of these assumptions can be tested by evaluating the w values (i.e. the height of the energy barrier). For the straight line plots of V/R versus $\ln I$ the Mott and Cabrera's expression for ionic current can be written as

$$I = i_0 e^{-[w - qaE]/kT}$$

hence

$$\ln I = \ln I_0 - \frac{w}{kT} + \frac{qa}{kT} \cdot E$$

or

$$\ln I = \frac{qa}{kT} \cdot E + \ln I_0 - \frac{w}{kT} \cdot$$

The slope of this linear plot will correspond to qa/kT and the intercept, for $E = 0$, will be equal to $[\ln I_0 - w/kT]$.

For any particular impressed voltage the value of $\ln I_0$ can be calculated from the initial current in the anodizing circuit. It then allows us to calculate the w, value for different experimental runs under different impressed voltages. The w values and those of other relevant parameters, for a representative set of experiment, are included in Tables 4 and 5. These results indicate that w values thus calculated fall within the order of values earlier reported by Nigam and Arora[3] from citric, tartaric, phosphoric and sulphuric acids baths. Further, it will be seen that these fundamentally important parameters can be calculated by this new method, employing a simple anodizing assembly wherein the

use of constant current device has been done away with. Some other important properties of the anodic films formed in the carbonate-borate electrolyte with water-dioxane, mixtures as solvents are being communicated separately.

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