Kinetics of Anodic Oxidation of Zircaloy - 2 in Lithium Salt Solutions

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Anodic oxidation of zircaloy - 2 has been studied at constant current density in Li_2SO_4, $Li_2B_4O_7$, CH_3COOLi and Li_3PO_4 solutions. Thickness estimates were made from capacitance data. The formation rate, ionic current efficiency and differential field were higher when zircaloy - 2 was anodized in Li_2SO_4. The concentration was exponentially related to the breakdown voltage. Radiotracer studies using active sodium sulphate gave insight to the mechanism of film formation.

The kinetics of anodic oxidation of zirconium and its alloys (zircaloy - 2 and zircaloy - 4) were studied in different electrolytes [1-5]. The present work deals with the comparison of the kinetics of anodization of zircaloy - 2 in 0.1M solution of Li_2SO_4, $Li_2B_4O_7$, CH_3COOLi and Li_3PO_4 at a constant current density of 8mA.cm^{-2} and at room temperature.

EXPERIMENTAL

Zircaloy - 2 samples (0.125 mm thick and about 99.7% purity) were supplied by N.F.C., Hyderabad. Specimens were cut with the help of a punch to give a working area of 1 cm^2 and a tag 2 cm long. The tag of the specimen was anodized in 0.1 M Na_2CO_3 (upto 300 V). One end of the tag was filed away to make electric contact. Specimens were chemically polished (in a freshly prepared mixture of one part of HF, 3 parts of HNO_3 and 3 parts of distilled water) and used.

Closed cells of 200 ml capacity were used. The platinum cathode had 30 cm^2 superficial area (to make the double layer capacitance as large as possible). The electrolyte was 0.1 M solution of one of the following salts: Li_2SO_4, $Li_2B_4O_7$, CH_3COOLi and Li_3PO_4. Specimens were immersed vertically in solution from the heavily anodized tag.

Radiotracer studies were made using active sodium sulphate. ^{35}S was received as dilute sodium sulphate solution with an activity of 5 mc/mm. An end-window G.M. tube with an automatic timer and counting equipment were used to measure the ^{35}S content of the film. The Geiger Counting system (GCS 16) had an efficiency of 1% and a dead time of 250 microseconds and due allowance was made for lost counts. The amount of back-scattering was estimated by counting active sodium sulphate on a thin lense tissue stretched across a plastic ring with and without a sheet of zircaloy - 2 in contact with it.

Thinning of anodic films was carried out by mechanical polishing on a glass plate using 0.5 microns diamond paste (supplied by Macneil and Mager Limited, India). Anodic films formed in active sodium

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sulphate were thinned by abrasion with a tissue paper impregnated with the a diamond paste. Uniform layers of the oxide film could be removed this way as judged from the interference colours. After each abrasion, specimens were washed with distilled water and dried. The thickness remaining was estimated from capacitance data and the activity remaining was measured with the end - window G.M. counter.

RESULTS AND DISCUSSION

Zircaloy - 2 specimens were anodized in 0.1M solution of Li_2SO_4, $Li_2B_4O_7$, CH_3COOLi and Li_3PO_4 at a constant current density of 8 $mA.cm^{-2}$ and at room temperature. The plots of formation voltage *vs* time (Fig. 1) were found to be linear upto breakdown voltage in case of CH_3COOLi, $Li_2B_4O_7$ and Li_2SO_4. (Breakdown occurs when a certain range of thickness is reached). Formation rate remains constant in these cases and independent of film thickness. However in the case of Li_3PO_4, the rate of film formation was initially 1.12 V sec^{-1} and beyond 20 volts it falls to 0.31 V sec^{-1}. The plots of reciprocal capacitance *vs* time (Fig. 2) were found to be linear and from these plots the ionic current efficiency and differential field were calculated [2]. The values are summarised in Table 1.

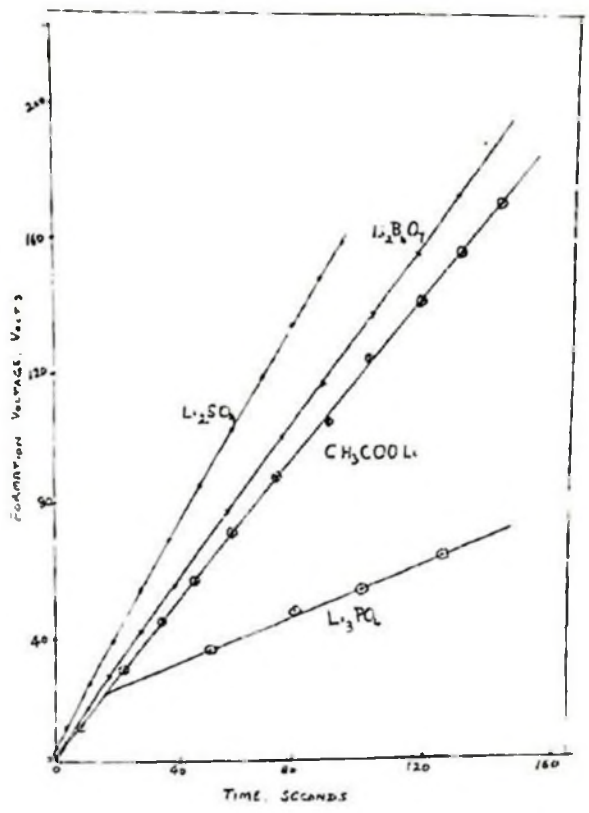


Fig 1 Formation Voltage (V) *vs* Time (Sec) for Zircaloy 2 in 0.1M Electrolytes

The linear plot of 1/Capacitance *vs* time (Fig 2) shows that field strength required to maintain a constant ionic current through the film is independent of the thickness of the film.

Table 1

Anodization Parameters for Zircaloy 2

Electrolyte	Formationrate (V/S)	Current Eff. &	Differential field (mV/cm)
Li_2SO_4	1.80	68.47	6.87
$Li_2B_4O_7$	1.39	56.04	5.71
CH_3COOLi	1.28	54.1	5.07
Li_3PO_4	1.12	49.8	4.63

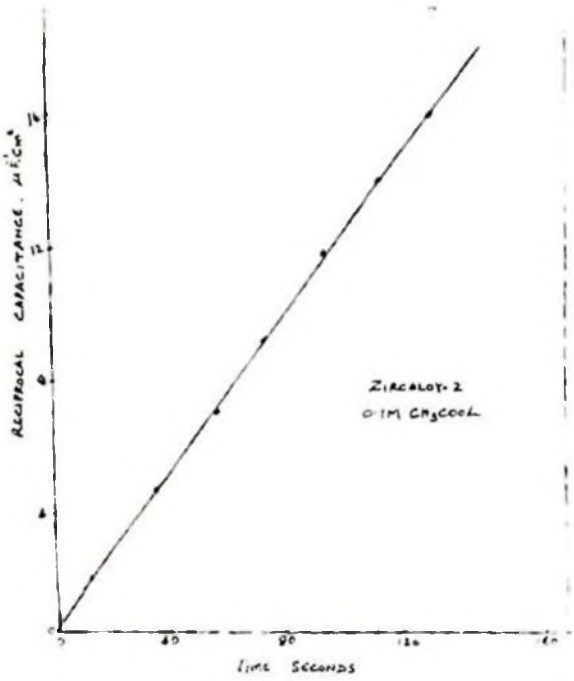


Fig 2 Reciprocal Capacitance *vs* Time (Sec) for Zircaloy 2 in 0.1 M CH_3COOLi

The formation rate, ionic current efficiency and differential field were found to be more when the anodization was carried out in Li_2SO_4 than in the other cases. Rogers *et. al.* [10] demonstrated the incorporation of anions containing carbon, sulphur, and boron in the anodic films formed on Zr in carbonate, sulphate and borate electrolytes. Incorporation of anions from the electrolytes in the anodic films have been studied earlier by Bonter [6] and Shehata [7]. The variation in formation rate, ionic current efficiency and differential field may be attributed to the amount of anion incorporation [9] which might be more in case of anodization in Li_2SO_4 than in $Li_2B_4O_7$, CH_3COOLi or Li_3PO_4.

Breakdown voltage of anodic films on Zr - 2 as a function of CH_3COOLi concentration at a constant c.d of 8 $mA.cm^{-1}$ are given in Table 2. The breakdown voltage is found to fall linearly with log (concentration) of anions present in the electrolyte. (Figur is not given). This behaviour is in agreement with the extensive studies of Gunther-Schulze and Betz [10]. Vermilyea [11] explained this by assuming that the number of electrons starting to move at the film/solution interface is proportional to the ion concentration. Young [2] showed that the breakdown of anodic oxide films on Al, Ta and Ti are associated with crystallization.

Table 2

Anodic Films Formed on Zircaloy-2 in 0.1M CH_3COOLi

Sl.No.	1	2	3	4
Molarity (M)	1.0	0.1	0.01	0.001
Breakdown Voltage (BV)	75	110	160	200

Kadary and Klein [12] observed that when the breakdown rate during the anodic growth of Ta_2O_5, was plotted as a function of oxide thickness at a constant field (F), the breakdown characteristics shift to lower thicknesses for an increase in field or a decrease in temperature. Radiotracer experiments were carried out using active sodium sulphate to know the mechanism of film formation. Anodic films were formed on Zr - 2 in 0.1 M CH_3COOLi on separate samples to a formation voltage of 60 V & 100 V and further anodized successively in 0.1 M $Na_2{}^{35}SO_4$ (actively 5 mc_i/mm) to a formation voltage of 150 V & 180 V. Anodic films formed in these transfers are found to consist of two discrete layers as the kinetics of anodization in Na_2SO_4 are found to be independent whether formed directly on the specimen or on the pre-formed film

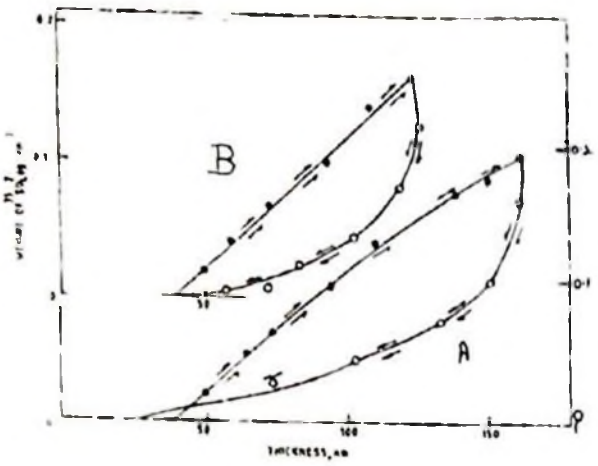


Fig 3 Weight of $^{35}SO_4^{2-}$ *vs* Thickness of the film formed on Zircaloy 2
A Film formed in CH_3COOLi (0-100V) followed by $Na_2{}^{35}SO_4$ (100-180 V)
B Film formed in CH_3COOLi (0-60V) followed by $Na_2{}^{35}SO_4$ (60-150 V)
o Uptake o Distribution

in CH_3COOLi. The rate determining step is thus assumed to be at the oxide/electrolyte interface. The films were later thinned gradually using 0.5 micron diamond paste. The thickness and uptake of S were measured at different stages. The uptake and distribution of sulphate ions *vs* thickness of anodic films are shown in figure 3.

It can be seen that as the outer layers are removed, S content decreases steeply. Thus the distribution of SO_4^{2-} across the oxide is found to be concentrated in the outer layers. The distribution in the inner layers is approximately uniform and in the reverse order of the uptake of $SO_4^{2-}/V/cm^2$. Thus the mechanism of anodic film formation might be *via* interstitial movement [9].

Assuming the films formed are duplex, i.e., the differential field acting in each layer remains the same as when formed individually, the integral field across the whole oxide can be calculated from the equation :

$$F = \underbrace{\frac{V}{D_L + D_{S_1} + D_{S_2}}}_{\text{(Experimental)}} = \underbrace{\frac{F_L D_L + F_{S_1} D_{S_1} + F_{S_2} D_{S_2}}{D_L + D_{S_1} + D_{S_2}}}_{\text{(Calculated)}}$$

Where D_L, D_{S_1}, D_{S_2} are the thicknesses of CH_3COOLi and Na_2SO_4 and F_L, F_{S_1} and F_{S_2} are the differential fields of CH_3COOLi and Na_2SO_4 at D_L, D_{S_1} and D_{S_2}. The experimental values are in coincidence with the calculated values. Hence the fields formed can be considered to be duplex in nature.

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