Duplex Experiments : Transferring the Specimen (Zirconium) from 0.05 M Oxalic Acid to 0.05 M Sodium Sulphate – Its Kinetic and Radio-Tracer Studies Using S^{35}

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THE kinetics of anodic film formation on zirconium have been studied at a constant current density of 4.1mA cm^2 and at room temperature by transferring the specimen from 0.05M oxalic acid to 0.05M sodium sulphate. In these transfers it is found that the kinetics of film formation in the subsequent electrolyte (Na_2SO_4) depend on the thickness laid down in the pre-formed film in oxalic acid. From radio-tracer measurements, the distribution of $S^{35}O_4^{--}$ across the oxide is found to consist of outer highly concentrated layer and a inner uniformly distributed layer of sulphate ions.

THE kinetics of anodic oxidation of zirconium and zircaloy-2 in 0.05 M oxalic acid and in 0.05 M sodium sulphate have been reported in our previous papers[1,2,3,4]. In the present work, duplex experiments were carried cut by transferring the zirconium specimen from oxalic acid to sodium sulphate to investigate the dependence of kinetics of film formation in a subsequent electrolyte i. e. Na_2SO_4 on the pre-formed film in oxalic acid.

EXPERIMENTAL

Zirconium specimens were cut from 0.125 mm thick Van Arkel zirconium (I.M.I) sheet 1 cm^2 working area and with a tag of 2 cms. Specimens were chemically polished and the procedure used was as described in our previous papers[1,2]. Specimens were suspended from heavily anodized tags (to 350 V) and a minimum amount of it was immersed in the electrolyte. The platinum cathode used had a 20 cm^2 superficial area to make the double layer capacitance as large as possible. The electrolytes used were 0.05 M oxalic acid, 0.05 M Na_2SO_4 and 0.05 M $Na_2S^{35}O_4$. Anodic films were formed at a constant current density of 4.1 mA cm^{-2} on separate samples of zirconium in 0.05 M oxalic acid to 40, 80 and 120 V respectively and each was further anodized in 0.05 M $Na_2S^{35}O_4$ to 265 V. Closed cells of 200 ml capacity were used for inactive solutions and the experiments with active solutions i.e., $Na_2S^{35}O_4$ were carried out in a specially designed cell of 20 ml capacity, with a cathode of platinum sheet 1 cm × 3 cm bent into a 'U' shape, each side of which was 1 cm. The anodes were suspended vertically and roughly parallel to the sides of U shaped platinum cathode.

A digital LCR meter (Type VIC 6) built by Vasavi Electronics, Hyderabad, was used at 1 KHz to measure the capacitance data and the thickness of the dielectric were calculated from these, assuming the oxide formed a parallel plate capacitor with a dielectric constant of 24.7[5]. The density of bulk zirconium oxide has been taken as 5.7 g/cm^3. All experiments were carried out at room temperature (300°K),

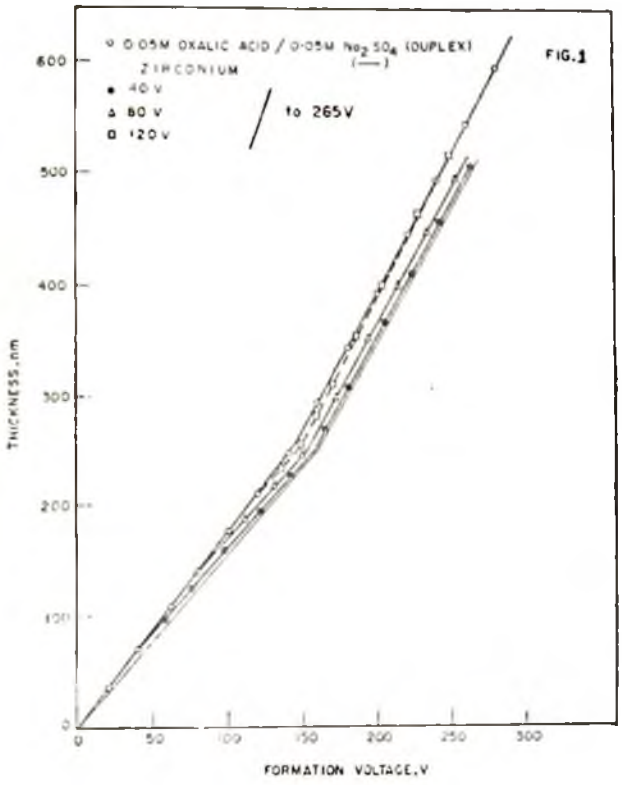
An end-window G.M. counter built by ECIL, Hyderabad, India, with an automatic timer and counting system was used to measure the $S^{35}O_4^{--}$ content of the film. The films were thinned by abrasion with a tissue paper impregnated with 0.5μ diamond paste to examine the distribution of SO_4^{--} impurities in depth. The active electrolyte used was 0.05 M $Na_2S^{35}O_4$ (Specific activity 0,26 mC/mM).

RESULTS AND DISCUSSION

Anodic films were formed on three separate samples of zirconium in 0.05 M oxalic acid to 40, 80 and 120 V respectively and each was then further anodized in 0.05 M $Na_2S^{35}O_4$ to 265 V. In these transfers further growth began almost at the same voltage and there was an instantaneous

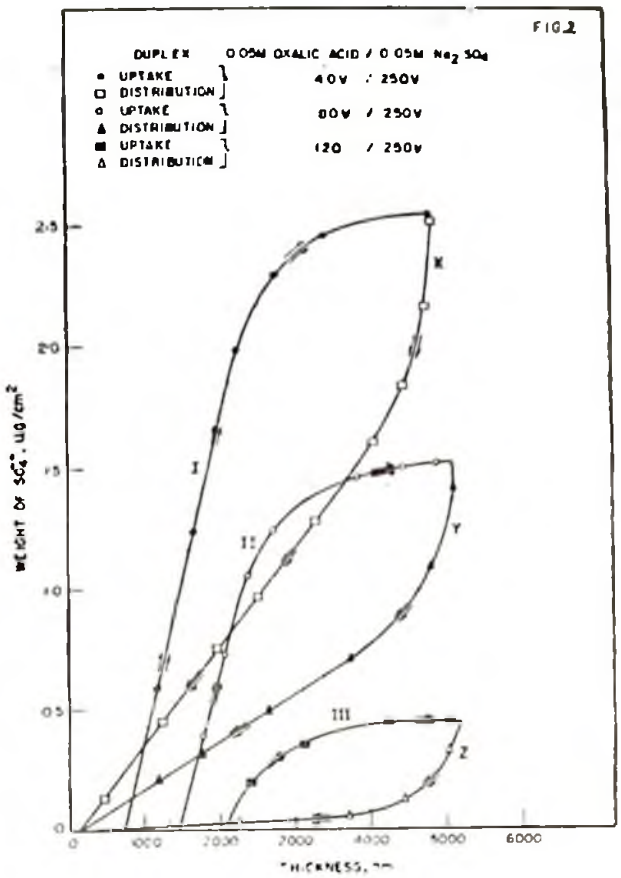
change over in the kinetics of film formation to that of Na_2SO_4.

Plots of thickness vs voltage are shown in Fig. 1. A decrease in differential field was observed in all cases, after formation to a total thickness of about 250 mm. The breakdown voltage was found to be about 265 V in all cases. As in 0.05 M Na_2SO_4 alone[6], the voltage vs thickness plots in Na_2SO_4 are made up of two straight lines and there is a decrease in apparent differential field to $4 \pm 0.1 \times 10^6$ cm/V after forming to a total thickness of 250 nm in oxalic acid and then in Na_2SO_4 (Fig. 1). This was observed



to coincide with the thickness at which the change over in the differential field occurs in oxalic acid alone. A sudden fall in the uptake of SO_4^{--}/V was observed in all cases after forming to a total thickness of 250 nm (Oxalic acid + Na_2SO_4).

Thinning experiments were carried out using 0.5μ diamond paste. Curves x, y and z in Fig 2 show the sulphate ion distribution/cm^2 in depth across the film for the three samples grown partly in 0.05 M oxalic acid and partly in 0.05 M $Na_2S^{35}O_4$. They refer to films grown to 40, 80 and 120 V in 0.05 M oxalic acid and further anodized in 0.05 M $Na_2S^{35}O_4$ to 250 V.



The distribution of SO_4^{--} across the oxide is found to consist of outer highly concentrated layer and the inner uniformly distributed layer of SO_4^{--} ions. However the outer concentrated layer is about 80 to 90 nm thick in all cases. This thickness also corresponds to cubic oxide layer in H_2SO_4[6,7]. The distribution in the outer layer is roughly the reverse of the uptake of SO_4^{--}/V/cm^2 in the initial formation voltage in all the three cases.

The sudden change in the differential field observed at a total thickness of 250 nm laid down in oxalic acid and sodium sulphate can be explained by assuming a fixed maximum ratio of thicknesses of cubic to monoclinic modifications[6,7,8] being reached when formed in sodium sulphate on a pre-formed film in oxalic acid. Hence, from the electrochemical and radio-tracer studies it is concluded that the films do not remain completely as discrete layers and the kinetics of film formation in the subsequent electrolyte do depend on the thickness laid down in oxalic acid in such a manner that at a total thickness of 250 nm the maximum ratio of cubic to monoclinic, (0.515)[6,7,8] is always maintained whether formed in oxalic acid alone or in sodium sulphate on a pre-formed film in oxalic acid.

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REFERENCES

1. M. L. Narayana and K. S. Sastry, *J. Electrochem. Soc. India*, 26-3 (1977) 31.
2. M. L. Narayana and K. S. Sastry, *J. Electrochem. Soc. India*, 27-3 (1978) 153.
3. M. L. Narayana and K. S. Sastry, *J. Electrochem. Soc. India*, 28-3 (1979) 135.
4. K. S. Sastry and P.H.G. Draper, *J. Electrochem. Soc. India*, 24-3 (1975) 121.
5. L. Young *Anodic Oxide Films*, Academic Press, London (1961).
6. K. S. Sastry, *Ph.D. Thesis*, University of London (1971).
7. K. S. Sastry, *J. Electrochem. Soc. India*, 22-3 (1973) 161.
8. P. H. G. Draper and E. A. Kellett (Private Communication).