Dependence of Breakdown Voltage on Anion Concentration in the Electrolyte, Na_2So_4

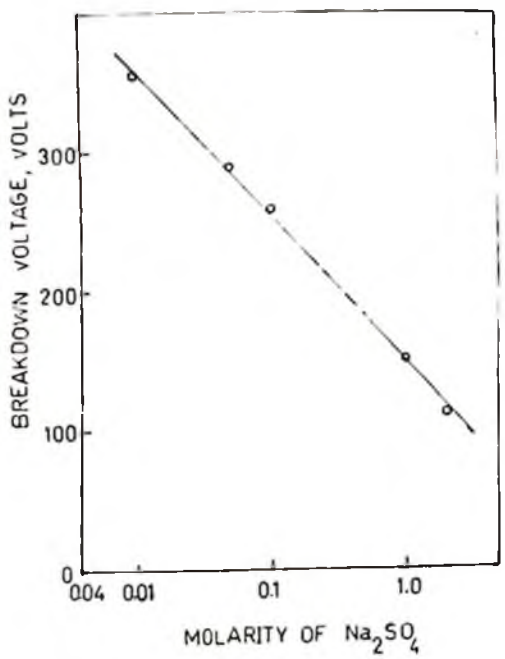
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Anodic films are formed on Zr in Na_2So_4 ranging from 10^{-3}M to 2M concentrations at a constand Current Density of 4mA. Cm.$^{-2}$ and at room temparature. The breakdown voltage is found to fall linearly with log concentration of anions present in the electrolyte.

Anodic films are formed when Zr is anodically polarised in a suitable electrolyte. The formation of the film is normally limited by a 'breakdown', which occurs when a certain range of thickness is reached. This thickness for a given metal etc., is dependent upon temparature and the nature and concentration of the ionic species present in the electrolyte.



Guntherschultze and Betz[1] gave extensive details of this process. As formation voltage is increased, a point is reached where short bursts of gas arise at different sites followed finally by visible sparks and permanent breakdown.

Experimental & Results

Experiments were carried out using 0.125 mm thick, annealed rolled sheet Van Arkel Zirconium of 99.8% nominal purity supplied by Imperial Metal Industries Ltd., Samples used were cut to a 1 cm^2 working area on either side and a tag about 2cm long. Samples were then chemically polished in a freshly made up mixture of one part of HF, 3 parts of HNO_3 and 3 parts of H_2O. Samples were kept in the mixture until brown fumes were evolved, leaving the surface bright, and quenched in concentrated HNO_3. Finally specimens were washed several times with distilled water and dried with tissues.

The tags were heavily anodized at 350v in 0.05M Na_2CO_3 at 4 mA.Cm $^{-2}$ leaving 1 Cm.^{2} working area on either side. A small portion of film towards the terminal end of the tag, was filed away to make electrical contact.

Anodizations were carried out at a constant current of 4MA.Cm.^{2} and the constant current generator was a stabilised power supply, built by GARGYA RESEARCH INSTRUMENTS (NEW DELHI) Anodic films were formed in Na_2SO_4 at various concentrations ranging from 10^{-3}M to 2M at room temparature till the breakdown voltage was reached. The breakdown voltage was found to fall with the increase in concentration of the electrolyte. A log plot of concentration of Na_2SO_4 vs. breakdown voltage gives a linear relationship as shown in figure 1.

Discussion

The breakdown voltage is found to fall linearly with log concentration of anions present in the electrolyte.

This relationship is in agreement with the extensive studies of Guntherschultze and Betz. The breakdown voltage is a function of both the nature and concentration of ions in the electrolyte and perhaps of the conductivity

of the film. The log-dependence upon anion concentraion in the electrolyte has been explained by Vermilyea[2] by supposing that if the number of electrons which start to move at the film-solution interface is proportional to the ion concentration then the spark voltage, will depend the logarithm of the ion concentration in the solution. Young[3] has suggested that breakdown is due to the heat produced by conduction in the electrolyte within the imperfections of the film. O Dwyer has proposed that all dielectric breakdown must be in a sense thermal, Yahalom and Zahavi[4] have recently reported that breakdown of anodic films on Al and Ta is associated with Crystallization.

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