KINETICS OF ANODIC OXIDATION ON Zr AND ZIRCALOY-2 IN 0.05 M SODIUM SULPHATE ELECTROLYTE

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The Kinetics of anodic Oxidation of Zr and Zircaloy -2 have been studied at a constant and varying current densities. Thickness estimates of the anodic films were made from the capacitance data and the differential field and current efficiency were calculated. The differential field of formation, for a given ionic current density was found to be more with Zircaloy-2 than with Zr, whilst the current efficiency With Zr was more than with Zircaloy -2. The parameters were estimated applying the Cabrera-Mott type theory.

The Kinetics of anodic oxidation of zirconium in 0.1M KOH and 0.05 oxalic acid have been reported in our previous papers [1,3]. In the present work an attempt is made to study the kinetics of anodic film formation in 0.05M Na_2SO_4 of Zircaloy -2 and to compare it with those of zirconium[4].

EXPERIMENTAL

Zirconium was of 99.85% nominal purity. The main impurities were hydrogen (<10 ppm), nitrogen (20 ppm) and titanium (30 ppm). Zircaloy-2 was a gift sample from Nuclear Fuel Complex, Hyderabad. The nominal analysis was Cr (500 to 1500 ppm), Fe (700 to 2000 ppm), Ni (300 to 800 ppm), oxygen (1000 to 1400 ppm) and Sn (1.2 to 1.7%). Specimens were cut from thin sheets of 0.125 mm thickness to give working area of 1 cm^2 and with a tag of 2 cms. Chemically polished samples were used as described earlier[3,5]. Anodizations were carried out in 0.05M Na_2SO_4 at various constant current densities and at room temperature in closed cells of 200 ml capacity. Specimens were suspended from the heavily anodized tag (about 350V), the minimum of it being immersed in the electrolyte. The platinum cathode had a 20 cm^2 superficial area to make the double layer capacitance as large as possible. The constant current generator used was a stabilised power source. A universal Impedance Bridge at 1 KHZ was used to measure the capacitance, and the thickness of dielectric was calculated assuming the oxide formed a parallel plate capacitor with a dielectric constant of 24.7[6].

RESULTS AND DISCUSSION

Anodic films were formed on Zr and Zircaloy-2 in 0.05M Na_2SO_4 at various constant current densities ranging from 2 to 8m A/cm^2. The current was interrupted at regular voltage increments to obtain the impedance and there was an interval of about 30 seconds prior to the reading of capacitance. The plots of voltage vs time reciprocal, capacitance vs time and voltage vs reciprocal capacitance were linear below a formation Voltage of 140 V. From the plots, the differential field and ionic current density were calculated. Plots of log ionic current density vs differential field gave a fairly linear relationship with Zr and Zircaloy -2 and they are almost parallel to each other as shown in Fig 1. The linearity of the plots confirms that, to a good approximation, the usual single barrier, empirical equation[7] i. e.

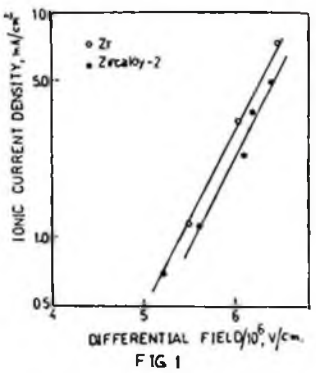


FIG 1

Relationship between ionic c. d. and differential field for Zr and Zircaloy-2.

$$i_i = A_i \exp B_i F \ldots\ldots\ldots (1)$$

is obeyed. In this i_i is the ionic current density and A_i and B_i are temperature-dependent constants for a particular metal. This has been observed for zirconium as reported in our earlier communication[3]. Applying the Cabrera-Mott type theory, assuming that the rate determining step is at the Oxide/Electrolyte interface, the equation is

$$i_i = nvq \left[\exp\text{-}(W - qaF)/kT \right] \ldots\ldots\ldots (2)$$

where n is the number of cations/cm^2 of metal surface able to undergo anodic transfer into the

film = 1.212×10^{15}/cm², ν (nu) is the vibrational frequency of a moving ion = 10^{13}/sec. W is the height of the energy barrier at the metal-oxide interface: T is the temperature, 300°K and q = 2e. The value of q is taken as 2e as anion mobility is predominant for oxide growth on zirconium[8].

Comparing equations (1) and (2)

$$A_i = n\nu q \exp(-W/kT) \quad \ldots\ldots(3)$$

$$B_i = qa/kT \quad \ldots\ldots(4)$$

B_i is an inverse Tafel constant. The parameters obtained are summarized in Table I

Table I. Estimates of Parameters (Control by Oxide/Electrolyte barrier)

Specimen	A_i, A/cm²	B_i, Cm/v	W, eV	a, A°
Zr and Zircaloy-2	3.162×10^{-8}	1.89×10^{-6}	0.93	2.44

The value for jump distance 'a' deduced is larger than the mean separation of oxygen ions in ZrO_2[6], 1.66° A°. Willis et al[9] obtained values the kinetic parameters via constant potential measurements Using 0.25M Na_2SO_4 as electrolyte, the barrier half distance was found to vary between 3.5A° and 4.6A° (q = 4e) with temperature ranging from 6.5° C to 60°C with Zr. Adams et al[10], found using 1 N Na_2SO_4 as electrolyte in constant voltage experiments that 'a' varied from 3.4A° to 4.4A° (q = 4e) with temperature from 6.5°C to 65°C, at high potential formation fields. They deduced a value of 1.04 eV for the activation energy somewhat arbitrarily assuming, however, a value of 2.5A° for the barrier half width. These values of 'W' and 'a' are comparable with the values of 0.93 eV and 2.44A° respectively deduced in the present work.

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