KINETICS OF ANODIC OXIDATION OF ZIRCONIUM IN 0.05M OXALIC ACID

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(Presented at the Conference on Industrial Metal Finishing ; Oct. 1976)

The kinetics of anodic oxidation of zirconium in 0.05M oxalic acid have been studied at constant current density of 4.1 mA/cm^2 and at room temperature. Thickness estimates of anodic films were made from the capacitance data and the differential field and current efficiency were calculated below a formation voltage of 120V.

The kinetics of anodic film formation were also studied at various current densities to investigate the exponential dependence of ionic current density on the field across the oxide. A plot of log ionic current density vs differential field gave fairly a linear relationship. The parameters were estimated applying the Cabrera-Mott theory.

The kinetics of the anodic oxidation of zirconium in different eloctrolytes were studied by Adams et al[1,2], Willis et al [3], Young [4], Charlesby [5] and others and also by us[6,7].

Adams et al[1,2] and Willis et al[3] used Chemically polished specimens which gave higher values of current efficiency at higher current densities.

In the present work the kinetics of the anodic film formation of zirconium were studied at constant current density in 0.05M oxalic acid and at room temperature.

Experimental

Zirconium specimens were cut from 0.125mm thick Van Arkel zirconium (I.M.I.) to give 1 cm^2 working area. Specimens were chemically polished in a mixture of 1 part of HF, 3 parts of HNO_3 and 3 parts of H_2O.

Anodizations were carried out in 0.05M oxalic acid. The constant current generator used was a stabilised power supply, built by GARGYA RESEARCH INSTRUMENTS (New Delhi).

Thicknesses of anodic films formed were measured by impedance method. An Universal Impedance Bridge (Toshniwal) was used to measure the capacitance. The measurements were made at 1kHZ and the thicknesses of dielectric were calculated assuming the oxide formed a parallel plate capacitor with a dielectric constant of 24.7[8]. The density of bulk zirconium oxide has been taken as 5.7 g/cm^3.

Results and Discussion

Anodic films were formed in 0.05M oxalic acid at various current densities ranging from 1 to 10mA/cm^2. The plots of voltage vs time, reciprocal capacitance vs time and voltage vs reciprocal capacitance were linear up to a formation voltage of 120V. From the plots, the differential fields and current efficiencies were calculated and are reported in Table. 1

TABLE—1 Anodic films formed to 120V in 0.05M Oxalic Acid

Total c.d., mA/cm^2	i_i, mA/cm^2	Current effy $=\eta_i$ %	Differential Field/10^6, V/cm
8.2	8.0	97.5	6.00
4.1	3.61	88	5.70
2.5	1.95	78	5.42
1.5	0.95	66.7	5.15
1.0	0.40	40	4.8

A plot of log ionic current density vs differential field gives a fairly linear relationship; the linearity of the plots confirms, to a good approximation, the usual single barrier, empirical equation[9], viz.

$$i_i = A_i \exp B_i F \quad \text{.....(1)}$$

where 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 ziroconium [3,4,10].

Applying the Cabrera – Mott type theory, assuming that the rate – determining step is at the oxide/electrolyte interface, the equation is

$$i_i = n \nu q \exp [-W-qaf/kT] \quad \text{.....(2)}$$

where n, the number of cations/cm^2 of metal surface able to undergo anodic transfer into the film = 1.212×10^{15}/cm^2 ; ν, the Vibrational frequency of a moving ion = 10^{13}/Sec; W, the height of the energy barrier at the metal — oxide interface; T = 300°K; and q = 2e. The value for q is taken as 2e as anion mobility is predominant for oxide growth on zirconium[11].

Comparing equations (1) & (2)

$$A_i = n \nu q \exp (W/KT) \quad \text{.....} \quad (3)$$

$$B_i = qa/KT \quad \text{.....} \quad (4)$$

B_i is an inverse Tafel constant; The parameters obtained are summarized in Table 2.

TABLE—2 Estimates of parameters.

Electrolyte	Formation Voltage	A_i, A/cm²	B_i, cm/V	W, eV	a,Å
0.05M Oxalic Acid	Below 120V	3.31×10^{-9}	2.45×10^{-6}	1.13	3.16

The value of the jump distance, 'a', is larger than the mean separation of the oxygen ions in ZrO_2[8], 1.66 Å.

Willis et al[3] obtained values of the kinetic parameters, vis constant potential measurements. Using 0.25M Na_2SO_4 as electrolyte, the barrier half-distance was found to vary between 3.5 Å and 4.6Å (q = 4e) with temperature from 6.5° to 60°C.

Young[4] found that the field calculated from the optical thickness increased with thickness, despite the fact that the plots of reciprocal capacitance against voltage were fairly linear. He deduced that the values of 'a' and 'W' varied from 2.3 to 3.7 Å (q = 4e) and 1.34 to 1.84 eV respectively with increase in thickness from 222 to 1476 Å.

Charlesby[5] obtained a value of 3.4×0^{6} cm/V for B_i and a deduced value of 2.14 Å for 'a' (q = 4e). Adams et al [1] using 1N Na_2SO_4 as electrolyte in constant voltage experiments found that 'a' varied from 3.4Å to 4.4Å (q = 4e) with temperature from 6.5°A 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 2.5Å for the barrier half-Width. This value is comparable with 1.13 eV, deduced in the present work.

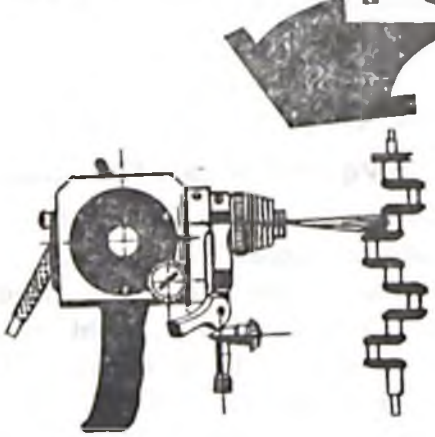
Acknowledgements: The authors wish to thank Prof. T. Navneet Rao, Head, Department of Chemistry for his keen interest.

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