Kinetics of Anodic Film Growth on Zirconium in 0.1 M Ammonium Persulphate

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The kinetics of anodic film growth on zirconium in 0.1 M ammonium persulphate have been studied at a constant current density. Thickness estimates of anodic films were made from capacitance data. The current efficiency and differential field of formation were calculated below a formation voltage of 150 V (240 ± 10 nm).

The kinetics of formation of anodic films in different electrolytes on zirconium were studied by Charlesby(1), Young(2), Adams et al.(3,4), Willis et al.(5) and by us(6,7).

In the present work an attempt is made to study the kinetics of anodic film formation of zirconium in 0.1 M ammonium persulphate at various constant current densities ranging from 2 to 10 mA/cm^2 and at room temperature.

EXPERIMENTAL

Specimens were cut from 0.1 mm thick Van Arkel zirconium (I.M.I) to give one square centimeter working area. The principal impurities were hydrogen (10 ppm), nitrogen (20 ppm) and titanium (30 ppm). Specimens were chemically polished in a mixture of 1 part HF, 3 parts HNO_3 and 3 parts of water, rinsed in concentrated HNO_3 and finally cleaned several times in distilled water. The tags were anodized in 0.05 M Na_2CO_3 to about 350 V and the terminal ends of the tag was filed off for the purpose of electrical contact.

The constant current generator used was a stablised power supply, built by Instruments Techniques Pvt. Ltd., Hyderabad. Digital LCR meter (Type VLCR 6) supplied by Vasavi Electronics, Hyderabad was used for the capacitance measurements. Thickness of the anodic films were estimated from capacitance measurements.

The density and dielectric constant of ZrO_2 were taken as 5.7 g/cc and 24.7 respectively(8).

RESULTS

The kinetics of anodic film growth on zirconium in 0.1 M ammonium persulphate were studied at a constant current density of 6 mA/cm^2 . During the film formation, interference colours were observed and the formation was smooth until the breakdown voltage (200 V) reached.

The plots of formation voltage vs time and thickness vs formation voltage were made up of two

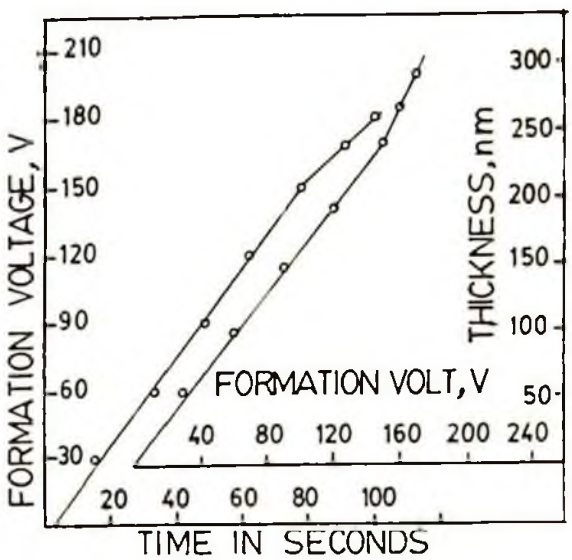


Fig. 1 Formation voltage vs time for the anodization of zirconium in 0.1M ammonium persulphate at 6mA/cm^2

straight lines (Fig. 1) intersecting at about 150 V (240 ± 10 nm). The differential field across the oxide decreased very markedly with the increase in the thickness beyond 240 nm at a constant ionic curent density. The plots of reciprocal capacitance vs time were linear upto the breakdown voltage (200 V or time 100 sec) showing that the ionic current density was constant and the current efficiency was fond to be 90.27%. The film grew initially at a differential field of 6.54 mV/cm but this fell to 3.92 mV/cm beyond a thickness of 240 nm.

Anodizations were also carried out at various constant current denstities ranging from 2 to 10 mA/cm^2 . From the plots of formation voltage vs time, reciprocal capacitance vs time and reciprocal capacitance vs formation voltage, the current efficiency and differential field were calculated and are summarized in Table - 1.

TABLE 1

ANODIZATION OF ZIRCONIUM IN 0.1 M AMMONIUM PERSULPHATE
(THICKNESS FROM CAPACITANCE MEASUREMENTS)

Total current density, mA/cm^2	Ionic Current density mA/cm^2	Current efficiency, η (%)	Differential field, F, mV/cm^2
2	1.30	65.0	5.49
3	2.49	84.0	5.98
4	3.43	85.8	6.36
6	5.42	90.3	6.54
8	7.25	90.7	6.63
10	9.13	91.0	6.87

The plots of log (ionic current density) vs differential field gave fairly a linear relationship. The linearity of the plots confirms, to a good approximation, the usual single barrier, empirical equation (9), viz.,

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

where i_i is the ionic current density, A_i and B_i are temperature dependent constants for a particular metal. This has been observed for zirconium. (2,5,10)

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

$$i_i = n\nu q \exp(-W - qaF/kT) \quad \ldots (2)$$

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; a, the half-jump distance; T = 301°K. The value for q is taken as 2e, as anion mobility is predominant for oxide growth on zirconium(11).

Comparing the equations (1) and (2)

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

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

B_i is an inverse Tafel constant. The parameters obtained are summarised in Table-2.

TABLE 2

ESTIMATES OF PARAMETERS IN 0.1 M AMMONIUM PERSULPHATE (CONTROLLED BY OXIDE/ELECTROLYTE INTERFACE)

Formation voltage	A_i , A/cm^2	B_i , cm/V	a, Å	W, eV
Below 150 V	1.0×10^{-6}	1.4×10^{-6}	1.82	0.93

DISCUSSIONS

In 0.1 M ammonium persulphate at 6 mA/cm^2 , the ionic curent efficiency is virtually constant as the plots of reciprocal capacitance vs time is linear. The relationship between thickness and formation voltage in 0.1 M ammonium persulphate consists of two straight lines intersecting at about 240 nm. Beyond 240 nm, the differential field across the film falls from 6.54 MV/cm to 3.92 MV/cm. This decrease in the field beyond 240 nm is clearly associated with the fall in persulphate ion uptake.

Sastry and Draper (6,13) observed similar behaviour while investigating the kinetics of anodic film formation on zirconium in 0.05 M H_2SO_4 and 0.05 M Na_2SO_4. In both the electrolytes they observed a fall in the differential field of formation at a thickness of 250 nm. From the radio-tracer studies, they concluded that the mechanism of anodic oxidation is via vacancy diffusion of oxygen ions plus some exchange interstitial capture below thickness of 250 nm. The fall in differential field of formation at a thickness of 250 nm was attributed to reaching a fixed maximum ratio of cubic to monoclinic modifications (12).

The value of half-jump distance 'a' deduced in the present work is comparable to the mean seperation of oxygen ions in ZrO_2, 1.66 Å.

Charlesby(1) obtained a value of 3.4×10^{-6} cm/V for B and a deduced value of 2.14 A for 'a' (q = 4e). Adams et al(4) using 1N Na_2SO_4 as electrolyte in constant voltage experiments found that 'a' varied from 3.4 to 4.4 A (q=4e) with temperature from 6.5 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 2.5 A for the barrier half-width.

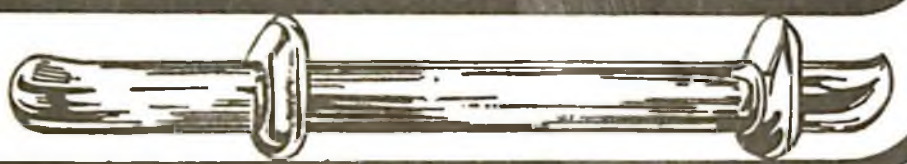
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REFERENCES

1. A. Charlesby, Acta.Met., 1, (1953) 340.
2. L. Young, Trans Faraday/Soc., 55, (1959) 632.
3. G.B. Adams, P. Van Rysselberghe and M. Maraghini, J. Electrochem. Soc., 102, (1955) 502.
4. G.B. Adams, T.S. Lee, S.M. Draganov and P. Van Rysselberghe, J. Electrochem. Soc., 105, (1958) 650.
5. G.C. Willis, G.B. Adams and P. Van Rysselberghe, Electrochim. Acta., 9, (1964) 79,93.
6. K.S. Sastry, J. Electrochem. Soc. India., 22, (1973) 161.
7. A.N. Chary, Ph.D. Thesis, Osmania University (1984).
8. L. Young, "Anodic Oxide Films, (Academic Press, London 1961).
9. A. Guntherschultze and H. Betz, Elektrolytkondensaboren, (2nd Ed) (1952), (Berlin, Herbert, Cram).
10. A.L. Bacarella and A.L. Sutton, Electrochem. Tech., 4, (1966) 117.
11. J.A. Davies, B. Domoij, J.P.S. Pringle and F. Brown, J. Electrochem. Soc., 112, (1965) 675.
12. K.S. Sastry, Ph.D. Thesis, University of London (1971).
13. K.S. Sastry and P.H.G. Draper, J. Electrochem. Soc. India., 24, (1975) 161.

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