Growth Kinetics of Anodic Oxide Films Formed on Zircaloy-2 in Various Electrolytes

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Abstract: The Kinetics of anodic oxidation of zircaloy-2 have been studied at current densities ranging from 4 to 12 mA cm⁻² at room temperature in order to investigate the dependence of ionic current density on the field across the oxide film. Thickness of the anodic films was estimated from capacitance data. The formation rate, current efficiency and differential field were found to increase with increase in the ionic current density for zircaloy-2. Plots of logarithm of formation rate vs. logarithm of current density is fairly linear. From linear plots of logarithm of ionic current density vs. differential field and applying the Cabrera - Mott theory, the half - jump distance (a) and height of energy barrier (W) were deduced.

Keywords: Anodization, Current density, Differential field, Cabrera-Mott theory, Zircaloy-2.

Introduction

When valve metals such as zirconium and its alloys like Zr-2, Zr-4, *etc.* are anodically polarized, interference colored oxide films is formed. These smooth and mechanically perfect anodic films can act as dielectrics in capacitors. The phenomenon of anodic oxidation plays a basic role in micro - circuitry¹ and in thin film methods². Anodic oxide films formed on valve metals are useful in the field of electrical and electronic components (such as capacitors, resistors, dioxides and photoelectric devices), corrosion protection and for decorative purposes. Applications of anodic films have been reviewed³. Guntherschultze and Betz⁴ were the first to investigate the kinetics and mechanism of the anodic oxidation of metals. Temperature and current density were found to exert a marked influence on the anodizing characteristics of metals⁵⁻⁸ such as zirconium, its alloys, niobium, hafnium, titanium *etc.*

Hoar⁹, Young *et al*¹⁰ Vermilyea¹¹ and Diggle *et al*¹² Panasa Reddy *et al*¹³ Lavanya¹⁴ have reviewed the work from various view points. Radiotracer studies were also done by using labeled phosphorous (³²P) to understand the mechanism of anodic film formation¹⁵⁻¹⁸.

In the present work, an attempt is made to study the effect of current density on the kinetics of formation of oxide films on zircaloy-2 in 0.1 M solutions of sulphamic acid, potassium malonate and ammonium hydroxide.

Experimental

The specimen used in the present work were punched from 0.1 mm thick, annealed rolled sheet of zircaloy -2 supplied by the Nuclear Fuel Complex, Hyderabad as a gift sample. The specimens had a working area of 1 cm² on each side and a tag 2 cm long. The specimens were polished to mirror finish by using chemical polishing mixtures, which consisted of HF and HNO₃ in definite volume ratios.

Adams *et al*¹⁹⁻²⁰ & Willis *et al*²¹⁻²² used chemically polished specimens which gave higher values for current efficiency at higher current densities. For anodization, a closed cell of 100 mL Pyrex glass beaker was used. The cathode was a platinum mesh of 20 cm² superficial area, specifically chosen to make the double layer capacitance as large as possible. The constant current generator used was a stabilized power supply unit (Powertronics, Hyderabad) capable of supplying constant current in the 0-100 mA range. Capacitance measurements were made with a digital LCR meter (Vasavi Electronics, Hyd). Current was measured on a digital milliammeter and the potential directly across the cell on a digital voltmeter. Thicknesses of the anodic films were estimated from capacitance measurements. For this, the constant current was interrupted at regular voltage increments (20 V) by reversing a DPDT switch. An interval of about 30s was allowed to lapse prior to reading a capacitance data.

Results and Discussion

Formation rate-current density relationship

The kinetics of the anodic oxidation of zircaloy-2 were studied in 0.1 M solutions of sulphamic acid, ammonium hydroxide and potassium malonate at constant current densities ranging from 4 to 12 mA cm⁻² and at room temperature. The formation rate (dV/dt) was estimated from plots of formation voltage *vs* time drawn at each current density for these electrolytes. The plots of logarithm formation rate *vs*. logarithm current density are found to be linear, as shown in Figure 1.

Values of slopes and intercepts in these plots are given in Table 1. The formation rate is expressed in V s⁻¹ and the current density in mA cm⁻². The linearity between log (dv/dt) and log (i) shows that they are related by the empirical relation.

$$dV /dt = a (i)^b \quad (1)$$

Table 1. Parameters in equation (1) for Zr-2.

Electrolyte	Slope, b	Intercept, log a
Sulphamic acid	0.98	2.24
Ammonium hydroxide	1.24	2.70
Potassium malonate	1.34	3.04

Where, a and b are constants. A similar relationship was given by Vermilyea¹¹ for the dependence of d δ /dt on *i* for tantalum, where δ is the thickness of the oxide film. The theoretical basis for the empirical relationship was given by Ammar and Kamal²³ and Lavrenko and Chekhovskii²⁴. Ammar and Kamal²³ found that the values of slopes were independent of acid concentration in H₂SO₄, HNO₃ and HCl, whilst in H₃PO₄ the value was

found to vary with the acid concentration. The slopes deduced were 1.18 in H_2SO_4 , 1.26 in HNO_3 , 1.16 in HCl , 1.20 in 0.1N and 1N solution of H_3PO_4 and 1.34 in 5N solution. Similar linear relationships were established by Anjaneyulu²⁵ and Shyamala Devi *et al*²⁶ for Ti in electrolytes such as propionic acid and ammonium citrate. Raghunath Reddy *et al*⁷ got similar linear relationships for zircaloy-4 and Niobium in electrolytes such as mandalic acid, ammonium borate and potassium hydroxide

Figure 1. Variation of formation rate (dV/dt) with current density (i)
 B = Sulphamic acid C = Potassium malonate D = Ammonium hydroxide

Ionic current density and differential field strength

The growth kinetics involves the study of variation of differential field with the ionic current density and calculation of kinetic parameters half-jump distance (a) and height of energy barrier (W) assuming that the rate determining step lies at the interfaces or within the bulk of the oxide. In the present study it was assumed that the highest energy barriers are situated at the interfaces and that the Cabrera-Mott type theory was applicable. From plots of formation voltage *vs.* time and reciprocal capacitances *vs.* time, the formation rate (dV/dt), current efficiency (η), Ionic current density (i_i) and differential field ($F.D$) were calculated for zircaloy-2 in the three electrolytes (Table 2, 3, 4). The current efficiency and field strength can be seen to be increasing with the increase in current density. Plots of logarithm ionic current density (i_i) *vs.* differential field ($F.D$) were drawn for each current density and were found to be fairly linear as shown in Figure 2. Using the empirical relation proposed by Guntherschultz and Betz⁴

$$i_i = A_i \exp[B_i F] \quad (2)$$

The temperature dependent constants A_i and B_i were found. Comparing with Cabrera-Mott equation²⁷

$$i_i = n v q \cdot \exp [(-W - q a F) / k T] \quad (3)$$

Where,

n is the number of mobile ions ; q is the charge of the mobile ion ;

ν is the vibrational frequency ; F is the field acting upon a mobile ion
 K is the Boltzmann Constant ; T is the absolute temperature

With equation (1) the expressions for A_i and B_i can be written as

$$A_i = \nu q \cdot \exp[-W/kT] \quad (4)$$

$$B_i = qa / kT \quad (5)$$

Table 2. Data on the anodization of Zr-2 in 0.1 M sulphamic acid.

Current density, i , mA.cm ⁻²	Formation rate, dv/dt, Vs ⁻¹	Current efficiency, η %	Ionic current density, i_i , mA.cm ⁻²	Log. Ionic current density, log i_i	Differential field, F.D, MV.cm ⁻¹
4	0.78	26	1.04	0.017	6.51
6	1.14	36	2.16	0.334	6.83
8	1.60	45	3.64	0.561	7.02
10	1.94	51	5.10	0.707	7.16
12	2.35	58	7.02	0.846	7.34

Table 3. Data on the anodization of Zr-2 in 0.1 M ammonium hydroxide.

Current density, i , mA.cm ⁻²	Formation rate, dv/dt, Vs ⁻¹	Current efficiency, η , %	Ionic current density, i_i , mA.cm ⁻²	log. Ionic current density, log i_i	Differential field, F.D, MV. cm ⁻¹
4	0.44	37	1.48	0.170	5.785
6	0.77	40	2.40	0.380	6.025
8	1.12	43	3.44	0.536	6.189
10	1.62	47	4.70	0.672	6.350
12	2.12	52	6.24	0.795	6.542

Table 4. Data on the anodization of Zr-2 in 0.1 M potassium malonate.

Current density, i , mA.cm ⁻²	Formation rate, dv/dt, Vs ⁻¹	Current efficiency, η , %	Ionic current density, i_i , mA.cm ⁻²	log. Ionic current density, log i_i	Differential field, F.D, MV. cm ⁻¹
4	0.57	39.00	1.56	0.193	5.300
6	1.01	45.50	2.70	0.431	6.026
8	1.51	48.75	3.90	0.591	6.542
10	2.04	54.00	5.40	0.732	6.960
12	2.65	62.40	7.48	0.873	7.387

The value of half-jump distance, 'a' deduced in 0.1 M solutions of sulphamic acid and ammonium hydroxide electrolytes for zircaloy-2 are larger than the mean separation of oxygen ion in ZrO₂ (1.66 Å). The value of 'a' is less in 0.1 M potassium malonate for zircaloy-2. The high value of 'a' found in the case of sulphamic acid and ammonium hydroxide could probably be due to the migration of oxygen ions via interstices, grain boundaries *etc.* in which case the mean jump distance could be more than the interatomic distance. The values of A_i , B_i , W and a are deduced for zircaloy-2 in 0.1 M sulphamic acid, 0.1 M ammonium hydroxide and 0.1 M potassium malonate Table 5.

The differences in the field of formation to grow films²⁸ on zirconium at a constant current density were observed in different electrolytes^{4,29-31}. Radio tracer and Infrared absorption studies have shown that the anions are incorporated as such in the films³²⁻³⁵ and that the nature and concentration of the anions has a marked influence on the ionic and

electronic conductivity of the films³⁴⁻³⁶. Such anions have been found to be absorbed as a consequence of anodization process and concentrate in the outer layers of the film. They affect the percentage ionic current density and hence the energy barrier for ionic movement^{34,35,37}. These observations support the present results.

C=Sulphamic acid E=Potassium malonate B = Ammonium hydroxide

Figure 2. Variation of log ionic current density ($\log i_i$) with differential field (F.D).

Table 5. Anodization of Zr-2 in 0.1 M solutions. Estimation of kinetic parameters of high field ion conduction (Control by oxide/ Electrolyte barrier).

Electrolyte, 0.1 M	A_i , mA.cm ⁻²	B_i , cm.V ⁻¹	Height of the energy barrier, W, eV	Half jump distance, a, ⁰ A
Sulphamic acid	1.267×10^{-11}	2.77×10^{-6}	1.20	3.58
ammonium hydroxide	0.933×10^{-8}	2.06×10^{-6}	1.04	2.67
Potassium malonate	2.395×10^{-5}	0.77×10^{-6}	0.84	1.00

A_i and B_i are temperature dependent constants.

Nageshwar Rao³⁸ obtained a value of 2.81×10^{-6} cmV⁻¹ for B_i and deduced the value of 3.65 ⁰A for 'a' [$q=2e$]. He also obtained a value of 2.6×10^{-9} Acm⁻² for A_i and deduced a value of 1.086 eV for 'W' in 0.1 M sodium salicylate for zircaloy-2. The values obtained for zircaloy-2 in 0.1 M solutions of sulphamic acid, ammonium hydroxide & potassium malonate are comparable with the results of earlier workers³⁸⁻⁴² more over the values of the kinetic parameters 'a' and 'W' obtained in the present work are comparable with the values for zirconium and its alloys.

Young *et al*¹⁰ found that the variation observed in 'W' was largely due to the variation in 'a' value. He further reported that the value 'W' increase with the increase in 'a' value. These observations support the present work results

Conclusions

The kinetic results are seen to have improved with zircaloy-2 in sulphamic acid and ammonium hydroxide as compared to the case in potassium malonate. Log-log relationships are found between the formation rate and current density. An exponential dependence of ionic current density on differential field was observed. The variations in half-jump distance and height of energy barrier are explained in terms of movement of mobile ions via interstices and grain boundaries

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