GROWTH KINETICS OF ANODIC FILM FORMATION OF ZIRCONIUM AND TITANIUM IN 0.1 M SULFOSALICYLIC ACID

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Anodic film formation occurs when the value metals such as Zr and Ti were anodically polarised in a suitable electrolyte. The kinetics of anodic film growth of Zr and Ti in different electrolytes have been reviewed by Young [1] , Hall and Hackermann [2], Johansen et al [3] and also by us [4,5].

In the present work, an attempt is made to investigate the kinetics of anodic film growth on Zr and Ti in 0.1 M sulfosalicyclic acid at various current densities ranging from 2 to 10 mA/cm^2 and at room temperature.

EXPERIMENTAL

Zirconium and Titanium specimens of 1 sq cm area prepared from 0.125 mm thick sheets of zirconium and titanium, supplied by Imperial Metal Industries and Knight Strip Metals Limited (England). The nominal analysis given for Zr was 10 ppm H, 20 ppm N and 30 ppm Ti. Titanium contained 0.025% C and 0.12% Fe. Before anodization,the specimens were chemically polished [4]. The cathode used was a platinum mesh of 20 cm^2 superficial area to make the double layer capacitance as large as possible. Thickness of the anodic films were estimated from the capacitance data. The density and dielectric constant of ZrO_2 was taken as 5.7 g/cc and 24.7; Titanium had the values 3.84 g/cc and 47 [1,6].

The constant current generator used was a stablised power supply unit built by Gargya Research Instruments, New Delhi. The capacitance bridge used was a Digital LCR meter (Type VLCR 6) supplied by Vasavi Electronics, Hyderabad.

RESULTS AND DISCUSSION

In the case of titanium the plots of formation voltage vs time were drawn at each current density. Assuming 100% current efficiency [7] during the initial stages of the film formation, the differential field across the oxide is calculated from the unitary rate[8] $(\frac{1}{i}\frac{dV}{dt})$ at each current density and the details are given in Table 1.

TABLE 1

ANODIC FILMS FORMED ON Ti AND Zr IN 0.1 M SULFOSALICYCLIC ACID

Total current density mA/cm^2	Ionic current density mA/cm^2		Current efficiency %		Differential field, mV/cm	
	Ti	Zr	Ti	Zr	Ti	Zr
2	2	1.481	↑	74.1	3.107	6.520
4	4	3.120	≈100%	78.0	3.492	6.836
6	6	4.836	≈	80.6	3.710	7.010
8	8	6.552		81.9	3.865	7.156
10	10	8.520	↓	85.2	3.975	7.300

In the case of Zirconium the formation voltage vs time, reciprocal capacitance vs time and reciprocal capacitance vs formation voltage were drawn at each current density and from these plots the ionic current efficiencies and the differential fields of formation were calculated and also summarised in Table 1. The plots of log (ionic current density) vs differential field gave fairly a linear relationship in both the cases. The linearity of the plots confirm, to a good approximation, the usual single barrier, empirical equation [9] viz.,

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

Where i_i is the ionic current density, A_i and B_i are temperature dependent constants for a particular metal. Applying Cabrera-Mott [10] type theory, the equation is

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

where 'n' is the number of cations/cm^2 of the metal surface able to undergo anodic transfer into the oxide film ($\neq 4.597 \times 10^{15}/cm^2$ for Ti) and ($\neq 1.212 \times 10^{15}/cm^2$ for Zr); 'ν' the vibrational frequency of a moving ion = 10^{13}/s; 'W' the height of the energy barrier at the metal-oxide interface; k is Boltzmann constant; 'a' is the half-jump disance; T = 300°K and q = 4e (for Ti) [10] and q = 2e (for Zr) [11], since the cation mobility is predominant for oxide growth on titanium and the anion mobility is predominant for oxide growth on zirconium.

Comparing equations (1) and (2)

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

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$$B_i = qaF/KT \quad ...(4)$$

B is an inverse Tafel constant. The kinetic parameters, half-jump distance 'a' and height of the energy barrier 'W' A_i and B_i deduced in the present work are summarised in Table 2.

TABLE 2

ESTIMATION OF PARAMETERS (CONTROLLED BY OXIDE/ELECTROLYTE INTERFACE)

Electrolyte 0.1 M sulphosalicylic acid

Metal	Formation Voltage	A_i A/cm^2	B_i cm/V	w eV	a A^o
Ti	< 45 V	5.0×10^{-6}	1.91×10^{-6}	0.94	1.24
Zr	<140 V	6.21×10^{-9}	1.89×10^{-6}	1.03	2.45

The values of kinetic parameters deduced in the present work are comparable with values obtained by earlier workers [12-15].

ACKNOWLEDGEMENTS

The authors are grateful to Prof. T. Navaneeth Rao, Vice-Chancellor, Osmania University and Prof. B. Sethuram, Head, Department of Chemistry, Osmania University for their keen interest and encouragement. The author (APR) expresses his gratitude to C.S.I.R. for the award of S.R.F.

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