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RESEARCH ARTICLE

Kinetics of Anodic Film Growth on Zr-4 in Ammonium Tartrate

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Abstract: The kinetics of anodic film growth on Zr-4 in 0.05 M ammonium tartrate has been studied at different current densities at room temperature under galvano static condition. The kinetic parameters like rate of film formation(dV/dt), ionic current density(i_i),current efficiency(η) and field of formation(F) were calculated. Using Cabrera-Mott theory the kinetic parameters such as half-jump distance(a), height of the energy barrier(W) were deduced. It is also established an exponential relation between ionic current density(i_i) and field of formation(F).

Keywords: Anodization, Zircaloy-4, current efficiency(η), Cabrera-Mott theory

Introduction

The anodic film formation takes place when a valve metal or their alloy anodized in a suitable electrolytes[1-4]. The anodic oxide film formed is corrosion resistant and mechanically stable. It is used as a dielectric of a capacitor and plays an important role in thin film methods[5]. The anodic oxide films are also used in micro-circuitry and electronic industry[6, 7]. In the present work an attempt is made to study the effect of current density on the kinetics of anodic film growth on Zr-4 in 0.05 M ammonium tartrate.

Experimental

The anodizations were carried out at different current densities ranging from 2 mA/cm^2 to 10 mA/cm^2 at room temperature. The electrolyte used was AR grade ammonium tartrate and the solution is made with double distill water.

The Zircaloy-4 specimens of 1 cm^2 area prepared from 0.1mm thick sheet supplied by Nuclear Fuel Complex, Hyderabad. The nominal purity of Zr-4 was Sn(1.44%), Fe(0.13%), Cr(0.07%) and remaining Zirconium. These specimens were chemically polished in a mixture of 1 part of HF(49%), 3 parts of HNO_3(70%) and 3 parts of distill water and dried. The specimens were suspended vertically in the cell containing 0.05 M ammonium tartrate electrolyte. The anode used was chemically polished Zr-4 and the cathode was Platinum foil of 20 cm^2 superficial area to make the double layer capacitance as large as possible.

The anodizations were carried out using regulated power supply(DC) supplied by Powertronics, Hyderabad. The thickness of anodic films was made from capacitance measurements using digital capacitance meter supplied by Devi Electroncis, Hyderabad, India.

Results and Discussion

Anodization of Zr-4 was carried out in 0.05 M ammonium tartrate at different current densities, *i.e.* 2, 4, 6, 8 and 10 mA/c.m^2 at room temperature. The chemically polished Zircaloy-4 specimens were used as anode and Platinum foil of 20 mA/cm^2 were used as cathode and the electrolyte is 0.05 M ammonium tartrate. During the anodization the reaction that occurs at anode[8] is

$$Zr + 2\,H_2O \rightarrow ZrO_2 + 4H^+ + 4e^-$$

The rate of film formation(dV/dt), ionic current density(i_i), current efficiency(η) and field of formation(F) were calculated from the plots formation voltage(V) *vs*. time(t), reciprocal capacitance (1/C) *vs*. time(t), and reciprocal capacitance(1/C) *vs*. formation voltage(V) shown in Figure 1-3 and their values are reported in Table 1.

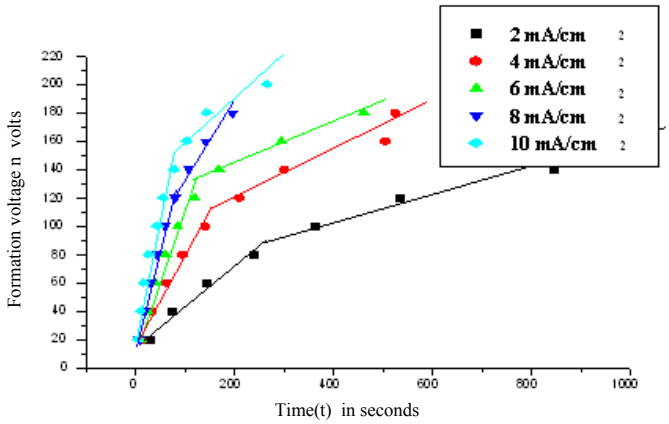

Figure 1. The plot of formation voltage(V) *vs*. time(t)

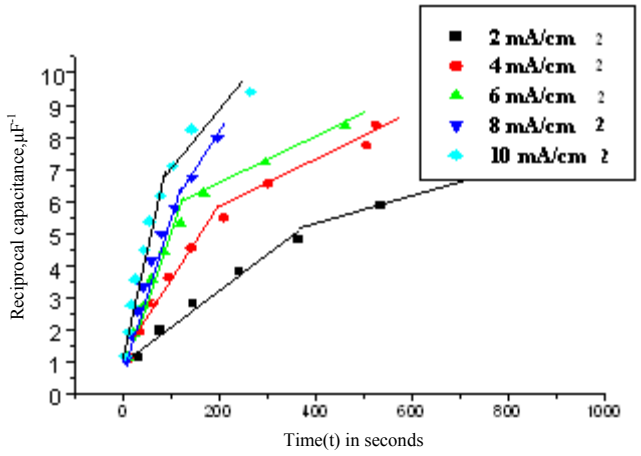

Figure 2. The Plot of reciprocal capacitance(1/C) *vs*. time(t)

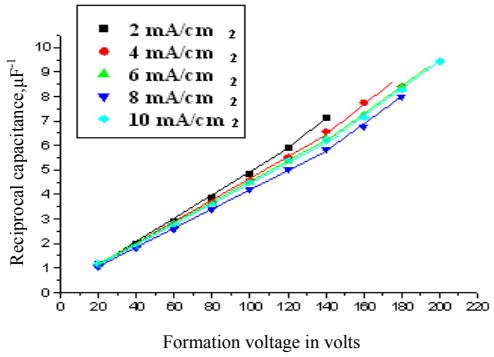

Figure 3. The plot of reciprocal capacitance(1/C) *vs*. formation voltage(V)

Table 1. Effect of current density on the anodization of zircaloy-4 in 0.05 M ammonium tartrate

S.No	Current density mA/cm^2	Formation rate(dV/dt) V.s^{-1}	Field of formation(F) MV/cm	Current efficiency η, %
1	2	0.182	4.66	40.23
2	4	0.645	5.20	42.90
3	6	0.96	5.32	53.30
4	8	1.4	5.87	61.62
5	10	2.85	6.12	94.38

The growth kinetics involves the study of variation inionic current density(i_i)with the field of formation(F) and calculation of kinetic parameters half-jump distance(a) and height of the 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 barrier is situated at the interfaces and the Cabrera-Mott theory was applicable.

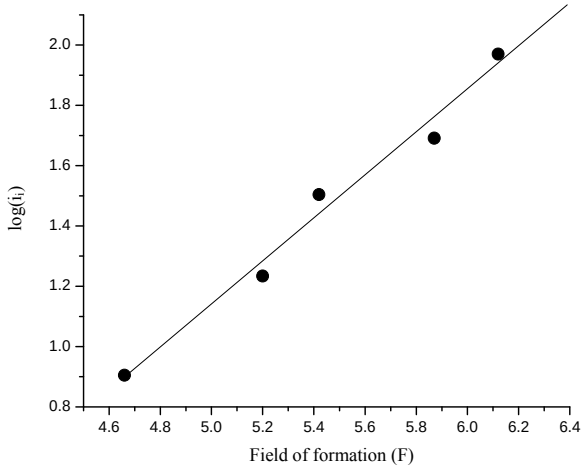

Figure 4. The plot of log(i_i)*vs*.field of formation (F)

The plot of log i_i *vs*. field of formation(F) gave fairly a linear relationship shown in Figure 4. The linearity of the plots confirms to a good approximation, the usual single barrier empirical equation[9] is

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

Where, A_i and B_i are inverse Tafel constants and temperature dependent constants for a particular metal. This has been observed for Zr[10]. Applying Cabrera-Mott theory assuming the rate determining step is at the oxide/electrolyte interface, the equation is

$$i_i = nvqexp\ –(W–q.a.F/k.T) \quad (2)$$

Where n = the number of cations /cm^2 of metal surface able to undergo anodic transfer into the film.ν = Vibrational frequency of ion from equation 1 and 2,

$$A_i = nvqexp – (W/k.T).$$

$$B_i = q.a/k.T.$$

The kinetic parameters half-jump distance(a) and height of the energy barrier(W) were deduced and reported in Table 2. The above observed kinetic parameter values are comparable with the earlier workers[11-13].

Table 2. Estimation of kinetic parameters of Zr-4

A_i $mA.cm^{-2}$	B_i $cm.V^{-1}$	Height of the energy barrier (W), eV	Half jump distance(a), A^0
$5.750x10^{-4}$	$1.616x10^{-6}$	0.770	2.095

Conclusion

It has found that the rate of anodic film formation, current efficiency and field of formation increases with the increase in current density. The kinetic parameters like half-jump distance and height of the energy barrier values are found to be comparable with earlier workers.

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