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**TEMPERATURE DEPENDENCE OF TAFEL
SLOPE IN THE FORMATION OF VERY THIN
ANODIC OXIDE FILMS ON NIOBIUM**

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TEMPERATURE DEPENDENCE OF TAFEL SLOPE IN THE
FORMATION OF VERY THIN ANODIC OXIDE FILMS ON NIOBIUM

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ABSTRACT

A kinetic study was made of the formation of very thin anodic oxide films on niobium at constant current over the temperature range -10 to 70°C .

Formation voltages were limited to the range below the oxygen evolution potential to eliminate possible interaction of an electronic component of the current with the measured formation field.

It was found that the measured temperature dependence of Tafel slope agreed with that predicted by the theory of Mott and Cabrera. Using this theory, a zero field interfacial barrier height of 1.19 ev and a half-jump distance of $2.40 \text{ \AA}$ were obtained.

Values of the differential formation field are reported at current densities of 1000 , 100 , 10 and $1 \mu\text{a}/\text{cm}^2$ at ten degree intervals over the temperature range studied.

INTRODUCTION

Several investigators (1), (2), (3), working with tantalum, niobium, and zirconium, respectively, have reported an essentially temperature-independent Tafel slope in the kinetics of formation of anodic oxide films on these metals.

The simple single-barrier theory of Mott and Cabrera (4), (5) is therefore not in agreement with their results, but Dewald's theory (6) which incorporates the assumption of ionic space charge formation in the oxide film is capable of explaining their results.

These investigators worked with oxide films ranging in thickness from several hundreds to several thousands of angstroms. Under these conditions it is probable that a space charge is established in the steady state; some experimental evidence for the presence of space charge has been obtained by Young (2).

The Mott and Cabrera theory for formation of very thin oxide films on metals contains the assumption that no space charge is established in very thin films ($\leq 100 \text{ \AA}$). With the additional assumptions that the rate determining step in the formation of the oxide is the high-field migration of metal ions from active surface sites on the metal across a metal-oxide interfacial potential energy barrier of height, Φ , and half-jump distance, b , into interstitial positions in the insulating oxide film, the following equation is derived:

$$F = \frac{\Phi}{bq} + \frac{kT}{bq} \ln (I/A_0) \quad (1)$$

where F is the electrostatic field acting across the oxide film,

q is the charge per metal ion,

I is the ionic current density,

m_s is the surface concentration of metal ions at active surface sites on the metal,

ν_s is the vibrational frequency of a surface metal ion

and $A_0 = q m_s \nu_s$.

The aim of the present work was to test this theory with an applicable system, namely, for the growth of very thin anodic oxide films in which the metal ion is the mobile species in an otherwise insulating film.*

*It is assumed that the niobium ion, because of its small size, is the mobile species in the oxide film (2). The glassy film has an extremely low electronic conductivity (2).

EXPERIMENTAL

The experimental techniques employed in this work have been described previously (7), (8).

Electrodes were made up from half-inch annealed niobium rod (Fansteel research grade) cut into half-inch lengths, and each fitted with a vertical brass rod for handling and electrical contact. This assembly was then masked with six individual coatings of baked Formvar enamel. The plane circular face of each electrode was exposed by abrasion, to give a nominal area of 1.265 cm^2 .

Electrode surfaces were prepared initially on a metallographic polishing wheel with #280 and #600 grit aluminum oxide abrasive slurries and finished with Linde B polishing alumina, to a highly reflecting surface. Electrodes were repolished after each run with polishing alumina.

The electrolyte was made up of 0.1 N sulfuric acid in 35% ethyl alcohol. This electrolyte was also used in the mercury-mercurous sulfate reference electrode. The solution was stirred mechanically during each run and renewed every eight hours.

Temperature was regulated to within $\pm 0.1^\circ \text{C}$ over the range -10 to 70°C with a Wilkens-Anderson refrigerated constant temperature bath.

Current densities from 1 to $100 \mu\text{a}/\text{cm}^2$ were regulated to within $\pm 0.5\%$ with an electronic current regulator described previously (9). Current density of $1000 \mu\text{a}/\text{cm}^2$ was regulated with a regulator described by Teeter (10).

Current was measured to within 0.5% with a Weston precision low resistance microammeter, model 627. Voltage was recorded on a Leeds and Northrup AZAR recorder using their model 7664-N electronic millivoltmeter as a high-input-impedance preamplifier.

Runs made at $1.0 \mu\text{a}/\text{cm}^2$ were obtained by first polarizing at $100 \mu\text{a}/\text{cm}^2$ and then dropping back to $1.0 \mu\text{a}/\text{cm}^2$ on the same electrode surface. It was observed that there was considerably more scatter among the individual formation rates for these runs than for runs made at higher current densities.*

All voltage measurements were limited to the range below the potential for reversible evolution of oxygen. By restricting voltage measurements to this range, possible complications involving the action of electronic current on the observed field are avoided, since the ionic current efficiency is then unity.

* When making a $1.0 \mu\text{a}/\text{cm}^2$ run the electrode is immersed continuously for an interval of more than an hour. At the higher temperatures it became necessary to recoat the electrode on one occasion because gross leakage had developed between the enamel mask and the rim of the electrode face. Slight leakage of this sort would give field values that were too low at the higher temperatures. The $1.0 \mu\text{a}/\text{cm}^2$ runs would be affected to the greatest extent, because of the protracted immersion times required and the greater percentage effect for a given leakage.

RESULTS

If equation (1) is obeyed, a plot of field versus absolute temperature should be linear for constant current runs, and the slopes of the regression lines should increase with increasing current density. In addition the lines should extrapolate to a common intercept, Φ/bq , at the absolute zero of temperature.

Equivalent statements are that the Tafel slope, $[\partial F / \partial \ln I]_T$, should vary in direct proportion to the absolute temperature, or that the half-jump distance, b , should remain constant with temperature.

The results of this investigation are presented in Table I and in Figure 1.

Each point is the average of at least five individual runs. The lines shown are the least square regression lines. Equations for these lines, with standard deviations of slopes and intercepts are as follows:

$$F_{1000} = (9.88 \pm 0.16 \times 10^6) - (1.65 \pm 0.06 \times 10^4)T$$

$$F_{100} = (9.91 \pm 0.27 \times 10^6) - (1.80 \pm 0.09 \times 10^4)T$$

$$F_{10} = (10.00 \pm 0.26 \times 10^6) - (2.02 \pm 0.09 \times 10^4)T$$

$$F_1 = (11.15 \pm 0.44 \times 10^6) - (2.59 \pm 0.15 \times 10^4)T$$

The half-jump distance, b , was calculated from Tafel slopes (obtained from the regression lines as $(\frac{F_{1000} - F_{10}}{4.606})$, assuming a pentavalent niobium ion. Values of b so obtained ranged from 2.44 to 2.36 Å, with a mean of 2.40 Å.

TABLE I

Variation of Field with Current and Temperature in the Formation of Very Thin Anodic Oxide Films on Niobium.

$T^{\circ}K$	$F_1 \times 10^{-6}$ (volts cm^{-1})	$F_{10} \times 10^{-6}$ (volts cm^{-1})	$F_{100} \times 10^{-6}$ (volts cm^{-1})	$F_{1000} \times 10^{-6}$ (volts cm^{-1})
263	4.19 ± 0.05	4.62 ± 0.03	5.09 ± 0.03	5.53 ± 0.03
273	4.06 0.05	4.47 0.01	4.97 0.04	5.41 0.05
283	3.92 0.03	4.32 0.02	4.89 0.01	5.17 0.02
293	3.67 0.02	4.09 0.03	4.73 0.02	4.97 0.01
303	3.23 0.04	3.97 0.02	4.46 0.01	4.88 0.01
313	3.03 0.06	3.78 0.01	4.17 0.01	4.75 0.04
323	2.90 0.07	3.51 0.01	4.07 0.01	4.59 0.01
333	2.51 0.09	3.23 0.01	3.87 0.01	4.38 0.01
343	2.12 0.06	3.01 0.02	3.75 0.02	4.17 0.01

(Oxide density, $5 \text{ gm cm}^{-3}(2)$)

Using the mean half-jump distance, $2.40 \text{ \AA}$, and the mean intercept of the field-temperature regression lines for the three highest currents, $9.91 \times 10^6 \text{ volts cm}^{-1}$, the interfacial barrier height, Φ , is 1.19 ev.

From the slopes of the regression lines at each current density, A_0 can be determined. The resulting values are 1.0, 0.9, 1.9 and $500 \times 10^7 \text{ amp cm}^{-2}$, in order of decreasing current density.

Taking $m_s \leq 8 \times 10^{14} \text{ atoms cm}^{-2}$ and $\nu_s = 10^{13} \text{ sec}^{-1}$ (2), one computes $A_0 \leq 6 \times 10^9 \text{ amp cm}^{-2}$, which is satisfactory, since m_s may be considerably less than the value estimated from the density of the metal.

DISCUSSION

The values of differential formation field reported in Table I are in agreement with those of Young (2), who worked with chemically polished electrode surfaces and high-voltage films.

The half-jump distance of 2.40 Å reported here is much smaller than the 4 Å value reported by Young (2) for high voltage films. The smaller value is the more reasonable, however, in view of the probable lattice parameters involved.

Runs taken at the lowest current density were not used in evaluating ϕ and b . Considerably less precision was obtained with these runs, both individually and in the fit to the regression line.

For the remaining runs, variation in the slopes of the regression lines with current density are of the same magnitude as standard deviations of slope. The three intercepts, however, all agree within their respective limits of error.

Unfortunately, the precision obtained in this work is not as good as that for equivalent measurements on high-voltage films (2). Nevertheless, it is felt that the present work is significant and that the single-barrier theory of Mott and Cabrera is adequate to explain present results for anodic growth of very thin niobium pentoxide films.

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Fig. 1 Temperature dependence of field at 1000, 100, 10 and $1 \mu\text{a}/\text{cm}^2$.