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ELECTROCHEMICAL MEASUREMENTS ON NIOBIUM AT ELEVATED TEMPERATURES

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Electrochemical Measurements on Niobium at Elevated Temperatures

H. S. Gadiyar, A. L. Bacarella, A. L. Sutton

The anodic oxidation properties of niobium have been studied by many investigators¹⁻⁹ at either 25°C or up to 100°C, where the thin films formed have been analyzed as homogeneous dielectrics. A preliminary investigation on the electrochemistry of film formation on chemically polished Nb at 200°C has been made and is reported.

Experimental.

A cylindrical type electrode 2.25" (long), ~0.11" (dia.) was prepared from an electron beam melted ingot of purity greater than 99.9%. The specimen was first mechanically polished up to 600 grit emery paper, thoroughly degreased and etched in a 5:2:2 (vol) solution of H₂SO₄ (95%), HNO₃ (70%) and HF (48%) to obtain a bright surface. It was then washed in running distilled water before being introduced into the cell. The cell used for measurements has been described by Bacarella.¹⁰

The measurements included current-voltage characteristics, and rate of film growth at constant anodic potential of + 0.1V (vs Pt/O₂) as a function of time at 200°C in oxygenated* 0.05M K₂SO₄ and H₂SO₄ solutions. Also capacitance measurements were made during film growth and AC impedance studies of the film were made at room temperature following the high temperature exposure.

Results.

The passive region on the niobium electrode at 200°C was determined from current-voltage measurements over a range of potentials (- 0.35V to

* 250 psig O₂ at room temperature.

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+ 0.8) using the potentiostat.¹¹ The passive regions found after 70 and 1,375 min of film growth at the constant anodic potential are shown in Fig. 1. Above + 0.1V (vs Pt/O₂) the film growth in the anodic region was produced with 100% efficiency.

The rates of film growth at constant anodic potential of + 0.1V (vs Pt/O₂) in oxygenated 0.05M K₂SO₄ and 0.05M H₂SO₄ solutions at 200°C are plotted in Fig. 2. The thickness of the film was calculated by integrating anodic current and by assuming $1 \text{ amp} \cdot \text{min}/\text{cm}^2 = 4.8 \times 10^3 \text{ } \mu\text{gm of O}_2$ and $1 \text{ } \mu\text{g O}_2/\text{cm}^2 = 70 \text{ } \text{\AA}$ of Nb₂O₅ film (using the density of Nb₂O₅ - 4.57 gm/cm³). An initial thickness of 70 Å was assumed to be formed during heating up process.

The capacitances measured by pulse technique¹¹ are presented as a function of time and integrated thickness in Table 1. The interference color of a corroded specimen at the end of the experiment was compared with anodic films formed at 25°C assuming thickness of 26.7 Å/volt.⁶ The thickness observed from comparison of color (Appendix 1 and Table 1) was found to be lower than that obtained from integrated thickness for the specimen corroded in K₂SO₄ solution. In the case of the specimen corroded in H₂SO₄ solution, white oxide was observed. The capacitance measured as a function of temperature after corroding the specimen in 0.05M K₂SO₄ for 5,620 min at constant potential + 0.1V (vs Pt/O₂) at 200°C is presented in Table 2.

After completion of the high temperature exposures, the AC impedance characteristics of the specimen corroded in K₂SO₄ were determined. The specimen was removed from the T1 cell, immersed in 0.05M K₂SO₄ in a glass cell at room temperature, and using a gold tube as a subsidiary electrode

C_s and loss tangent as a function of frequency were measured using a General Radio 1615 A capacitance bridge. The exposed area of the specimen was 0.55 cm^2 . The data obtained are plotted in Figs. 4(a), (b) and (c).

Discussion.

During film formation in $0.05\text{M K}_2\text{SO}_4$ at 200°C (curve 1, Fig. 2), the rate steadily decreased first up to about 100 min and then became somewhat steady, changing from 1.0×10^{-6} to $5.5 \times 10^{-7} \text{ amp/cm}^2$ from 110 to 5,600 minutes. The fact that rates somewhat level off after 100 min implies either of these possibilities - existence of porous film, the dissolution of the film at the outer surface, or transformations occurring in the oxide film. Using the reciprocal capacitance, which is a function of film thickness, and the rate of film growth, the data (Table 1A) have been analyzed for kinetics of film growth; the growth does not follow logarithmic, cubic or hyperbolic sine function relationships. Also on plotting integrated thickness vs $1/c$, no linear relationship was observed. The thickness shown by the color at the end of the run was less than the integrated thickness. This again is consistent with formation of a porous film or film dissolution. However, except for the initial point, a straight line behavior (Fig. 3) is observed on plotting the rate vs capacitance (which is a function of reciprocal film thickness). This shows that the thickness corresponding to measured capacitance can be expressed by parabolic kinetics of film growth.

The corrosion rates (at anodic potential + 0.1V) in $0.05\text{M H}_2\text{SO}_4$ (Fig. 2, curve 2) decreased to about $3.2 \times 10^{-6} \text{ amp/cm}^2$ after 60 to 70 min exposure at 200°C , remained steady in the region for sometime up to

Table 1

Film Growth Rate, Capacitance Per Unit Area and Total Integrated Thickness
as a Function of Time for Niobium
Temperature of Corrosion = 200°C.

A = 0.05M K ₂ SO ₄ + 250 psig O ₂				B = 0.05M H ₂ SO ₄ + 250 psig O ₂			
Time	Film Growth	Capacitance	Total	Time	Film Growth	Capacitance	Total
(min)	Rate (γ)	per unit	Integrated	(min)	Rate (γ)	per unit	Integrated
	amp/cm ²	Area	Thickness		amp/cm ²	Area	Thickness
		(μf/cm ²)	(X _T) _Å			(μf/cm ²)	(X _T) _Å
20	4.95x10 ⁻⁶	3.96	134	20	6.62x10 ⁻⁶		143
120	9.74x10 ⁻⁷	3.24	208	50	3.42x10 ⁻⁶		194
350	7.10x10 ⁻⁷	2.57	273	70	3.23x10 ⁻⁶	4.96	216
1470	5.96x10 ⁻⁷	2.41	519	380	3.05x10 ⁻⁶	4.68	543
3010	5.48x10 ⁻⁷	2.23	815	700	8.54x10 ⁻⁶		737
4190	5.27x10 ⁻⁷	2.22	1023	1600	1.00x10 ⁻⁵	6.97	1300
5620	5.44x10 ⁻⁷	2.10	1273				

[The observed thickness from the color after 5,620 min corrosion was between 700 and 1000 Å]. [White oxide was observed on the specimen].

around 300 min, and then again increased to values of 1×10^{-5} amp/cm² at 900 to 1000 min exposure. Capacitance values also decreased for around 500 min and then increased at 1000 min (Table 1B). White oxide was observed on the specimen on examining after 1,600 min corrosion. These results indicate breakdown of the film after short exposure in the H₂SO₄ solution.

The AC impedance results correspond to straight line behavior in plots of $1/C_s$ vs $\log_{10} f$, $\tan \delta/C_s$ vs f and R_T vs $1/f$ as shown in Figs. 4 (a), (b) and (c). The ratio of the slopes of the $1/C_s$ and R_T plots was 9.4 (close to the value of 9.2 predicted by Young² in his studies on various anodic oxide films). The $\tan \delta$ values for the film varied from 0.234 at 1 KHz to 0.173 at 10 KHz. These values are higher than those observed for ZrO₂ films. (Values between 0.03 and 0.04 were observed for ZrO₂ films for X_T between 1000 Å to 1800 Å). The results of the plots indicate that the oxide has good dielectric properties as discussed by Young.¹ However, lower frequency measurements would be required to establish whether pores were present.

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Table 2

Capacitance Per Unit Area as a Function of Temperature. Film Grown in
 0.05M K_2SO_4 + 250 psig O_2 (Thickness $X_T \sim 1000 \text{ \AA}$) at Constant
 Anodic Potential + 0.1V vs Pt/ O_2 for 5,620
 Minutes.
 Temperature = 200°C
 (Measured in the Ti Cell by Pulse Technique)

Temperature (°C)	Capacitance per Unit Area $\mu f/cm^2$ (calculated from total surface area 4.92 cm^2)
198	2.10
186	2.08
180	2.07
175	2.01
170	2.00
160	1.985
146	1.98
133	1.975
58	1.75
40	1.69
25	1.67

APPENDIX I

Colors observed during anodic oxidation of Nb Specimen in 0.5%

K_2SO_4 Solution

<u>Color</u>	<u>Formation voltage</u>
Gold	10V
Straw	13
Purple	17.5
Blue	20
Very Light Blue	30
Pale Gold	40
Light Gold	45
Deep Gold	55
Burgundy	60

Thickness $\text{\AA}$ per volt = 26.7.

(Obtained by wt gain measurements)

(Colors were obtained by R. E. Pawel, private communication).

Fig. 2. Corrosion Rate (r) vs. Time (t).

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Niobium; Films grown at constant anodic potential + 0.1V vs Pt/O₂.

1. $\Theta = 0.05M K_2SO_4 + 250$ psig O₂; 2. $\bar{A} = 0.05M H_2SO_4 + 250$ psig O₂; Temperature = 200°C.

Fig. 3. Corrosion-rate (r) vs. capacitance (c, μf) Niobium metal; Film grown at constant anodic potential + 0.1V vs Pt/0.5M K_2SO_4 ; Temp. = 200°C

Fig. 4(a) $1/C_s$ as a function of frequency for Nb oxide film X_T 700 Å

Fig. 4(b). $\tan \delta / C_s$ as a function of f for Nb_2O_5 film formed by anodic film growth at 200°C in $0.05M K_2SO_4$
 (at $+0.1V$ vs Pt/O_2) (Area measured = 0.55 cm^2) 100 mv amplitude.

Fig. 4(c). R_T as a function of $1/f$ for Nb_2O_5 X_T 700 Å. Measured in 0.05 M K_2SO_4 at electrolyte at 25°C; glass cell.

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