27 cup
.5 $ NTIS

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OXIDATION OF THORIUM IN OXYGEN, HUMID AIR, AND HUMID NITROGEN

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OXIDATION OF THORIUM IN OXYGEN, HUMID AIR, AND HUMID NITROGEN

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(Presented at the 15th meeting of JOWOG-12, June 18-21, 1974,
AWRE, Aldermaston, England)

ABSTRACT

The oxidation of two different grades of thorium, each with two different surface treatments, by water vapor at a pressure of 13.33 kPa has been studied in both air and nitrogen between 353 and 415 K. The dependence of the oxidation rates on the partial pressure of water vapor at 415 K was also investigated for these two grades of thorium.

The oxidation of the lower-purity, arc-melted thorium was studied in 6.66 kPa oxygen between 373 and 433 K. The dependence of the oxidation rate on the partial pressure of oxygen was determined at 415 K for the arc-melted thorium.

Experimental: Thorium, like many metals, corrodes when exposed to oxygen or moist gases. An understanding of the thorium water-vapor reaction and the oxidation of thorium is essential before thorium can be used in nuclear applications in the presence of oxygen and/or water vapor.

The flow corrosion test apparatus used to test the two grades of thorium in a stream of moist gas has been previously documented.[1] It consisted of a heated test chamber capable of holding six samples suspended in the flowing test gas, a gas humidifier, and an analytical balance. In the static system, used for the studies in pure oxygen, the sample was suspended from a recording thermobalance

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[1] C. A. Colmenares, D. R. McKenzie, and T. E. Shell, J. Phys. E: 6, 1121 (1973).

in a thermostatically controlled test chamber. The entire system, including the thermobalance, was evacuated to 480 μPa before the test gas was introduced.

The high-purity electron-beam-melted (EB) thorium contained less than 600 ppm impurities, while the lower-purity, arc-melted (AM) thorium contained 3500 ppm impurities. Prior to testing, the "degreased" thorium samples were polished on 600-grit paper, ultrasonically cleaned for 15 min. in trichloroethylene, and then ultrasonically cleaned in absolute ethanol. The "etched" thorium samples were prepared by etching for 10 min. in 50 vol% nitric acid, containing 0.5 vol% hydrofluoric acid, at room temperature for the EB samples and at 311 K for the AM thorium samples.

Results: The reaction of thorium with water vapor, as followed by weight gain, showed three distinct regions: an initial portion, followed by an accelerated transitional region and a final linear portion.[2] The weight gain per unit surface area in the initial region was found to be proportional to a fractional power of time. However, the weight gain in the initial region, if extended slightly, can also be approximated as a linear function of time. We have analyzed the data both ways. The activation-energy results are presented in Table 1, and the pressure exponents in Table 2. The confidence limits for the activation energies and pressure exponents were calculated using small sample statistics (t-test).

The electrical conductivity of thorium, or any material, is the product of mobility, concentration, and charge. This conductivity should be directly proportional to changes in concentration of the charge carriers at constant temperature, since the mobility of these charge carriers should be relatively insensitive to changes in concentration. Considering only cases where defects arising from oxidation

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[2] 14th meeting of JOWOG-12, October 3-5, 1972. Union Carbide Y-12 Plant, CNC-2-698.

or reduction predominate the pressure dependences shown in Table 3 can be derived.[3] The possible controlling defects associated with the oxidation of the various grades of thorium are also listed in Table 2.

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[3] R. W. West, N. M. Tallan, and W. C. Tripp, J. Am. Ceram. Soc., 47 (12) 635-40 (1964).

TABLE 1. Activation energies for the oxidation of thorium in oxygen, humid air and humid nitrogen.

Thorium	Treatment	Gas mixture	Time exponent, (n)[a]	Oxide thickness mg/cm^2	Activation energy		
					Mean kJ/mole	Confidence limits, kJ/mole	Confidence level, %
AM	Degreased	Air/H_2O	0.69	0.0-0.14	68.36	± 5.50	95
			1.0	0.0-0.53	93.08	± 2.15	95
			1.0	2.7-8.0	72.39	± 8.43	95
		N_2/H_2O	0.67	0.0-0.27	64.32	± 3.93	95
			1.0	0.0-0.50	92.59	± 2.96	95
			1.0	4.3-8.0	77.32	± 4.18	[c]95
		O_2	---	0.0-3.3	134.54	±16.65	80
AM	Etched	Air/H_2O	0.67	0.0-0.04	54.99	± 6.09	70
			1.0	0.0-0.04	84.40	±19.18	70
			1.0	2.5-8.0	67.19	±13.77	80
		N_2/H_2O	0.33	0.0-0.06	34.67	±13.21	70
			1.00	0.0-0.06	94.52	±19.41	70
			1.0	3.5-8.0	67.91	±4.88	80
EB	Degreased	Air/H_2O	0.69	0.0-0.20	72.00	± 5.48	90
			1.0	0.0-0.50	99.59	± 5.53	95
			1.0	3.0-6.0	69.27	± 6.08	90
		N_2/H_2O	0.67	0.0-0.24	53.43	± 3.43	95
			1.0	0.0-0.45	73.27	± 7.96	90
			1.0	4.5-7.5	55.57	± 4.40	90
EB	Etched	Air/H_2O	0.67	0.0-0.11	63.09	± 5.59	90
			1.0	0.0-0.20	94.21	± 0.97	95
			1.0	3.0-6.0	71.37	± 8.92	80
		N_2/H_2O	1.0	0.0-0.30	78.63	±12.15	60
			1.0	3.0-6.0	63.25	± 5.30	95

[a] From $(\Delta W/A) = C + Kt^n$, where $(\Delta W/A)$ = weight gain/unit area, K = rate constant, t = time, and n = time exponent.

TABLE 2. Pressure exponents for the oxidation of thorium in oxygen, humid air and humid nitrogen.

Thorium	Treatment	Gas mixture	Time exponent (n)[a]	Oxide thickness mg/cm^2	Pressure exponents		Confidence level, %	Controlling defect
					Mean	Confidence limits		
AM	Degreased	Air/H_2O	1.0	0.0-0.46	0.225	±0.029	80	V_{Th}-3, ⊕ } n=1/4 O_i-1, ⊕ }
								V_{Th}-4, ⊕ n=1/5
			1.0	2.7-8.0	0.444	±0.072	80	V_{Th}-1, ⊕
		N_2/H_2O	1.0	0.0-0.39	0.170	±0.090	70	O_i-2, ⊕
			1.0	4.3-8.0	0.252	±0.072	70	V_{Th}-3, ⊕
								O_i-1, ⊕
		O_2	1.38	0.0-2.7	-0.153	±0.036	60	V_O+2, ⊖
AM	Etched	Air/H_2O	1.0	0.0-0.023	0.810	----	----	----
			1.0	2.5-7.7	0.332	±0.129	60	V_{Th}-2, ⊕
		N_2/H_2O	1.0	0.0-0.047	0.245	±0.508	60	V_{Th}-3, ⊕
								O_i-1, ⊕
			1.0	4.0-8.5	0.280	±0.116	60	V_{Th}-3, ⊕
								O_i-1, ⊕
EB	Degreased	Air/H_2O	1.0	0.0-0.50	0.400	±0.046	80	V_{Th}-2, ⊕
			1.0	3.0-6.0	0.318	±0.067	60	V_{Th}-2, ⊕
EB	Etched	Air/H_2O	1.0	0.0-0.20	0.502	±0.154	60	V_{Th}-1, ⊕
			1.1	3.0-6.0	0.473	±0.070	60	V_{Th}-1, ⊕

[a] From $(\Delta W\ A) = C + Kt^n$, where K = rate constant, t = time, n = time exponent; $(\Delta W/A)$ = weight gain/ unit area.

TABLE 3. Pressure exponents for the oxidation of thorium for various possible defects under oxidation-reduction conditions

$$\text{Rate} = K\left(P_{O_2}\right)^{x}$$

Predominant defect	Pressure exponent
V_O^{+m}, $\ominus$ (m = 1,2)	-1/4, -1/6
Th_i^{+n}, $\ominus$ (n = 1,2,3,4)	-1/2, -1/3, -1/4, -1/5
V_{Th}^{-p}, $\oplus$ (p = 1,2,3,4)	1/2, 1/3, 1/4, 1/5
O_i^{-q}, $\oplus$ (q = 1,2)	1/4, 1/6

V = vacancy, I = interstitial, $\oplus$ = positive holes, $\ominus$ = electrons.

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