17. ✓ Alkali-Metal Corrosion of High-Temperature Materials

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Auxiliary electrical or ion-propulsion requirements for space vehicles necessitate power plants of high efficiency that will operate at high temperatures. Nuclear power systems have been proposed for these applications in which alkali metals transfer heat from the reactor, power a turbogenerator, and lubricate rotating components.¹ Accordingly, we are studying the corrosion properties of candidate alkali metals, specifically lithium and potassium, under conditions of interest for space applications. Because of the relatively high temperatures ($>1000^{\circ}\text{C}$), the studies are largely concerned with refractory-metal container materials.

COMPATIBILITY OF BOILING ALKALI METALS WITH REFRACTORY ALLOYS

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A program to investigate the compatibility of refractory metals with boiling alkali metals has been in progress using refluxing capsules, natural-circulation loops, and forced-circulation loops.² Tests are being conducted at 1100 to 1400°C with durations ranging from 100 to 5000 hr. Materials under investigation include alloys based on niobium, tantalum, molybdenum, and tungsten.

The major part of our investigation of boiling and condensing conditions has involved refluxing capsules and natural-circulation loops. Both types of tests incorporate insert specimens in the condenser section to provide quantitative data on the

rate of dissolutive attack. To obtain a better simulation of boiling circuitry we are also operating engineering-scale pumped loops that provide data on the corrosion-erosion resistance of potential nozzle and turbine blade materials.

Table 17.1 summarizes the conditions and results of tests conducted during the past year. These tests have effectively completed our study of developmental niobium- and tantalum-base alloys in potassium and have brought the cumulative operating time for refractory-metal-boiling-potassium systems to over $90,000$ hr. Examinations of these systems showed almost negligible dissolutive attack in either the boiler or condenser regions at temperatures up to 1300°C and for times as long as 5000 hr.

Included in our experimental program this year was a 3000 -hr pumped loop (FCL-6) fabricated of Nb-1% Zr. The loop contained a TZM nozzle-blade test section, which operated at an 1100°C vapor inlet temperature. Metallurgical examination is still in progress, but we have found that each of three blade specimens showed a slight weight gain and a thin deposit. Slight erosion damage was noted on the blade impingement area adjacent to the low-quality (82%) high-velocity (3000 ft/sec) nozzle. The other two blade specimens, which were subjected to much higher quality vapor, showed no evidence of attack or erosion. Another pumped loop (FCL-8) of a similar design is presently operating. This loop, fabricated of D-43 and containing D-43 nozzle-blade specimens, has completed 2000 hr at 1200°C test-section inlet temperature.

Future study of refractory metals in potassium will be directed toward tungsten-base alloys and toward the role played by oxygen in the corrosion of niobium and tantalum.

¹A. P. Fraas, *Nucleonics* 22(1), 72 (1964).

²J. H. DeVan, J. R. DiStefano, and D. H. Jansen, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1966*, ORNL-3970, pp. 176-77.

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Table 17.1. Summary of Boiling-Potassium-Refractory-Alloy Compatibility Tests

Material ^a		Temperature (°C)		Test Duration (hr)	Condensing Rate (g min ⁻¹ cm ⁻²)	Weight Change (mg/cm ²)	Results
Insert	Container	Boiler	Condenser				
Refluxing Capsules							
T-111	T-111	1200	1180	5000	0.32	-0.1 to -1.7	No evidence of attack
TZM	TZM	1300	1250	5000	0.32	-0.3 to -1.6	No evidence of attack
Nb-1% Zr	Nb-1% Zr	1190	1170	5000	0.35	-0.3 to +1.5	No evidence of attack
C-129Y	C-129Y	1325	1250	5000	0.36	+0.6 to +1.1	~1 mil attack on end of one insert
W	W	1315	1240	5000	0.33		Examination in progress
Nb	Nb		1200	1500	0.31		Test in progress
Nb-1% Zr	Nb-1% Zr	1240	1210	1100	0.30		Test in progress
Natural-Circulation Loops							
T-111	T-111	1250	1040	3000	0.47	-0.4 to +2.5	No attack. C and O pickup by loop material
TZM	D-43	1250	1040	3000	0.35	+0.3	No attack. O pickup in loop material in areas of decarburization
FS-85	FS-85	1250	750	1200	0.26	+2.5 to -23	Loop being repaired
TZM	TZM	1240	1160	200	0.29		Test in progress
Forced-Circulation Loops							
TZM	Nb-1% Zr	1200	450	3000	165 g/min		Examination in progress
D-43	D-43	1300	840	<i>b</i>	280 g/min		Test in progress

^aCompositions of alloys identified here and in the text of this chapter by commercial names are listed in Table 15.1.

^bLoop has completed 2000 hr of a scheduled 3000-hr test.

CORROSION OF REFRACTORY ALLOYS BY LITHIUM

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Interest in lithium stems from the attractive properties of this metal as a heat-transfer fluid in high-performance nuclear reactor systems. Refractory alloys based on niobium, tantalum, tungsten, or molybdenum have demonstrated low solubilities in lithium, and, by virtue of their superior high-temperature strength, appear ideally suited for containing lithium. Accordingly, we are investigating the detailed corrosion behavior of refractory metals in lithium from the standpoint of mass transfer resistance and the effects of oxygen on grain-boundary penetration.

We are investigating mass transfer in thermal-convection loops, which circulate lithium for 3000 hr at maximum temperatures in the range 1200 to 1300°C. Weight changes of insert specimens placed end-to-end around the loop are recorded for all loop positions after the test. Operating conditions of tests completed or in progress during this past year are shown in Table 17.2. We are correlating the results of a Nb-1% Zr loop (TCL-5R), which operated at 1300°C, with results of earlier 1200°C loops³ to evaluate the effects of hot-leg temperature on mass transfer rates. Figure 17.1 compares the weight change profiles obtained for the Nb-1% Zr alloy at the two test temperatures. The total amount of material lost (0.4 g) in

³J. H. DeVan and C. E. Sessions, "Mass Transfer of Niobium-Base Alloys in Flowing Nonisothermal Lithium," *Nucl. Appl.* 3, 102-9 (February 1967).

Fig. 17.1. Comparison of Nb-1% Zr Weight Change Profiles for 1200 and 1300°C Lithium Thermal Convection Loop Tests.

Table 17.2. Operating Conditions for 3000-hr Thermal-Convection Loops Used to Test Refractory Metals in Lithium

Loop	Alloy	Temperature (°C)		Lithium Flow Rate (fpm)
		Maximum	Minimum	
		Hot Leg	Cold Leg	
TCL-5R	Nb-1% Zr	1315	1115	4.8
TCL-6R ^a	T-222	1350	1150	5.0

^aLoop currently operating.

the 1300°C test was twice that lost at 1200°C; however, the maximum weight loss at 1300°C was ten times that in the 1200°C test. Both loops showed a depletion of zirconium from hot-leg surfaces and an enrichment of zirconium, primarily as ZrN, along cold-leg surfaces. For the maximum weight loss area, electron microprobe analyses revealed depths of zirconium depletion 0.002 and

0.007 in. in the 1200 and 1300°C loops, respectively. Zirconium diffusion rates at these two temperatures, based on the assumption of a constant surface concentration, were calculated to be 3.5×10^{-13} and 6×10^{-12} cm²/sec respectively. The values of diffusivity at these temperatures agree with published data in which short-circuiting along grain boundaries accounts for the bulk of the material transport.

These thermal-convection loop results will be supplemented by mass-transfer studies under forced flow. We have undertaken the design, pump development, and construction of a T-111 alloy loop to operate at temperatures in the range 1370 to 1650°C. The loop is being designed as a test-bed system to accommodate removable insert specimens and will operate with a maximum fluid velocity of 20 ft/sec at a flow rate of 6 gpm. Following each test series, the heater and economizer sections along with insert specimens will be replaced with various tantalum- and tungsten-base alloys. Preliminary to this pumped loop experiment, we conducted a series of static capsule

tests to evaluate the effect of oxygen contamination in T-111 and T-222 welds during exposure to lithium. Coupons of each alloy were doped with oxygen to approximately 500 ppm, welded in argon, and tested in lithium at 750 and 1200°C for 100 hr. No corrosion was found within the weld bead of either alloy at the 500 ppm O level; however, intergranular corrosion was observed for both alloys in the base metal away from the heat-affected zone. Heat treatment at 1300°C, which precipitates oxygen as HfO_2 , effectively eliminated the base-metal attack.

EFFECT OF OXYGEN IN THE TANTALUM-POTASSIUM SYSTEM

R. L. Klueh

Our studies of the role played by oxygen in the corrosion of refractory metals by potassium have shifted from the niobium-potassium system to the tantalum-potassium system. A series of static capsule tests at 600, 800, and 1000°C has been programmed to investigate (1) the partitioning of oxygen between tantalum and potassium, (2) the dissolution of the tantalum in potassium, (3) the formation of corrosion products, and (4) the kinetics of these processes. Oxygen effects are being investigated from the standpoint of the concentration of oxygen in the tantalum as well as in the potassium.

Preliminary results for the Ta-O-K system at 600 and 800°C have followed closely the patterns observed for the Nb-O-K system. That is, although the thermodynamic properties of the known oxides of potassium and tantalum predict that oxygen should be gettered from potassium by tantalum, the opposite is observed. In capsule tests at

600°C, tantalum specimens with 50 ppm O exposed to potassium containing 100 to 3300 ppm O lost weight in proportion to the oxygen content of the potassium. After 500 hr, all of the tantalum specimens had lost oxygen, irrespective of the oxygen level of the potassium. Studies are now in progress to define the chemical reactions by which both the oxygen and tantalum enter potassium.

DETERMINATION OF OXYGEN IN ALKALI METALS

J. E. Strain⁴

J. H. DeVan

A fast-neutron activation analysis facility was completed during the past year to expedite the analysis of oxygen in alkali and refractory metals. However, operation of the system has been hampered by debugging problems encountered first with the counting equipment, subsequently with the sample vacuum system, and currently with the palladium leak valve within the neutron generator. The latter problem is associated with the leakage of Freon from the insulated accelerator dome into the valve. The cause of the leakage was located, and the manufacturer of the accelerator is sending a replacement valve and feed system to eliminate the problem. The sample stopping and unloading device was also redesigned to reduce the travel time of the sample from irradiation to counting position. A series of refractory-metal specimens with carefully documented oxygen levels was assembled to statistically evaluate the accuracy of the present system.

⁴Analytical Chemistry Division.