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 are used to transfer heat, drive a turbogenerator, and lubricate rotating components.¹ Accordingly, we are studying the corrosion properties of candidate alkali metals, primarily 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 POTASSIUM 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 $^{\circ}\text{C}$ with durations ranging from 100 to 5000 hr. Materials under investigation include alloys based on Nb, Ta, Mo, and W.

The investigation of corrosion under boiling conditions has involved refluxing capsules and both natural- and forced-circulation loops. Most tests incorporate insert specimens to provide quantitative data on the rate of dissolutive attack. Engineering-scale forced-circulation loops also provide data on the corrosion-erosion resistance of potential nozzle and turbine-blade materials.

¹W. O. Harms and A. P. Litman, "Compatibility of Materials for Advanced Space Nuclear Power Systems," paper 67-WA/AV-1 presented at the meeting of the American Society of Mechanical Engineers, Pittsburgh, Pa., November 1967, and accepted for publication in *Nuclear Applications*.

²J. R. DiStefano, D. H. Jansen, and B. Fleischer, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1967*, ORNL-4170, pp. 93-94.

Table 17.1 summarizes the conditions and results of tests conducted during the past year. These tests have effectively completed the original objectives set for our potassium program and have brought the cumulative operating time for refractory-metal-boiling-potassium systems to over 100,000 hr. Potassium studies for the coming year will be limited to the completion of tests on tungsten- and molybdenum-base alloys.

Capsule Test Examinations

Capsule tests now in progress or recently completed are summarized in Table 17.1. Experiments with unalloyed niobium have shown an interesting contrast to our earlier capsule studies with niobium alloys. As discussed previously,^{2,3} the alloys of niobium, which as a class contain a minimum of 1% Zr, were resistant to attack in boiling potassium at temperatures up to 1300 $^{\circ}\text{C}$ for times as long as 5000 hr. Unalloyed niobium, on the other hand, exhibited heavy attack in refluxing potassium initially containing less than 10 ppm O and was virtually destroyed in potassium to which 300 ppm O was added. As seen in Table 17.1, a similar oxygen addition had very little effect on Nb-1% Zr under comparable test conditions.

Unalloyed tungsten, like niobium, showed extensive attack in a 5000-hr refluxing capsule test at 1300 $^{\circ}\text{C}$. The test used tungsten with two different fabrication histories — insert specimens had been made by the chemical vapor deposition (CVD) process and the capsule by extrusion of powder-metallurgically produced material. Corrosion effects in this capsule were identified more with mass transfer occurring between the CVD and extruded material than with any concentration gradient that may have existed between condenser and boiler regions. Likewise, in an arc-cast

³J. H. DeVan, A. P. Litman, J. R. DiStefano, and C. E. Sessions, "Lithium and potassium corrosion studies with refractory metals," pp. 675-95 in *Alkali Metal Coolants* (Proceedings of a Symposium, Vienna, 28 November-2 December, 1966) International Atomic Energy Agency, Vienna, 1967.

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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							
W ^b	W	1315	1240	5000	0.33	-93 to +188	Mass transfer between CVD inserts and powder metallurgically produced capsule
Nb ^c	Nb		1200	5000	0.32	<i>d</i>	Very heavy attack
Nb	Nb		1210	5000	0.40	<i>d</i>	Heavy attack
Nb-1% Zr ^c	Nb-1% Zr	1230	1210	5000	0.38	-3 to +1	No evidences of attack
<i>e</i>	W-25% Re		1180	5000	0.30		Examination in progress
<i>e</i>	W-25% Re	1250	1210	5000	0.33		Mass transfer deposit near top of vapor zone
Nb-1% Zr	Nb-1% Zr	1215	1200	950	0.28		Test in progress
Nb ^b	Nb		1200	1200	0.30		Test in progress
Natural-Circulation Loop							
TZM	TZM	1240	1160	<i>f</i>	0.29		Test in progress
Forced-Circulation Loops							
TZM	Nb-1% Zr	1200	450	3000	165 g/min		Nozzle-blade specimens showed negligible attack; mass transfer of loop components limited to zirconium migration from boiler to vapor and condenser regions
D-43	D-43	1300	840	10,000	280 g/min		Examination in progress

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

^bChemically vapor deposited material.

^cPotassium contained approximately 300 ppm O before test.

^dInsert specimens bonded to capsule.

^eNo insert specimens available.

^fLoop has completed 4000 hr of a scheduled 5000-hr test.

W-25% Re capsule (Table 17.1) we observed a heavy mass transfer deposit in the condenser region of the capsule, a mass transport effect opposite to that expected from concentration gradient considerations. We suspect that impurities, possibly halogens, may have given rise to gas transport effects that dominated the usual concentration gradient effects in these capsules.

Forced-Circulation Loop Studies

Metallurgical analysis of the Nb-1% Zr alloy loop FCL-6 containing a TZM nozzle-blade test section was completed (Table 17.1) and a summary report is being written. The examinations revealed excellent compatibility of potassium with Nb-1% Zr and TZM alloys under engineering conditions. Mass transfer and erosion were minimal. The only visual evidence of mass transfer deposits was noted in the nozzle and blade test section and in the boiler nucleation rings. The deposits in

the test section were mostly ZrO₂ and chromium, the chromium apparently coming from the stainless steel pump cell, which operated with inlet and outlet temperatures of 400 and 540°C, respectively. Zirconium migrated from the upper region of the boiler to all other parts of the system. Except for the zirconium-rich deposits in the test section, zirconium migration could be detected only by direct electron-beam microprobe analysis of the piping surfaces.

A pumped loop (FCL-8) of similar design, fabricated of D-43 alloy and containing D-43 nozzle-blade specimens, completed 10,000 hr of operation at design conditions (Table 17.1). The loop, operated by Reactor Division personnel, was shut down in June 1968 after having been on line 96% of the time since startup in March 1967. The down time was mostly associated with electrical and instrument problems external to the vacuum chamber. Examination of this loop is in progress.

CORROSION OF REFRACTORY ALLOYS BY LITHIUM

C. E. Sessions J. H. DeVan
B. Fleischer

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 Nb, Ta, W, and Mo have demonstrated low solubilities in lithium, and, by virtue of their superior high-temperature strength, appear ideally suited as container materials. 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.

Thermal-Convection Loop Tests

The thermal-convection loop affords a convenient means for studying mass transfer properties of liquid metals moving through a temperature gradient. Our current program makes use of the thermal-convection approach for the following purposes: (1) to compare the corrosion resistance of niobium, tantalum, and tungsten alloys in flowing nonisothermal lithium and (2) to measure in the niobium and tantalum systems the magnitude and the time dependence of corrosion reactions, which are controlled by solid-state diffusion processes.

In tests of the niobium-base alloys D-43, Nb-1% Zr, and FS-85 in circulating lithium, we have observed the following mass transfer effects:⁴

1. The alloy constituents zirconium and nitrogen are preferentially transferred from hotter to cooler surfaces in loop tests operated at maximum temperatures of 1200 and 1300°C.
2. Zirconium concentration gradients measured below the surfaces of hot-leg specimens indicate that zirconium depletion is controlled by a solid-state diffusion process. The gradients are of the same form as those computed under the assumption that zirconium surface concentrations remain fixed throughout the test.
3. Mass transfer of niobium is insignificant at 1200°C but accounts for a large fraction of insert weight

⁴C. E. Sessions and J. H. DeVan, "Thermal Convection Loop Tests of Refractory Alloys in Lithium," pp. 326-31 in 1967 IEEE Conference Record of the Thermionic Conversion Specialist Conference, October 30-November 1, 1967, Palo Alto, California, Institute of Electrical and Electronic Engineers, New York.

changes in loops operated at 1300°C. The higher rate of niobium transfer at 1300°C is also manifested by the appearance of niobium deposits at the heater entrance.

4. Mass-transfer profiles in these systems indicate that components of the refractory alloy enter and leave the lithium at commensurate rates. The solute concentrations in the lithium change very little from point to point around the loops, so that the corrosion rate is the same for any given temperature independent of location and direction of heat flux.

The corrosion properties of these niobium-base alloys are now being compared with those of tantalum alloys containing tungsten and hafnium. The first such test, that of the alloy T-222, is being examined after operating 3000 hr at 1350°C. Future tests have also been programmed to evaluate tungsten-base alloys.

Forced-Circulation Loop Studies

The mechanical, piping, electrical, and instrument design of the advanced forced-circulation liquid lithium loop (FCLLL-1) was completed. For economic reasons we adopted a test-bed-loop approach so that we can study the compatibility of several refractory alloys in lithium at 20 ft/sec. A simplified schematic of the basic loop system is shown in Fig. 17.1 and a general

ORNL-DWG 67-9135A

Fig. 17.1. Schematic Representation of Forced-Flow Liquid Lithium Loop.

description of the forced-circulation lithium loop program is presented in Table 17.2. Future loops, FCLLL-2 and -3, will be operated in the same test stand with the heater and economizer sections of FCLLL-1 replaced. Approximately 100 specimens have been fabricated for insertion in the loops to study changes in weight, composition, and mechanical properties. All supporting equipment for FCLLL-1 has been procured and fabricated.

Techniques were developed for making butt and nozzle-type welds, Nb-1% Zr to T-111 welds, and field welds. As-welded field-type joints have been exposed to lithium in capsule tests and show no evidence of

Table 17.2. Test Conditions and Materials for Forced-Circulation Lithium Loops with Maximum Velocity of 20 ft/sec

Loop	Maximum Temperature ^a (°C)	Materials ^b	
		Hot Leg	Specimens
FCLLL-1	1370	T-111	T-111
FCLLL-2	1370	T-111	Tungsten alloys
FCLLL-3	1540	Tungsten alloy	Tungsten alloys

^aMinimum: 1205°C.

^bCold leg: T-111.

Fig. 17.2. T-111 Helical Induction Pump and Associated Stainless Steel Containment.

corrosion damage. High-purity zirconium foil has been procured for hot-trap purification of lithium.

A T-111 pump cell for the helical induction pump was successfully fabricated and tested to 815°C in potassium to verify its structural integrity and establish its performance characteristics. A photograph of this pump cell is included in Fig. 17.2. Measured performance closely matched predicted behavior. Extrapolation to 1205°C, the operating temperature in lithium, indicated a satisfactory flow rate of 5.8 gpm at 450 v and 41 psi developed head. All T-111 material for FCLLL-1 has been procured and about 95% of the parts have been fabricated in preparation for welding of assemblies.

COMPATIBILITY OF NaK WITH TYPE 316 STAINLESS STEEL AND Nb-1% Zr ALLOY IN A HEAT REJECTION SYSTEM⁵

A. P. Litman W. J. Leonard

Evaluation of a SNAP-50-type dissimilar-metal radiator circuit with a stainless steel-to-refractory alloy surface area ratio of 5.5 was completed. The test system consisted of a parallel-tube, air-cooled radiator fabri-

⁵Summary of papers presented at the USAEC Corrosion Symposium, Columbus, Ohio, May 6-8, 1968, and at the American Nuclear Society, Toronto, Ontario, Canada, June 10-13, 1968.

Fig. 17.3. Effect of Time and Temperature on Carbon and Nitrogen Migration in Nb-1% Zr and Type 316 Stainless Steel Simultaneously Exposed to Polythermal Eutectic NaK.

cated from type 316 stainless steel and a heated section made from Nb-1% Zr. The loop, containing numerous replaceable and permanent refractory alloy and stainless steel specimens, circulated eutectic NaK (78% K) at 8.4 ft/sec (Reynolds number of 100,000 in the hot section) for 6000 hr with a heater outlet temperature of 680°C and a temperature difference of approximately 100°C.

Weight changes on the specimens were minimal (maximum approximately $0.1 \text{ mg cm}^{-2} \text{ month}^{-1}$), and dimensional changes were too small to be measured. The major corrosion effect was solid-state diffusion-controlled mass transfer of carbon and nitrogen from the stainless steel to form thin layers, approximately 0.0001 in. thick, of Nb₂N and NbC on the refractory alloy. The bulk movement of these interstitial elements as functions of time and temperature is shown in Fig. 17.3. Changes in the mechanical properties of the alloys are shown in Table 17.3 and indicate that adequate ductility and strength at room and elevated temperatures remained after test.

The experiment led to a better definition of acceptable residence times and temperature conditions for Nb-1% Zr alloy and type 316 stainless steel exposed together in NaK. A low system corrosion rate, no greater than 0.0001 in./year, plus satisfactory post-test mechanical properties, indicate high reliability for the dissimilar-metal heat rejection complex operating at 680°C — a reliability that can reasonably be extrapolated to 10,000 hr service life.

Table 17.3. Mechanical Properties of Type 316 Stainless Steel and Nb-1% Zr Alloy After Exposure in Bimetallic NaK System

Exposure Temperature (°C)	Test Temperature (°C)	Tensile Elongation (%)	Ultimate Tensile Strength (psi)
Type 316 Stainless Steel			
			$\times 10^3$
None	25	64	86
565	25	51	87
680	25	29	95
None	680	51	49
565	680	38	51
680	680	30	53
Nb-1% Zr Alloy			
None	25	22	56
605	25	44	40
680	25	43	40
None	680	10	43
605	680	22	29
680	680	30	29

INTERACTIONS IN REFRACTORY-METAL-ALKALI-METAL SYSTEMS CONTAINING OXYGEN

R. L. Klueh

Effect of Oxygen in the Tantalum-Potassium System

We are continuing⁶ to study the Ta-O-K system at 600, 800, and 1000°C. The effect of oxygen on the compatibility between tantalum and potassium depends upon whether the oxygen is in the potassium or the tantalum. An increase in the oxygen concentration of the potassium leads to an increase in the solubility of tantalum in potassium. We believe that this effect can be explained phenomenologically in terms of the effect of oxygen on the activity coefficient of tantalum in potassium, as discussed in the next section.

At each of the test temperatures there was a threshold oxygen concentration in the tantalum at which potassium penetrated the tantalum. This threshold oxygen concentration increased with temperature (between 100 and 600 ppm below 800°C and between 600 and 1000 ppm at 1000°C) and was unaffected by the oxygen concentration of the potassium. Examples of penetration at 600°C of tantalum containing 600 and 1300 ppm O are shown in Figs. 17.4 and 17.5, respectively. The amount of attack (and depth of penetration) increased with the initial oxygen concentration of the tantalum. Note that both transcrystalline and grain-boundary attack are present in Fig. 17.5. When the specimen shown in Fig. 17.4 was etched, only grain-boundary attack was detected.

Qualitatively, the results are similar to those obtained by DiStefano⁷ for the Nb-O-Li and Ta-O-Li systems. The chief difference is that a lower threshold oxygen concentration is required for penetration by lithium than by potassium.

Analysis of Corrosion Behavior in Terms of Solution Interaction Parameters⁸

Studies of the compatibility between refractory metals (principally niobium and tantalum) and the alkali metals sodium and potassium have shown that the

⁶R. L. Klueh, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1967*, ORNL-4170, p. 96.

⁷J. R. DiStefano, *Corrosion of Refractory Metals by Lithium*, ORNL-3551 (April 1966).

⁸Papers summarizing this work were presented at the NACE Annual Conference in Cleveland, Ohio, March 18, 1968, and at the USAEC Corrosion Symposium in Columbus, Ohio, May 6, 1968.

Fig. 17.4. Tantalum that Initially Contained 600 ppm O After Exposure to Potassium for 500 hr at 600°C. Unetched.

dissolution of the refractory metal in the alkali metal depends upon the concentration of oxygen in the alkali metal. Also, the experimentally determined oxygen equilibrium distribution coefficient at a given temperature (the ratio of the oxygen concentration in the refractory metal to that in the alkali metal at equilibrium) is generally much smaller than the theoretically calculated value. These observations have generally been explained by postulating the formation of a double oxide containing atoms of the refractory metal, alkali metal, and oxygen.⁹

As an alternative to the double oxide hypothesis, we propose that at equilibrium a liquid ternary solution exists in equilibrium with the solid and that oxygen affects the solubility of the refractory metal by decreasing the activity coefficient of the refractory metal in the liquid. Under this assumption, the system can be characterized in terms of the interaction

parameters developed by Wagner¹⁰ for the interaction between the refractory metal and the oxygen in the potassium. This interaction parameter for the Nb-O-K system is defined as

$$\epsilon_{Nb}^{(O)} = \left(\frac{\partial \ln \gamma_{Nb}}{\partial N_O} \right),$$

where γ_{Nb} is the activity coefficient of the niobium and N_O is the atom fraction of the oxygen in the potassium. Once $\epsilon_{Nb}^{(O)}$ is determined experimentally, solubility data for oxygen in pure potassium can be used to empirically represent the activity coefficient of oxygen in the ternary solution as a function of the niobium concentration of the solution.

The phase rule has been used to check the hypothesis for the Nb-O-K, Nb-O-Na, and Ta-O-Na systems. In all cases the solubility of the refractory metal increases with the oxygen concentration of the alkali metal.

⁹C. Tyzack, "The Behavior of Materials in Liquid Sodium," p. 251 in *Advances in Materials (Inter-Disciplinary Symposium)*, The Institution of Chemical Engineers, London, 1964.

¹⁰C. Wagner, *Thermodynamics of Alloys*, Addison-Wesley, Cambridge, Mass., 1952.

Fig. 17.5. Tantalum that Initially Contained 1300 ppm O After Exposure to Potassium for 500 hr at 600°C. Etched in a solution of H_2O , HNO_3 , and NH_4HF .

Furthermore, these tests show that the concentration of oxygen in solid solution finally achieved in the refractory metal increases regularly with the initial oxygen level of the alkali metal. Both observations suggest that there are two condensed phases present at equilibrium rather than the three phases required by the double oxide hypothesis. Also the activity coefficients derived by the interaction parameter approach offer a reasonable explanation for the distribution coefficient discrepancy discussed above.

PARTITIONING OF OXYGEN BETWEEN ZIRCONIUM AND POTASSIUM AND BETWEEN ZIRCONIUM AND SODIUM¹¹

R. L. Klueh

We have completed our investigation of the use of zirconium gettering of oxygen in alkali metals as an analytical technique for oxygen determination.¹² This investigation required an analysis of the oxygen parti-

tioning occurring between zirconium and liquid potassium and sodium. In both systems the partition coefficient (the ratio of the oxygen content in zirconium to that in the alkali metal) was relatively large ($>10^4$). Accordingly, under the conditions employed for these studies, essentially all of the oxygen initially in the liquid metal was gettered by the zirconium.

Therefore, one is able to determine the oxygen in potassium or sodium to very low concentrations simply by exposing the liquid metal to zirconium and directly measuring the amount of oxygen gettered. To test the technique we conducted recovery experiments at 800°C in which known oxygen additions were made to potassium and sodium, which were then exposed to zirconium tabs in molybdenum containers. Recoveries of 90% or greater were obtained for oxygen concentrations (in potassium or sodium) in the range of 100 to 1000 ppm.

¹¹ Abstracted from topical report in preparation.

¹² A. P. Litman and J. W. Prados, *Electrochem. Technol.* 3, 228-33 (1965).

DETERMINATION OF OXYGEN IN ALKALI METALS

J. H. DeVan J. E. Strain¹³

The fast-neutron activation facility described previously^{14,15} has been used routinely during the past year for the determination of oxygen in alkali and refractory metals. A unique feature of this facility is that the alkali metal is protected by an inert atmosphere rather than by the usual encapsulation procedure, so the oxygen background associated with the specimen holder is greatly reduced. Thus we have successfully determined oxygen in both lithium and potassium at levels of less than 20 ppm. Sodium has not yet

been analyzed for oxygen because of the high-energy beta radiation associated with ^{20}F , a product of fast-neutron reaction with sodium. However, we are presently evaluating different beta discrimination techniques that we believe will make this analysis feasible.

This system is also being used to measure the oxygen levels in our refractory metal corrosion specimens before and after exposure. This technique makes possible the nondestructive analysis of our whole test specimen ($1 \times 1/2 \times 0.040$ in.). The specimen is transported to and from the neutron generator in a polyethylene holder and under an argon atmosphere. Because the analysis is nondestructive, the same specimen can be analyzed before and after testing. Oxygen has been determined in the range of 27 to 2700 ppm in specimens of V, Nb, Ta, and Nb-Zr alloys, and the results show reasonable agreement with vacuum fusion analyses on the same specimens. A series of refractory-metal oxygen standards is being prepared by oxidizing tantalum and niobium test coupons to known oxygen levels and performing repetitive analyses.

¹³Analytical Chemistry Division.

¹⁴A. P. Litman and J. E. Strain, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1966*, ORNL-3970, pp. 82-83.

¹⁵J. E. Strain and J. H. DeVan, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1967*, ORNL-4170, p. 96.