Part III. Space Power Technology

24. ✓Alkali-Metal Corrosion of Refractory Metals

J. H. DeVan W. O. Harms

The purpose of this program is to investigate the chemical and metallurgical effects produced in refractory metals during exposure to alkali metals for primary and secondary circuits of space nuclear power systems. Principal emphasis during this report period was on studies of mass-transfer reactions in both primary lithium circuits and secondary (Rankine-cycle) power-conversion circuits involving boiling potassium.

Work on corrosion by sodium, aimed primarily at fast breeder reactor applications, is reported in Chapter 21.

LITHIUM CORROSION STUDIES

Lithium is of interest as a coolant for high-performance nuclear reactor systems.[1] Refractory alloys based on Nb, Ta, W, and Mo are ideally suited as container materials for these applications because of their low solubilities in lithium and their superior high-temperature strengths. We have investigated the corrosion behavior of refractory metals in lithium with respect to thermal-gradient mass transfer and the effects of oxygen on grain-boundary penetration.

Thermal-Convection Loop Tests

J. H. DeVan

We continued our study of the mechanisms that control the mass transfer of oxygen, nitrogen, and carbon in lithium–refractory metal systems. The results of thermal convection loop tests on niobium-base alloys that have been conducted over the past four years point to a link between the transfer of nitrogen and zirconium from hot to cold regions. We have now shown that the rate of transport of these two elements is limited by the solid-state diffusion of zirconium to surfaces of the loop where zirconium is being depleted.[2]

We procured sheet and tubing for the construction of thermal convection loops of unalloyed tungsten and of W–25% Re. A brazing procedure was developed to connect various sections of the loops to avoid the recrystallization problem associated with fusion welding of tungsten and its alloys. All connections were designed as socket joints to provide tight, overlapping fits between adjacent loop sections. For this application, the gas tungsten-arc process with Mo–50% Re filler alloy was determined to be superior to the electron-beam process using the same filler alloy.

Forced-Circulation Lithium Loop

B. Fleischer

A lithium outlet temperature of 1370°C and a temperature difference of 165°C were achieved[3,4] in

[1]W. O. Harms and A. P. Litman, "Compatibility of Materials with Alkali Metals for Space Nuclear Power Systems," *Nucl. Appl.* 5, 156–72 (1968).

[2]C. E. Sessions and J. H. Devan, "Thermal Convection Loop Tests of Nb–1% Zr Alloy in Lithium at 1200 and 1300°C," *Nuclear Applications & Technology*, to be published.

[3]J. H. DeVan and W. R. Huntley, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1970*, ORNL-4560, pp. 200–12.

[4]J. H. DeVan and A. P. Litman, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1969*, ORNL-4520, pp. 254–56.

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an engineering-scale, forced-circulation loop constructed of the tantalum-base alloy T-111 (Ta–8% W–2% Hf). Specimens of the T-111 alloy were placed in the system to measure the effects of mass transfer, including mechanical properties. Pertinent test parameters are presented below.

Temperature, °C	
Maximum	1370
Minimum	1205
Flow rate, gal/min	5.2
Maximum velocity of lithium, ft/sec	18
Maximum Reynolds number	89,000
Total system pressure drop, psi	36
Resistance heater power, kW	30
Volume of circulated lithium, in.^{3}	300
Number of Corrosion Specimens	
Flat	84
Annular	9

The loop was operated at design conditions for the scheduled test period of 3000 hr. However, the test was interrupted after 1735 hr when a lithium leak occurred in an auxiliary line leading from the hot leg to a surge tank.[3] Since the line was not essential, we removed it and sealed the opening where it adjoined the loop. This successful field repair constituted an important milestone in the application of tantalum-base alloys in high-temperature piping systems for space nuclear systems. Although we have not pinpointed the cause of the vent line leak, it appears to have been associated with the original condition of the vent line rather than to effects induced by the lithium.

The loop was instrumented with various types of thermocouples[5] to provide information on cost, reliability, and accuracy of high-temperature thermometry techniques. Thermocouples of W–3% Re vs W–25% Re showed no drift even when welded directly to the loop.[3] This experiment also demonstrated that the helical induction[2] pump affords a satisfactory means for circulating lithium at 1200°C.

The loop was designed so that the sections containing test specimens could be removed and new specimens substituted. We completed the fabrication of replacement specimens[4] of arc-cast tungsten, chemically vapor deposited tungsten, wrought chemically vapor deposited tungsten, W–25% Re, ASTAR 811C (Ta–8% W–1% Re–1% Hf–0.025% C), and T-111. In preparation for installing the second test section, we developed welding techniques for cutting into a tube filled with lithium and making a new field weld with automatic equipment.

[5] J. H. DeVan and A. P. Litman, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1969*, ORNL-4480, pp. 196–200.

EFFECT OF OXYGEN ON THE COMPATIBILITY OF REFRACTORY METALS WITH ALKALI METALS

R. L. Klueh

We continued our study of the effect of oxygen on the compatibility of niobium and tantalum with the alkali metals potassium, sodium, and lithium. Reactions with oxygen in these systems depend upon whether the oxygen is present in the refractory metal or alkali metal. Oxygen added to the refractory metal above a threshold concentration renders the metal subject to penetration by the alkali metal. Oxygen added to the alkali metal promotes dissolution of the refractory metal.

Alkali Metal Penetration

We showed that the rate of penetration of a refractory metal by an alkali metal was too rapid for a diffusion mechanism to apply and proposed a "wedging" mechanism to explain the observed penetration kinetics.[6] Wedging is caused by the formation of a corrosion product – presumably a ternary oxide – having a larger volume than the metal from which it forms.

[6] R. L. Klueh, paper presented at Symposium on Corrosion by Liquid Metals, Philadelphia, October 13–15, 1969, to be published by Plenum Press.

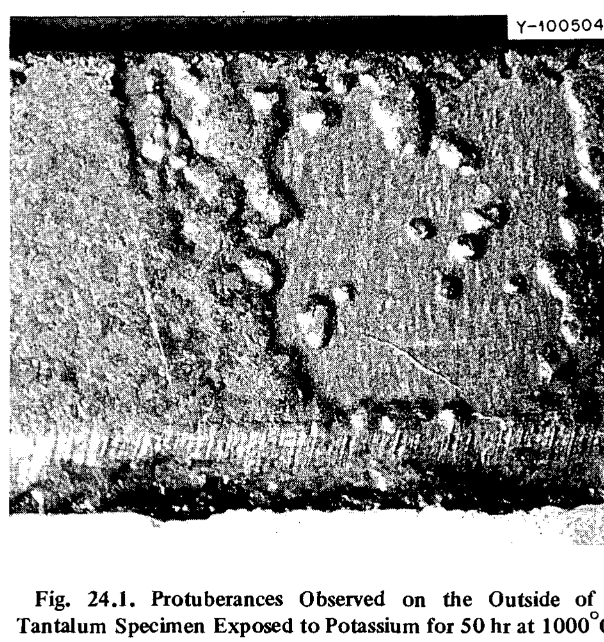

Fig. 24.1. Protuberances Observed on the Outside of a Tantalum Specimen Exposed to Potassium for 50 hr at 1000°C. The specimen contained 2000 ppm O before exposure. 25×. Reduced 28.5%.

We found evidence in the Ta-O-K and Nb-O-K systems that the formation of corrosion product does produce a volume expansion. Figure 24.1 shows protuberances on the external surface of a tantalum specimen that contained 2000 ppm O and was exposed to potassium at 1000°C. Sectioning this specimen (Fig. 24.2) revealed that the position of the subsurface corrosion products matched the locations of the surface protuberances. That is, the corrosion products distorted the external surface of the specimens when the stresses generated by the larger volume material could not be restrained by the surrounding material. We propose that penetration occurs when the pressure generated by the formation of corrosion products causes a crack and that subsequently liquid metal is drawn to the crack tip by both capillary action and the low-pressure region of the newly formed crack.

Effect of Oxygen on Dissolution of Refractory Metals in Alkali Metals

The effect of oxygen in potassium on the compatibility of tantalum and potassium was studied at 600, 800, and 1000°C in static capsules to which various amounts of K_2O had been added. Increases in the oxygen concentration of the potassium were accompanied by increased amounts of tantalum found in the potassium after test. Unlike the Nb-O-K and Nb-O-Na systems,[7,8] the oxygen content of the refractory metal did not depend on changes in the oxygen concentration of the potassium. This observation suggests that a ternary oxide phase was formed.

[7] R. L. Klueh, *Corrosion* 25, 416–22 (1969).

[8] R. L. Klueh, pp. 171–76 in *Proceedings of the International Conference on Sodium Technology and Large Fast Reactor Design, November 7–9, 1968,* ANL-7520, Part I.

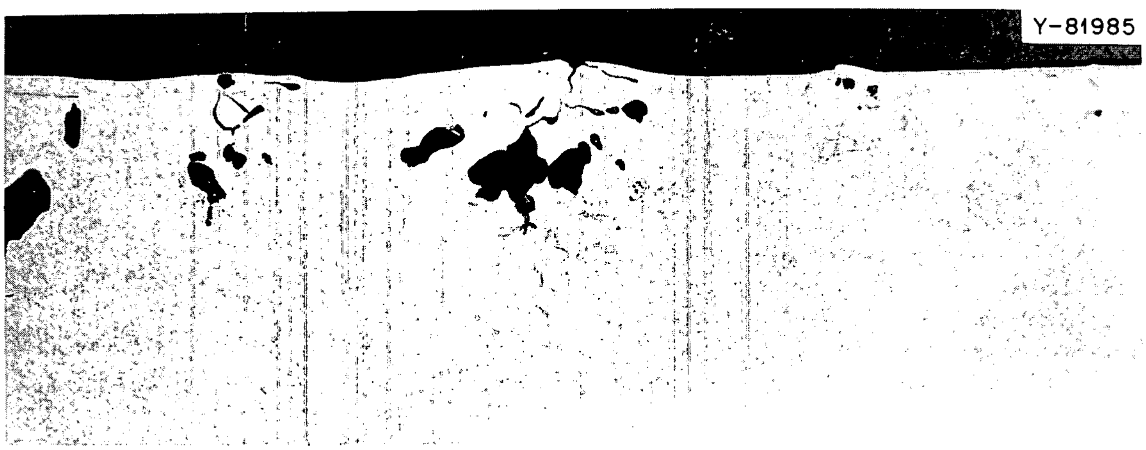

Fig. 24.2. Cross Section of Specimen Shown in Fig. 24.1. Note how protuberances are formed by stresses generated by subsurface corrosion products. 100×. Unetched.