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

J. H. DeVan A. P. Litman

The purpose of this program is to investigate the chemical and metallurgical effects produced in structural materials during exposure to alkali metals. Our experiments are designed to guide the selection of containment materials for both sodium-cooled fast breeder reactor (LMFBR) systems and lithium-cooled space-power systems in which boiling potassium serves as the Rankine-cycle fluid.

Studies in support of the sodium-cooled fast breeder reactor are designed (1) to determine the effects of interstitial impurities in sodium on the mechanical and corrosion properties of vanadium alloys and (2) to investigate the interactions of 300 series stainless steels, commercial insulation, and sodium in air at 600 to 800°C.

Studies in support of space-power systems are centered around refractory-metal containment materials, in particular, tantalum- and tungsten-base alloys. Our principal objective is to study the conditions affecting thermal-gradient mass transfer to refractory alloys in lithium in the temperature range 1200 to 1650°C. A small effort has been included on boiling potassium systems to bring this portion of the program to an orderly conclusion.

MASS TRANSFER OF INTERSTITIAL IMPURITIES BETWEEN VANADIUM ALLOYS AND SODIUM

As is true for refractory metals as a class, vanadium alloys are highly resistant to dissolutive attack by liquid alkali metals if these liquids remain free of impurities. The presence of oxygen, however, greatly increases the corrosion rate of vanadium alloys in sodium. Oxygen, together with carbon and nitrogen, also may be transferred by the liquid metal to the refractory alloy to cause important mechanical property changes.

Accordingly, we are studying the mechanisms by which vanadium alloys undergo attack in sodium at interstitial impurity levels typical of sodium-cooled

reactor systems. Our objectives are (1) to characterize the partitioning behavior of oxygen, nitrogen, and carbon between vanadium alloys and sodium as a function of alloy composition and sodium purity; (2) to determine mechanical property effects produced in vanadium alloys by interstitial impurities acquired from sodium; and (3) to determine the effect of oxygen in vanadium alloys and sodium on the dissolution behavior of the alloys.

Effect of Oxygen in Sodium on Vanadium and Vanadium Alloys

R. L. Klueh

Kinetics of Internal Oxidation. — Vanadium and its alloys readily absorb oxygen from liquid sodium at 600 to 700°C. The kinetics of oxygen absorption differs depending upon the composition of the alloy. Alloys containing titanium and aluminum absorb oxygen with the simultaneous formation of a subsurface hardened zone. The depth of this zone depends on time, temperature, oxygen content of the sodium, and composition of the alloy. Pure vanadium and vanadium containing chromium and niobium absorb oxygen somewhat faster and without the formation of a pronounced hardened zone.

The experimental observations on vanadium-titanium and vanadium-aluminum alloys suggested that these alloys were internally oxidizing in sodium and that the subsurface hardened zone represented a TiO_2 or Al_2O_3 precipitate band. We therefore interpreted the published results for these alloys in terms of an internal oxidation model and showed that the kinetics of the subsurface layer growth was consistent with models proposed by Rapp¹ in which solid-state diffusion of oxygen into the alloy controls the rate of oxide precipitation. We then extended this model to the

¹ R. A. Rapp, *Corrosion* 21, 382 (1965).

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consideration of alloy characteristics that would afford maximum nobility in a sodium service environment.

Oxygen Partitioning. — We exposed a series of vanadium capsules and insert specimens to sodium to gain an understanding of the effect of oxygen on the compatibility between vanadium and sodium and to compare these results with similar tests² in the niobium-sodium and tantalum-sodium systems.

Tests were conducted³ at 600 and 800°C with sodium containing from about 50 to 1300 ppm O. In all cases the oxygen was effectively gettered by the vanadium specimen and capsule, indicating a very large equilibrium distribution coefficient. After exposure the sodium contained about 40 and 200 ppm V at 600 and 800°C respectively. In contrast, the niobium-sodium and tantalum-sodium systems exhibit a markedly smaller oxygen distribution coefficient, and the solubility of niobium and tantalum in sodium increases more with increasing oxygen concentration in the sodium. Sodium did not penetrate vanadium that contained as much as 1900 ppm O; tantalum and niobium are penetrated under similar conditions.

Interstitial Effects on Mechanical Properties of Vanadium Alloys

R. L. Wagner

Interstitial contaminants in vanadium and its alloys significantly affect their mechanical properties. We are studying the effect of alloying elements on the nature and rate of interstitial contamination of vanadium and the effect of the contaminants on creep properties.

We measured the contamination of 0.020-in.-thick pure vanadium sheet specimens exposed to oxygen on both sides from 350 to 900°C. The oxygen concentration in the vanadium did not change significantly under a vacuum of 4×10^{-8} torr for 800 hr. Also, in the range 10^{-6} to 10^{-7} torr the oxygen concentration of the vanadium went through a maximum at approximately 550°C. Assuming the reaction rates to be linear in time, the rates for the maximum observed at 550°C were 0.5 and 0.1 ppm/hr at 2×10^{-6} and 2×10^{-7} torr O respectively.

Mass Transport of Interstitial Impurities Between 300 Series Stainless Steels and Vanadium Alloys

J. H. DeVan D. H. Jansen

We are investigating the partitioning of carbon and nitrogen between vanadium alloys and stainless steels in a sodium circuit. Test variables include the relative

surface areas and temperatures of stainless steel and vanadium and the chemical composition of the two alloy systems. The tests are being conducted in thermal convection loops designed⁴ so that all heated surfaces in contact with sodium are of vanadium, while all isothermal or cooled sections are of stainless steel.

Mass transfer rates and the effect of interstitial transfer on the mechanical properties of the alloys are determined from insert specimens positioned concentrically in the heated and cooled legs of the loop. Loops of types 304 and 321 stainless steel, each incorporating an unalloyed vanadium hot leg section, are currently operating at a 700°C sodium outlet temperature.

We are interested in comparing the rates of interstitial transport in these systems with those in a static, isothermal system and have constructed a series of stainless steel vessels that can accommodate sheet specimens of both vanadium and stainless steel for tensile tests. The relative surface areas of stainless steel and vanadium correspond to the ratios set for our thermal convection loops.

COMPATIBILITY OF STAINLESS STEEL AND INSULATION IN LMFBR SYSTEMS

C. D. Bopp⁵ A. P. Litman

Compatibility of insulating materials with stainless steels is an important consideration in the design of LMFBR systems. Accordingly, we are studying the possible reactions between commercial insulating materials and stainless steel.

The first phase of our program is concerned with the interactions of stainless steels and commercial alumina-silica insulation materials between 370 and 760°C. The second phase deals with the effects of sodium leaks in stainless steel systems surrounded by thermal insulation. Small leaks that may be self-sealing at lower temperatures are being investigated by methods similar to those used in the first phase. The effects of large leaks are being studied in heated, pressurized containers with artificial defects incorporated in the container wall.

²R. L. Klueh, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1968*, ORNL-4370, p. 83.

³R. L. Klueh, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1968*, ORNL-4350, pp. 87–91.

⁴W. O. Harms, J. H. DeVan, and A. P. Litman, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1968*, ORNL-4390, pp. 85–86.

⁵On loan from the Reactor Chemistry Division.

We completed a survey⁶ of the effects of insulating materials on stainless steel. This included a literature study, a compilation of ORNL experience with thermal insulations, and an examination of pertinent thermodynamic data. This survey indicates that, in the LMFBR temperature range, the oxides of iron, chromium, or nickel on stainless steel should not react with pure alumina or silica, the major components in suitable commercial insulations. However, the presence of low-melting and volatile oxides or of sulfur- or halogen-containing compounds could lead to catastrophic oxidation at the interface between base metal and oxide. We also found disagreement in explaining the details of the acceleration of oxidation by these impurities. Much of the information available is highly empirical and lacking in the areas of long-term, cyclic, and transient effects.

Except for some continuing long-term tests, we have completed our experimental study of the compatibility of insulation with stainless steel in the absence of sodium oxidation products.^{7,8} The test results are

⁶C. D. Bopp, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1968*, ORNL-4350, pp. 95-102.

⁷C. D. Bopp, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1968*, ORNL-4390, pp. 91-92.

⁸C. D. Bopp and A. P. Litman, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1969*, ORNL-4420, pp. 92-100.

summarized in Fig. 17.1. When some differences in experimental conditions are allowed for, the scaling kinetics in moist air are similar to those reported for oxygenated superheated steam. The similarity of scaling in moist air and steam was confirmed further by examination of the scale by metallography, elemental analysis, electron microprobe scan analysis, and x-ray diffraction. Our specific test findings were as follows:

1. Catastrophic oxidation (a rapid form of corrosion thought to result from fluxing of the scale by a liquid phase) was not found in tests with type 316 stainless steel to 815°C.
2. Type 304L stainless steel has superior scaling resistance to type 316 stainless steel in moist air in the range 700 to 815°C.
3. Alumina-silica "blanket" insulation did not enhance scaling even under conditions that produced extensive exfoliation of the oxidation products on types 304L and 316 stainless steel. In contrast, scaling was noticeably enhanced by amosite asbestos-diatomaceous silica insulation, probably from interaction of the sodium silicate binder or sulfur impurity with the scale.
4. Temperature cycling increased spalling substantially with relatively thick scales but did not affect the protectivity of the thinner scales formed under less stringent conditions.

Fig. 17.1. Oxidation of Stainless Steel Against Thermal Insulation in Moist Air.

5. Work hardening by machining gave a temporary improvement in the oxidation resistance of type 316 stainless steel over pickled material, lasting about 100 hr at 815°C and 2000 hr at 760°C.

Work has started on the second phase of this program, which involves the effect of a sodium leak on stainless steel-insulation compatibility.

CORROSION OF REFRACTORY ALLOYS BY LITHIUM

Interest in lithium stems from its attractive properties 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

J. H. DeVan

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 the magnitude and the time dependence of corrosion reactions governed by solid-state diffusion processes.

The sixth loop in this series, constructed of the tantalum alloy T-222, was examined following operation for 3000 hr at a maximum temperature of 1350°C. Weight change as a function of loop position was analogous to that observed⁹ in D-43 and Nb-1% Zr tests at 1200°C, where about two-thirds of the loop surface lost weight and one-third gained weight. Weight losses were relatively small (≤ 0.8 mg/cm²) and were attributable primarily to the transport of hafnium from the hotter to colder loop regions.¹⁰ The alloy also lost

oxygen at all positions and gained nitrogen in the cold regions.¹¹ A combination of thermal aging and nitrogen pickup significantly reduced room-temperature ductility in specimens exposed at 1270 to 1300°C (ref. 12). This ductility loss was not observed for specimens whose temperature was either higher or lower than 1200°C.

Forced-Circulation Lithium Loop

B. Fleischer

Fabrication of the initial forced-convection lithium loop⁹ (FCLLL-1) was completed, and shakedown operations began. Construction required the assembly of 50 T-111 component parts, involving about 75 ft of tubing and machined fittings.¹³⁻¹⁵ To join these parts required about 60 inert gas dry box welds and three field welds, which used previously described¹⁶ automatic inert gas equipment. The test section of the loop, shown in Fig. 17.2, contains about 90 T-111 corrosion specimens. This unit is designed so that it can be removed from the test bed loop and replaced with a new test section.

Early results of start-up and shakedown operation have shown that the lithium purification tank performed its task remarkably well. The oxygen and nitrogen contents of the lithium are at the detection limit of the analytical techniques (<5 ppm N and about 17 ppm O).

Before loop fabrication, we corrosion tested¹⁷ a series of T-111 and T-222 weld specimens in lithium at 750 and 1200°C. No attack of weld heat-affected zones was observed in samples containing up to 540 ppm O. However, we found attack to a depth of 0.010 in. in the base metal of these samples unless they had been heat-treated for 2 hr at 1300°C after welding. Lithium

¹¹J. H. DeVan, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1968*, ORNL-4390, pp. 100-4.

¹²J. H. DeVan, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1969*, ORNL-4420, pp. 105-6.

¹³B. Fleischer, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1968*, ORNL-4350, pp. 130-35.

¹⁴D. L. Clark and B. Fleischer, *Fuels and Materials Development Program Progr. Rept. Dec. 31, 1968*, ORNL-4390, pp. 104-9.

¹⁵D. L. Clark, C. W. Cunningham, and B. Fleischer, *Fuels and Materials Development Program Quart. Progr. Rept. March 31, 1969*, ORNL-4420, pp. 106-13.

¹⁶E. A. Franco-Ferreira and G. M. Slaughter, *Welding J. (N.Y.)* 45, 835-42 (1966).

¹⁷C. E. Sessions, *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1968*, ORNL-4330, pp. 104-10.

⁹C. E. Sessions, J. H. DeVan, and B. Fleischer, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1968*, ORNL-4370, pp. 78-80.

¹⁰J. H. DeVan, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1968*, ORNL-4350, pp. 127-30.

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Fig. 17.2. Alloy T-111 Test Section of FCLLL-1 Containing About 90 Specimens.

tests were also conducted on T-111 weld specimens that had been prepared simultaneously with the welding of the T-111 lithium pumped loop described above. Although not heat-treated, these welds showed no evidence of lithium attack.

Procurement of test materials for the replacement section (FCLLL-2) has begun. The test materials ordered include W-25% Re, ASTAR-811C, T-111, and both wrought and CVD tungsten.

COMPATIBILITY OF BOILING POTASSIUM WITH REFRACTORY ALLOYS

This year we concluded the major portion of our investigations¹⁸ of the corrosion of refractory metals

¹⁸J. R. DiStefano, D. H. Jansen, and B. Fleischer, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1968*, ORNL-4370, pp. 76-77.

by boiling potassium. A few refluxing capsules were conducted to investigate alloys or conditions not covered by our original studies. Also we completed our examination of two engineering-scale forced-circulation loops, which were operated to provide data on the corrosion-erosion resistance of potential nozzle and turbine blade materials.

Capsule and Natural-Circulation Loop Tests

J. R. DiStefano D. H. Jansen

Table 17.1 summarizes the conditions and results of potassium refluxing capsule tests conducted during the past year. An Nb-1% Zr capsule was operated under conditions that minimized the uptake of oxygen from the external environment. Corrosion results, however,

Table 17.1. Summary of Tests of Compatibility of Boiling Potassium with Refractory Alloys

Material	Temperature (°C)		Test Duration (hr)	Condensing Rate (g min ⁻¹ cm ⁻²)	Results
	Boiler	Condenser			
Refluxing Capsules					
W-25% Re ^a	1250	1180	5000	0.30	No evidence of attack
W-25% Re ^b		1210	5000	0.33	Mass transfer of tungsten from boiler to condenser
Nb ^c	1215	1200	5000	0.30	Very heavy attack
Nb-1% Zr		1200	5000	0.29	No evidence of attack
Ta		1205	5000	0.32	Test in progress
Natural-Circulation Loops					
TZM	1240	1160	4400	0.29	No evidence of attack
FS-85	1250	1200	1300	0.20	20 mg/cm ² gain in subcooler, stress corrosion in boiler

^aPowder product.^bArc melted.^cChemically vapor deposited (CVD) inserts in an arc melted capsule.

were similar to those of previous capsules,¹⁹ where small amounts of oxygen entered the system.

An unalloyed niobium capsule, which contained chemically vapor deposited (CVD) niobium inserts, exhibited heavy attack after exposure to potassium, and mass transfer of tungsten from the boiler to condenser region was found²⁰ in an arc melted W-25% Re capsule. Attack in both these latter capsules appeared to have been oxygen-induced and indicated that locally high oxygen concentrations had been produced at the boiler surfaces as a consequence of the boiling process.

Two natural-circulation boiling potassium loops were also examined after operation under conditions shown in Table 17.1. Neither loop showed any metallographic evidence of attack, and changes in interstitial concentration were relatively minor.^{21,22}

¹⁹J. R. DiStefano, *Refluxing Capsule Experiments with Refractory Metals in Boiling Alkali Metals*, ORNL-4322 (January 1969).

²⁰J. R. DiStefano, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1968*, ORNL-4350, pp. 103-7.

²¹D. H. Jansen, *Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1968*, ORNL-4330, pp. 84-86.

²²D. H. Jansen, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1969*, ORNL-4350, pp. 107-10.

Forced-Circulation Boiling Potassium Loop

B. Fleischer

A forced-circulation boiling potassium loop fabricated of D-43 was examined after 10,000 hr operation at a 1200°C maximum temperature.^{23,24} Inspections of the loop components showed mechanical distortion only in the pump cell. This was apparently caused by excessive temperatures resulting from the economizer effect of the two-pass design used for this pump. The expansion caused continuous loss of pump efficiency, which was reflected by a continuous need to increase pump voltage to maintain design flow during operation.

Examination of internal surfaces of the loop showed no corrosion effects other than in the nozzle-blade test section. The appearance of blade specimens from this section before and after test is illustrated in Fig. 17.3. The slight discolorations noted reflect some slight deposition. The maximum weight change was about 4.6 mg gain on blade 2. This was less than one-third of the

²³B. Fleischer and C. W. Cunningham, *Fuels and Materials Development Program Quart. Progr. Rept. Sept. 30, 1968*, ORNL-4350, pp. 110-20.

²⁴C. W. Cunningham and B. Fleischer, *Fuels and Materials Development Program Quart. Progr. Rept. Dec. 31, 1968*, ORNL-4390, pp. 94-95.

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Fig. 17.3. Blade Test Specimens Used in Forced-Circulation Boiling Potassium Loop FCL-8. Loop was fabricated of D-43 and operated 10,000 hr at a 1200°C boiler-condenser temperature. (a) Typical specimen before test. (b) After 10,000-hr test. Nozzle specimens showed no visible change.

maximum deposition experienced¹⁸ on blades tested in an Nb-1% Zr loop that operated 3000 hr at a maximum temperature of 1090°C.

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

R. L. Klueh

We continued our comparative study²⁵ of the effect of oxygen on the compatibility of niobium and tantalum with alkali metals (potassium, sodium and lithium) at 600°C. Reaction with oxygen in these systems differs depending upon whether the oxygen is present in the refractory metal or the alkali metal. When the oxygen concentration of the refractory metal exceeds some threshold concentration, the alkali metal penetrates the refractory metal. This effect was studied by making controlled oxygen additions to refractory metal samples and exposing the samples in a static capsule of the same material. When oxygen is in the

alkali metal, the effect is to increase the dissolution of the refractory metal. This latter effect was studied by the addition of oxygen to the alkali metal before testing in static capsules.

Alkali Metal Penetration

For penetration to occur, the oxygen concentration of the refractory metal must exceed a critical concentration, which is a function of temperature, the specific alkali metal, and the refractory metal. The effect of temperature has been studied²⁶ in the systems Nb-O-Li and Ta-O-Li and as well²⁵ in Ta-O-K. Penetration occurs in two modes, intergranular and transgranular, with each having a different threshold oxygen concentration.

²⁵R. L. Klueh, *Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1968*, ORNL-4370, pp. 81-83.

²⁶J. R. DiStefano, *Corrosion of Refractory Metals by Lithium*, ORNL-3551 (April 1966).

The penetration of tantalum and niobium by potassium, sodium, and lithium was compared at 600°C. The estimated threshold oxygen concentrations are shown in Table 17.2.

Effect of Oxygen on Dissolution of Refractory Metals in Alkali Metals

The effect of oxygen in the alkali metal was compared for niobium and tantalum in potassium, sodium, and lithium at 600°C. Increasing the oxygen concentra-

Table 17.2. Estimated Threshold Oxygen Concentrations for Penetration of Refractory Metals by Alkali Metals at 600°C

Corrosion Mode	Oxygen Concentration in Refractory Metal for Penetration by Liquid Metal ^a (ppm O by weight)		
	Potassium	Sodium	Lithium
Tantalum			
Grain boundary	500	300	150
Transgranular	1400	>1000	500
Niobium			
Grain boundary	1500	1000	400
Transgranular	>2400	>1600	1300

^aValues were estimated by metallographic examination and chemical analysis of refractory metals.

tion in lithium had no effect on the dissolution of either niobium or tantalum. For potassium and sodium, on the other hand, an increase in the oxygen concentration of the alkali metal led to increased dissolution of the refractory metal. For niobium in potassium²⁷ and niobium in sodium²⁸ this effect was attributed to an increase in the solubility of the niobium as a result of interactions between niobium and oxygen dissolved in the alkali metal (i.e., the oxygen decreases the activity coefficient of the niobium in the alkali metal). This interaction was characterized in terms of solution interaction parameters.²⁸ We now believe that the effect of oxygen in potassium on tantalum can be similarly explained, although the process is more complicated. The concentration of tantalum in sodium again increases with an increase in the oxygen concentration of the sodium. However, as the oxygen concentration of the sodium is increased oxygen migrates from the sodium to the tantalum, which in turn is penetrated by the sodium.

²⁷R. L. Klueh, *The Effect of Oxygen in Potassium on Niobium-Potassium Compatibility*, ORNL-TM-2476 (February 1969).

²⁸R. L. Klueh, "The Effect of Oxygen in Sodium on the Compatibility of Sodium with Niobium," 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.