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CORROSION MECHANISMS IN REFRACTORY METAL–ALKALI METAL SYSTEMS

J. R. DiStefano
E. E. Hoffman

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ABSTRACT

Liquid metals make excellent high-temperature coolants because of their low vapor pressures and excellent heat-transfer coefficients. These properties recommend their use in nuclear power reactors where very high heat fluxes are present from the nuclear fuel. Liquid metals are also most attractive coolants and working fluids for space power systems which require compact design.

The use of liquid metals, however, introduces solid-liquid metal interactions which are not primarily electrochemical, as found in systems involving aqueous media. The corrosion of solid metals by these coolants occurs as the system attempts to attain chemical equilibrium. The mechanisms by which this can occur are (a) dissolutioning, which results from the solubility relationships between the solid and liquid metals, and (b) impurity reactions, resulting from the presence of interstitial impurities, such as oxygen, nitrogen, and carbon, in the solid and liquid metals.

The manner in which dissolutioning proceeds gives rise to many types of attack ranging from simple solution to mass transfer of one or more constituents of an alloy. Some variables which influence the rate and type of dissolutive corrosion are: temperature, flow velocity, surface area to volume ratio, surface condition of solid metal, temperature gradient, and number of materials in contact with the same liquid metal.

The refractory metals tungsten, molybdenum, tantalum, and niobium, as well as other high-melting body-centered cubic metals, have excellent resistance to dissolutive attack by the alkali liquid metals at high temperatures. However, there are numerous occasions when it is desirable to utilize the unique capabilities of several structural materials in the same system. A few experiments have been conducted which show that, when more than one type of solid metal or alloy is in contact with an alkali metal, the tendency for the system to achieve equilibrium results in a number of complex interactions involving interchange of metallic and nonmetallic constituents. These interactions generally are deleterious and therefore material selection can be limited.

The most significant corrosion problem involving refractory metals appears to be the influence of the impurities, oxygen, nitrogen, and carbon. Experiments have been conducted to study the effect of such impurities in both the refractory metals and alkali metals. As an example, data are presented which show that the presence of small quantities of oxygen in either tantalum or niobium results in the penetration of these metals by lithium over a wide range of temperatures. It has also been found that oxygen in sodium increases its corrosion rate when in contact with niobium and other refractory metals. In addition, a method to predict the redistribution of impurities which are present in solution in either the solid or liquid metal is compared with experimental results.

The corrosion of solid metals by liquid metals often occurs in complex multicomponent systems. For this reason, further data on solubilities of single components, multicomponent effects, temperature coefficients of solubilities, and kinetics of dissolution and precipitation of solid metals are needed. It is also suggested that more emphasis be placed on analytical techniques for determining the concentrations of oxygen, nitrogen, and carbon in liquid metals in order that their effects upon various corrosion processes might be better understood.

CORROSION MECHANISMS IN REFRACTORY METAL–ALKALI METAL SYSTEMS

J. R. DiStefano and E. E. Hoffman

INTRODUCTION

The alkali metals lithium, sodium, potassium, rubidium, and cesium have many properties which make them attractive as coolants and working fluids for use in compact nuclear power sources. A review of the heat capacity, thermal conductivity, density, melting point, and vapor pressure of these metals indicates that they are generally superior to the "heavy" liquid metals lead, bismuth, and mercury as heat-transfer media, especially for aerospace applications.

A major interest in alkali metals at present is as heat-transfer and working fluids in Rankine cycle systems (vapor engines) to generate electric power for space applications.[1] As an example, a recent publication[2] describing a nuclear reactor designed to operate in space and provide electric power for instruments and ion engine propulsion stated: "Liquid lithium flows through the hot reactor core and emerges at 2000°F (1093°C). The tubes that carry it are made of zirconium-columbium alloy. The lithium is piped through a heat exchanger and turns liquid potassium (boiling point, 1400°F) to high-pressure gas that runs a turbine producing 300 kw to 1000 kw of electricity." In order to obtain maximum cycle efficiency and to minimize the size (and weight) of the waste-heat radiator, such systems must be operated at very high temperatures. The combination of properties required of the container materials to be used in the construction of these systems makes the refractory metals likely candidates for consideration.

Numerous investigations[3–5] have indicated that the refractory metals are more resistant than conventional metals and alloys to attack by alkali metals. However, most corrosion data available in the literature were obtained in static isothermal capsule tests. Corrosion tests of relatively large engineering systems with high flow velocities and large temperature differentials have been limited in number for the following reasons: (1) refractory-metal tubing has not been readily available, (2) fabrication and joining are difficult, (3) an inert test environment is required to prevent contamination of the refractory metal, and (4) the cost of these systems is high.

The purpose of this paper is to (1) discuss corrosion mechanisms which have been observed in alkali metal—solid metal systems, (2) present a brief summary of results that have been obtained on specific refractory metal—alkali metal systems, and (3) suggest areas of research on the latter systems which are needed to better understand the fundamental corrosion processes.

CORROSION MECHANISMS

Interactions that occur between liquid and solid metals have been the subject of numerous investigations in recent years. Several writers have classified the various types of corrosion phenomena which have been observed.[4,6–9] The authors of this paper describe briefly the corrosion mechanisms appearing to be operative in solid metal—alkali metal systems, but emphasize those processes of particular importance when the solid metal is either niobium, tantalum, molybdenum, or tungsten. Specific results obtained in corrosion studies of these refractory metal—alkali metal systems are cited in "Corrosion Results," this paper.

Dissolutive Corrosion Mechanisms

Dissolution of Solid Metal in Liquid Metal

Dissolution of a pure solid metal by a pure liquid metal proceeds according to the following reaction:

$$\text{A (solid metal)} \rightleftharpoons \text{A (in liquid B)}$$

The process will continue until the chemical potential of A is equivalent in the two phases. The rate of dissolution is influenced by the reaction rate at the solid-liquid interface and by the diffusion rate of the solute away from the liquid boundary layer. The dissolution rate in a polycrystalline metal is generally most rapid in high energy regions, and preferential dissolution of certain grain boundaries and twinned regions has been noted (Figure 1).[10]

The process of dissolutioning and variables which affect it have been discussed in considerable detail by other authors.[11,12]

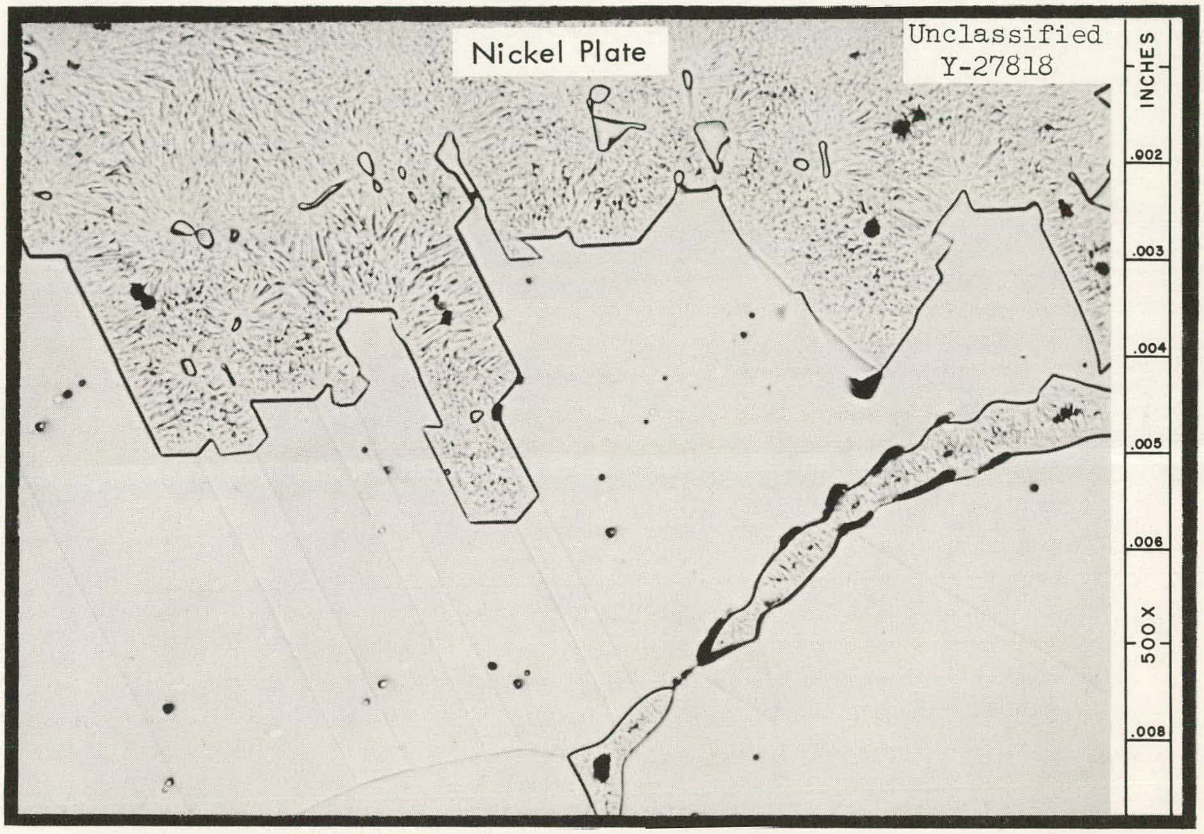

Figure 1. Surface of Nickel Specimen Following Exposure to Lithium for 100 Hours at 800°C. Note the preferential dissolution occurring along grain boundaries and along twin bands. Specimen nickel-plated following exposure to preserve edge during metallographic polishing. Etchant: KCN-H_2O_2 (90-10 volume %).

Alloying of Liquid Metal with Solid Metal

The alloying of a liquid metal with a solid metal to form a corrosion product phase is not a common process but has been noted in the iron-tin and thorium-bismuth systems.[13] Hoffman and Manly[14] reported the formation of a copper-sodium phase which completely penetrated the grain boundaries of a copper capsule (0.25 inch thick) in an experiment conducted at 1000°C.

Dissimilar-Metal Mass Transfer

When two or more solid metals or alloys are placed in contact with a common liquid metal, extensive interalloying often occurs between the solid metals even if there are small solute concentrations in the liquid metal. The driving force for this process is the thermodynamic requirement that the chemical potential of each element be equivalent in all phases that are in contact. Kinetic considerations usually limit the extent of alloying and, as would be expected, this corrosion process becomes increasingly more important as the system temperatures increase. An example of this type of corrosion[15] is given in Figure 2.

Temperature-Gradient Mass Transfer

Temperature-gradient mass transfer occurs in solid metal—liquid metal systems as a result of a temperature dependence of the solubility of the solid metal in the liquid metal. A coolant circulating in a heat-exchange system tends to dissolve the container metal in the hot zone and to transfer it to cooler zones where it may deposit and plug the circuit. Although kinetic factors such as diffusivities, rates of dissolution, and rates of crystal nucleation and growth have an important effect on the rate of mass transfer, it is recognized that the basic driving force for this process lies in the variation of solubility with temperature. The kinetic aspects of temperature-gradient mass transfer are discussed elsewhere.[16—17]

Since the solubility of a solid metal in liquid metal nearly always increases with temperature, temperature-gradient mass transfer must be considered as a serious compatibility problem in high-temperature

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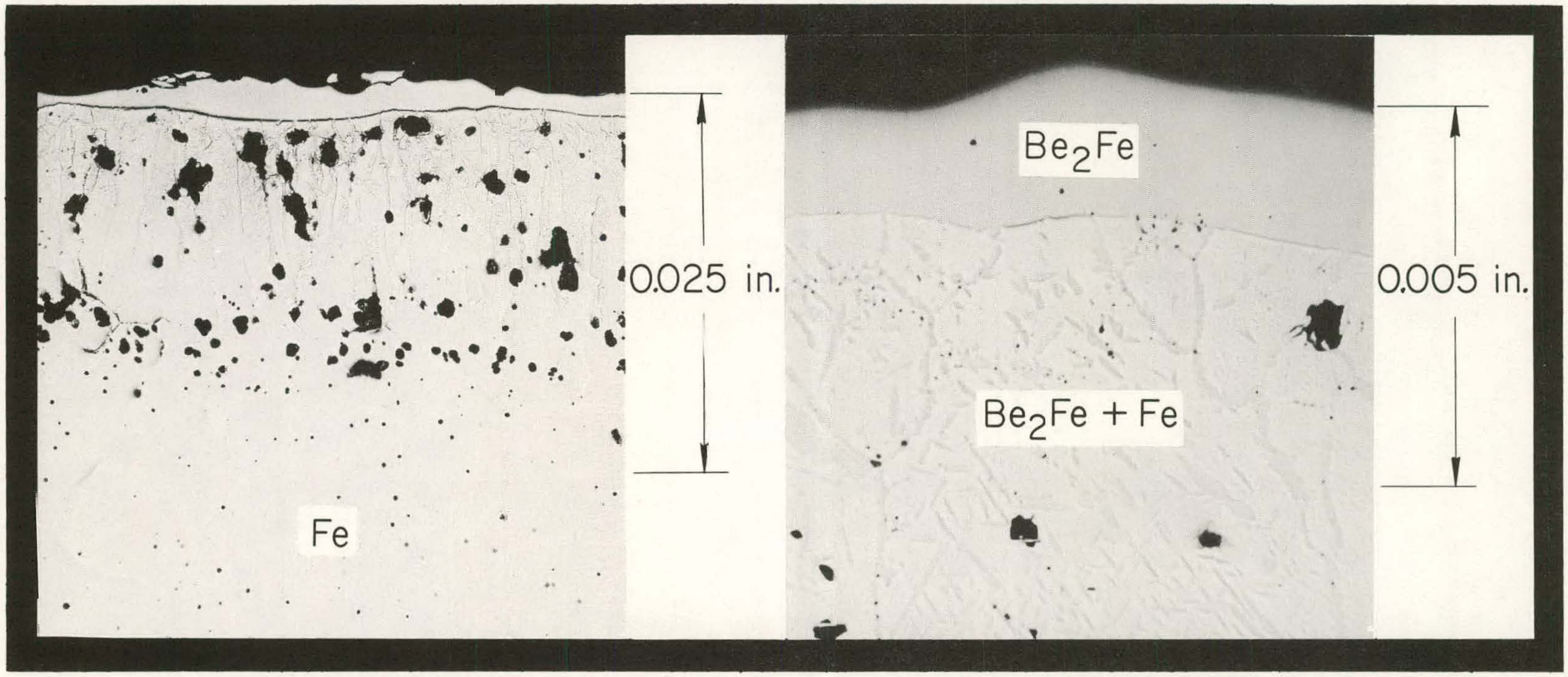

100X

500X

Figure 2. Wall of an Iron Container in Which a Beryllium Specimen Was Exposed to Lithium. Test conditions: static, 1832°F (1000°C), 100 hours. As-polished. Reduced 18%.

heat-transfer systems. The most important effect of temperature-gradient mass transfer in relatively compatible systems is generally not the removal of metal from the hot regions but the subsequent crystal deposition in the cooler regions of the systems. These deposits increase the pressure drop in circulating systems and can eventually restrict flow completely. An example of temperature-gradient mass transfer is illustrated in Figure 3, which shows the effect of hot-zone temperature on the extent of mass transfer in a type 446 stainless steel (27 wt % Cr—bal Fe)—lithium system.[18]

Dissolution of container materials in boiling alkali-metal systems may be a particularly serious problem since the solid metal in the condenser region will continuously be exposed to a pure solvent. Studies conducted in systems of this type have not been extensive enough to determine the magnitude of this problem.

Impurity Reactions

The presence of elements such as oxygen, nitrogen, carbon, and hydrogen in solid metal—liquid metal systems can often lead to accelerated corrosion. The mechanisms by which corrosion occurs are often complex and not well understood. However, explanations for some observed experimental phenomena have been proposed and are discussed below.

Liquid-Metal Impurities

Impurities in liquid metals have been found to increase the corrosion rate of some solid metals in alkali metals, presumably through the formation of soluble or loosely adherent compounds. It has been shown, for example, in iron-sodium systems that oxygen in the sodium leads to an increase in the amount of temperature-gradient mass transfer. Horsley[19] has suggested that oxygen in the sodium reacts with iron to form the complex compound $FeO \cdot (Na_2O)_2$. Since this double oxide is thermodynamically more stable with respect to oxygen dissolved in sodium at high temperatures than at low temperatures, it is suggested that oxygen in the sodium assists in the mass transfer of iron by the

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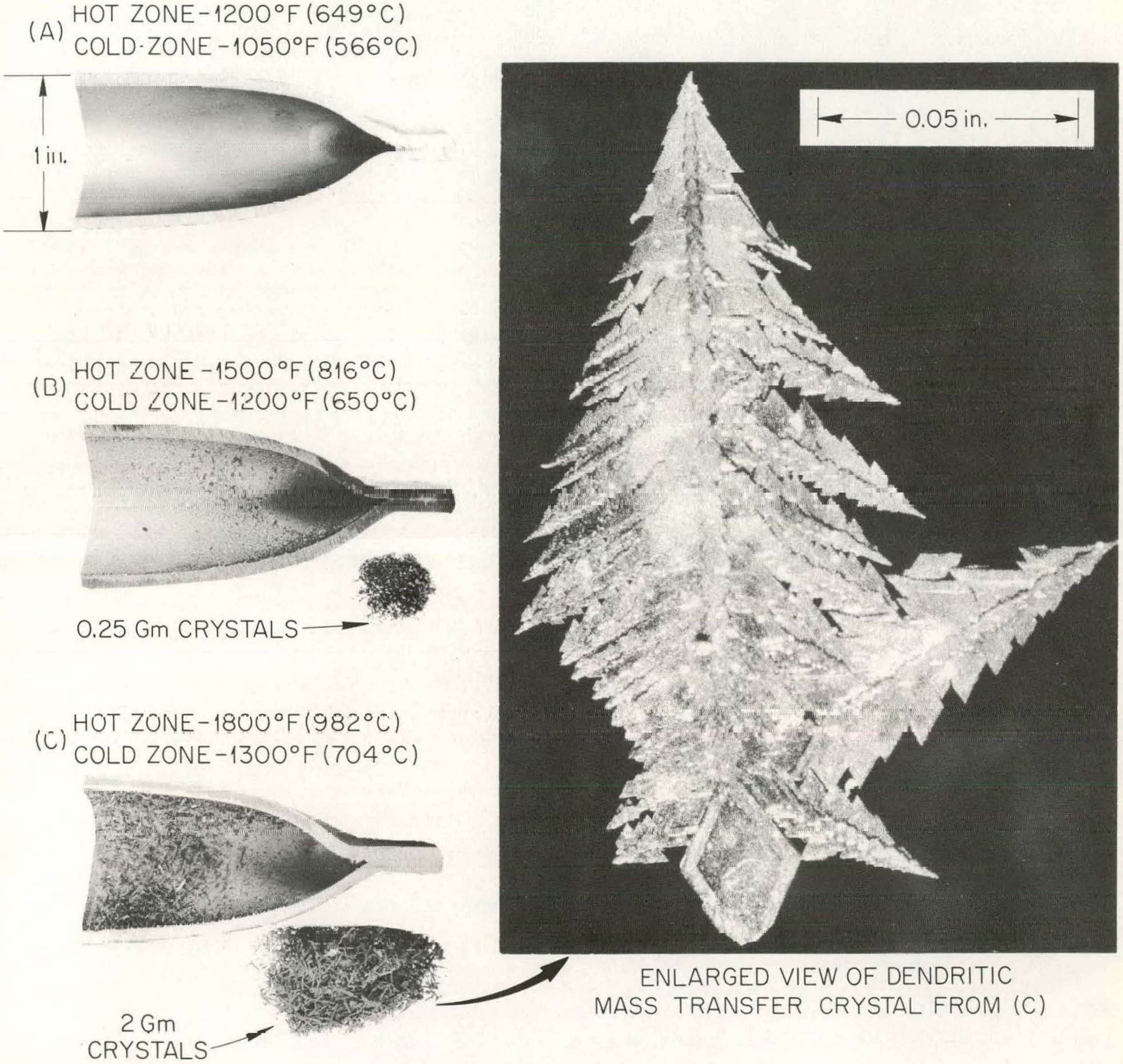

Figure 3. Cold-Zone Sections from Type 446 Stainless Steel (27 wt % Cr—Bal Fe) Seesaw Capsules Following Exposure to Lithium. Test conditions: 1 cycle per minute, 100 hours (6000 cycles).

successive formation and reduction of $FeO \cdot (Na_2O)_2$ in the hot and cold zones, respectively.

Baus and co-workers[20] measured the solubility of iron over the range 200 to 560°C in pure sodium and in sodium saturated with sodium monoxide. They found that iron was approximately four times more soluble in the oxygen-contaminated sodium. Weeks[21] estimated that $\Delta F^{O}_{FeO \cdot (Na_2O)_2}$ at 480°C is −9 kcal/mole and stated that the apparent increase in the solubility of iron could be due to the formation of this complex oxide, which then dissolves in the sodium. A similar effect was observed[22] in tests of austenitic stainless steel at 500°C which showed that increasing the oxygen concentration of the sodium from 30 to 100 parts per million (ppm) resulted in the rate of attack being increased by an order of magnitude.

Impurities in alkali metals also have a marked effect on the corrosion resistance of refractory metals. Free-energy considerations indicate that an impurity such as oxygen in sodium could react with a container material such as niobium to form niobium oxide surface films. High concentrations of oxygen in the sodium and removal of the oxide from the solid metal would result in high corrosion rates. Several investigators have discussed this corrosion process.[23–25]

Solid-Metal Impurities

The presence of oxygen, carbon, etc., in the solid metal has also been found to cause corrosion. Although pure iron generally has been found to be resistant to attack by lithium, Hoffman[26] reported that iron containing small amounts of carbon was penetrated intergranularly by lithium in certain temperature ranges. Corrosion was attributed to a reaction of lithium with carbon in the grain boundaries. Lyashenko et al.[27] noted similar results, reporting increased weight losses and lithium penetration as a function of increasing carbon content of some steels. The results indicated that corrosion occurred according to the following reaction:

$$2Fe_3C + 2Li \rightarrow Li_2C_2 + 6Fe$$

These results, as well as those cited in the previous section, show that the presence of unstable phases in either solid or liquid metal can be an important factor in the overall compatibility of the system. It is, therefore, always important to consider what impurities are present and to what extent they can be controlled.

Partitioning of Impurities Between Solid Metal and Liquid Metal

In the previous two sections the role of impurities in corrosion mechanisms was discussed as to the formation of soluble or loosely adherent complexes. It has recently been observed that these impurities in solid metal—liquid metal systems had still another effect: when oxygen* is in solution in two immiscible phases, it partitions itself between the two phases. This problem is especially important in refractory metal—alkali metal systems for two reasons: low oxygen concentrations in these metals are difficult to obtain and maintain and at the temperatures required for many applications oxygen diffusion rates are high.

In some systems a deleterious effect of oxygen partitioning is unfavorable modifications of the mechanical properties of the refractory metal due to oxygen increases. It is well known that the properties of these metals are quite often sensitive to oxygen concentration.[28] Another possible result of the partitioning of oxygen could be plugging (by precipitated alkali-metal oxides) of the cooler regions in flowing circuits if sufficient quantities of oxygen were leached from the refractory metal. These considerations point to the desirability of being able to predict the equilibrium distribution of oxygen in refractory metal—alkali metal systems. The method used by the authors and other investigators is outlined below.

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*Only oxygen is discussed here; in some systems, however, carbon, hydrogen, and nitrogen can behave in a similar manner.

Consider two immiscible solvents A and B in contact, both containing oxygen in solution. Then

$$\bar{F}_A = F_A^o + RT \ln a_A , \tag{1}$$

where $\bar{F}_A$ is the partial free energy of oxygen per gram atom; in A, F_A^o is the free energy per gram atom of oxygen in a reference state, and a_A is the activity of oxygen in A. Similarly, in solvent B the partial free energy of oxygen per gram atom can be written as

$$\bar{F}_B = F_B^o + RT \ln a_B . \tag{2}$$

Since at equilibrium $\bar{F}_A = \bar{F}_B$, it can be shown that

$$\ln \frac{a_B}{a_A} = \frac{F_A^o - F_B^o}{RT} . \tag{3}$$

A useful reference state for oxygen in this case is oxygen in solution in A or B which is in equilibrium with the oxides of A or B. For this choice of reference state F_A^o can be replaced by $\Delta F^o_{f(A \text{ oxide})}$ and F_B^o by $\Delta F^o_{f(B \text{ oxide})}$, where ΔF_f^o refers to the standard free energy of formation of the oxides of A or B. Therefore

$$\frac{a_B}{a_A} = \exp\left[\frac{\Delta F^o_{f(A \text{ oxide})} - \Delta F^o_{f(B \text{ oxide})}}{RT}\right] . \tag{4}$$

If the activity of oxygen in the dilute solutions involved can be expressed by an equation of the type

$$a_B = k_B N_B$$

where N_B is the atomic fraction of oxygen in B and k_B is a constant, then

$$a_B = \frac{N_B}{(N_B)_s} ,$$

since $a_B = 1$ when $N_B = (N_B)_s$ (atom fraction of oxygen soluble in B at temperature T), and similarly

$$a_A = \frac{N_A}{(N_A)_s} .$$

At low concentrations

$$a_A = \frac{C_A}{(C_A)_s} \text{ and } a_B = \frac{C_B}{(C_B)_s} \quad ,$$

where C stands for concentration. Equation (4) can therefore be expressed as

$$\frac{C_B}{C_A} = \exp\left[\frac{\Delta F^o_{f(\text{A oxide})} - \Delta F^o_{f(\text{B oxide})}}{RT}\right] \frac{(C_B)_s}{(C_A)_s} \quad . \tag{5}$$

The right side of Eq. (5) is a constant at a given temperature and is called the distribution coefficient κ_T,

$$\kappa_T = \frac{C_B}{C_A} \quad . \tag{6}$$

Numerous investigators[25, 29–31] have used thermodynamic treatments of this type to calculate the concentration limits of oxygen in sodium that must be maintained to prevent oxygen contamination of container materials. The correlation of calculated and experimentally determined distribution coefficients for oxygen in refractory metal–alkali metal systems is discussed in "Corrosion Results," this paper.

Stress Corrosion

The effect of liquid metals on the brittle fracture of stressed solid metals has been studied extensively by Rostoker _et al._[32] Diffusion penetration processes are not fundamentally implicit in this phenomenon since the severity of embrittlement generally increases with decreasing temperature, indicating that diffusion-controlled processes are not responsible. Rostoker[33] proposes that the liquid metal, through adsorption at the interface of the load-sustaining material, reduces the energy to initiate and propagate fracture to the extent that the plastic component of the process is virtually suppressed.

The only two examples of stress-corrosion cracking involving alkali metals have been reported for the lithium–AISI 4130 steel and lithium–copper systems.[32] This phenomenon has not been observed in refractory metal–alkali metal systems.

CORROSION RESULTS FOR REFRACTORY METAL–ALKALI METAL SYSTEMS

Tungsten, molybdenum, tantalum, and niobium, as well as other high-melting refractory metals, appear to have excellent resistance to dissolutive attack by the alkali metals at high temperatures. Although corrosion data are not yet available on many refractory metal–alkali metal test systems, some of the corrosion phenomena discussed in the previous section have been observed in these systems. Results which have been obtained are discussed under the following headings:

Dissolutive Corrosion

Solubility

The solubility information currently available[34–44] for refractory metal–alkali metal systems is summarized in Tables 1–4. It is emphasized that the available data were often not reported as equilibrium solubility information but rather as analyses of the alkali metal before and after a compatibility test with a particular refractory metal. When no data whatever were available, the results of theoretical predictions of qualitative solubility are given.

From these tabulations it is obvious that there is a dearth of solubility information. However, those available do provide a guide to indicate the relative inertness of the refractory metals compared with conventional structural materials as containers for alkali metals at high temperatures.

Strauss *et al.*[45] proposed that both the solubility and the temperature coefficient of solubility are strongly dependent on the disparity in the atomic radii of solvent and solute atoms. A comparison of the solubility of molybdenum in lithium to that of some other structural materials is given in Figure 4. In this study Leavenworth and Cleary[44] concluded that the relative atomic size of solvent and solute in dilute liquid-metal solutions does, as was proposed,[45] have an important effect on both the magnitude of the solubility and the temperature coefficient of the solubility. The size factor for the metals in Figure 4 is listed below:

Table 1. Solubility of Niobium in Alkali Metals

Alkali Metal	Temperature (°C)	Time (hours)	Niobium Concentration (ppm)	Remarks	Reference Number[a]
Lithium	500	100	< 30[b]	Armco Fe container	34
	735	100	80[b]	Armco Fe container	34
	1000	50–100	< 1[b]		35
	1015	50–100	900[b]	Armco Fe container	34
Sodium	900	8	93[c]	Nb–1 wt %[d] Zr container	36
	1150	2.5	24[c]	Nb–1% Zr container	36
	1200	720	50–110[e]	Nb–1% Zr container	37
	1250	3.5	53[c]	Nb–1% Zr container	36
	1370	3	41[c]	Nb–1% Zr container	36
Potassium	1150	8	1000[e]	Nb–1% Zr container	38
	1200	100	300[e]	Nb–1% Zr container	39
Rubidium				No data available, but low solubility predicted	40
Cesium				No data available, but low solubility predicted	40

[a] See Reference section at end of paper.

[b] Solubility experiment.

[c] Sodium density experiment.

[d] All percentages in this paper are based on weight, unless otherwise noted.

[e] Corrosion experiment.

Table 2. Solubility[a] of Tantalum in Alkali Metals

Alkali Metal	Temperature (°C)	Time (hours)	Tantalum Concentration (ppm)	Remarks	Reference Number[b]
Lithium	725	24	19	Armco Fe container	34
	1000	100	1850	Armco Fe container	34
Sodium	325	24	0.03	Tracer technique	41
	525	24	2.9	Tracer technique	41
Potassium				No data available, but low solubility predicted	42,43
Rubidium				No data available, but low solubility predicted	40
Cesium				No data available, but low solubility predicted	40

[a] All data obtained in solubility experiments.

[b] See Reference section at end of paper.

Table 3. Solubility[a] of Molybdenum in Alkali Metals

Alkali Metal	Temperature (°C)	Time (hours)	Molybdenum Concentration (ppm)	Remarks	Reference Number[b]
Lithium	550	100	< 15	Armco Fe container	34
	735	24	< 10	100 ppm N in Li	44
	860	100	< 25	Armco Fe container	34
	870	24	13	100 ppm N in Li	44
	980	100	140	Armco Fe container	34
	1000	50–100	< 1		35
	1200	20–100	300–1000		35
Sodium				No data available, but low solubility predicted	42,43
Potassium				No data available, but low solubility predicted	42,43
Rubidium				No data available, but low solubility predicted	40
Cesium				No data available, but low solubility predicted	40

[a] All data obtained in solubility experiments.

[b] See Reference section at end of paper.

Table 4. Solubility[a] of Tungsten in Alkali Metals

Alkali Metal	Temperature (°C)	Time (hours)	Tungsten Concentration (ppm)	Remarks	Reference Number[b]
Lithium	715	24	1050	Armco Fe container	34
Sodium				No data available, but low solubility predicted	42,43
Potassium				No data available, but low solubility predicted	43
Rubidium				No data available, but low solubility predicted	40
Cesium				No data available, but low solubility predicted	40

[a] Solubility experiment.

[b] See Reference section at end of paper.

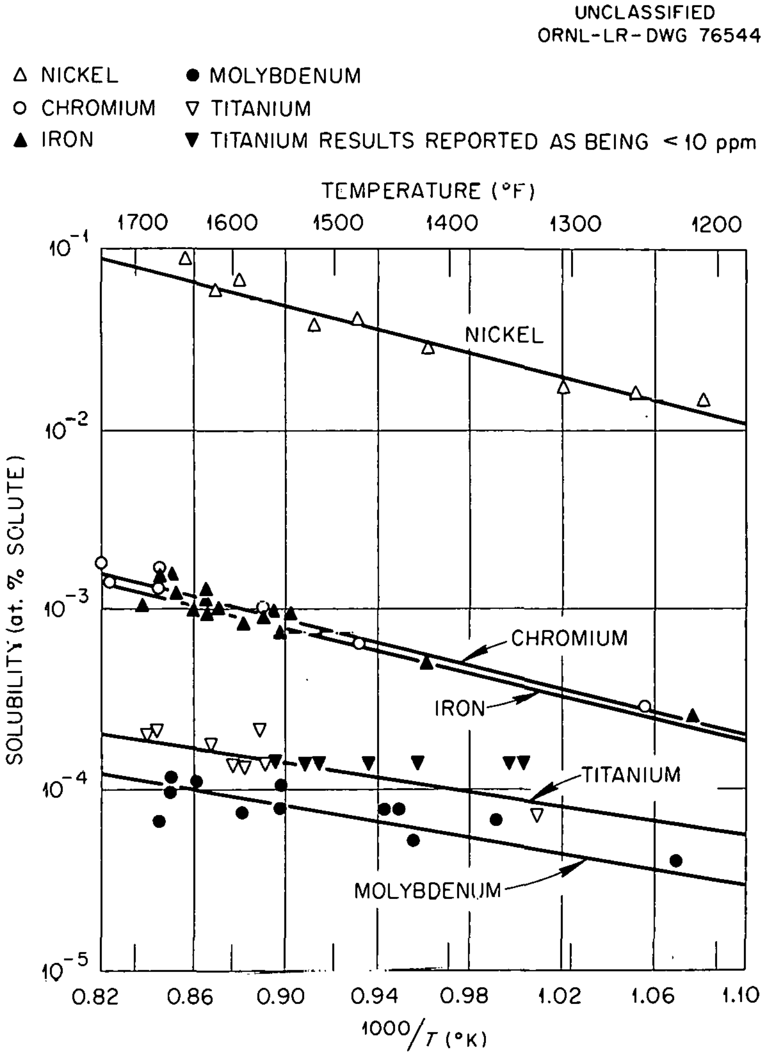

Figure 4. Variation of the Solubility of Some Metals in Lithium with the Reciprocal of the Absolute Temperature. Nitrogen contamination 50–100 ppm. [Data taken from H. W. Leavenworth and R. E. Cleary, "The Solubility of Ni, Cr, Fe, Ti, and Mo in Liquid Lithium," *Acta Metallurgica* **9**, 519–20 (May 1961).]

$$\text{Atomic size factor} = \frac{\text{atomic radius of solvent}}{\text{atomic radius of solute}}$$

$$\frac{\text{Li}}{\text{Ni}} = 1.26; \ \frac{\text{Li}}{\text{Cr}} = 1.22; \ \frac{\text{Li}}{\text{Fe}} = 1.24; \ \frac{\text{Li}}{\text{Ti}} = 1.07; \ \frac{\text{Li}}{\text{Mo}} = 1.12$$

Although many static corrosion tests have been conducted which were not considered to be solubility experiments, the results are useful insofar as they give qualitative indications of the extent of solubility. These results are presented in Table 5.[46–52] It may be noted that under a variety of thermal conditions the refractory metals are quite corrosion-resistant, indicating low solubilities.

Dissimilar-Metal Mass Transfer

Corrosion effects as a result of two or more metals in contact with a common alkali metal have generally been observed only after relatively long times at temperatures in excess of 700°C in the case of refractory-metal systems.

Early results were reported by Brasunas[53] from tests in which niobium, molybdenum, tantalum, or tungsten was tested for 400 hours at 1000°C in Armco iron capsules containing lithium or in nickel capsules containing sodium. These results are summarized in Table 6. The most severe corrosion effect was found in the molybdenum-sodium-nickel system in which a very hard (2990 diamond pyramid hardness) nickel-rich surface layer formed on the molybdenum. More recent results reported by Hoffman[54] indicate that this interaction also occurs in the molybdenum-sodium-Inconel (80% Ni–14% Cr–6% Fe) system. Figure 5 shows the surface of a molybdenum specimen following exposure to sodium in an Inconel container after 500 hours at 980°C.

In addition to mass transfer of metallic constituents, transfer of interstitial elements such as carbon and nitrogen from stainless steels or other materials which contain these elements has been observed in some refractory-metal systems. The authors investigated the niobium-sodium–type 316 stainless steel system in some detail and found this type of interaction to be the major one at temperatures up to 1000°C. Test results are summarized in Table 7, which indicate that when the

Table 5. Results of Corrosion Experiments of Refractory Metals in Various Alkali Metals

Test Material	Alkali Metal	Temperature (°C)	Time (hours)	Remarks	Reference Number[a]
Niobium	Lithium	815	100	No attack	46
		980	100	No attack	46
Niobium	Potassium	1090	300	No attack	47
		1150	100	No attack	47
		1200	140	No attack	47
Nb—1% Zr	Potassium	1090	300	No attack	47
		1150	100	No attack	47
Tantalum	Lithium		100	No attack	48
Molybdenum	Lithium	815	100	No attack	48
Molybdenum	Sodium	1500	100	$<$ 0.001-in. attack	49
Mo—0.5% Ti	Potassium	730	500	No attack	50
		900	500	No attack	50
		925	500	No attack	50
		980	500	No attack	50
Molybdenum	Cesium	1000	100	No attack	51
Tungsten	Lithium	815	100	No attack	52
	Potassium	540	1000	No attack	47
	Cesium	1000	100	No attack	47

[a] See Reference section at end of paper.

Table 6. Dissimilar-Metal Corrosion Results of Refractory Metals in Iron-Lithium and Nickel-Sodium Systems after 400 hr at 1000°C

Specimen	Container	Liquid Metal	Weight Change (gram/cm^2)	Metallographic Notes on Specimen
Niobium	Armco iron	Lithium		Thin surface film
Tantalum	Armco iron	Lithium	−0.003	Surface film identified at TaC by x ray
Molybdenum	Armco iron	Lithium	−0.011	Thin surface deposit; x ray of surface showed traces of Fe
Tungsten	Armco iron	Lithium	−0.071	No film visible but x ray of surface identified Fe_2W
Niobium	Nickel	Sodium	−0.060	Unidentified phase at some grain boundaries
Tantalum	Nickel	Sodium	+0.010	Dual film; x ray identified TaC
Molybdenum	Nickel	Sodium	+0.002	0.002-inch-thick Ni-rich intermetallic compound
Tungsten	Nickel	Sodium	−0.029	Extremely thin metallic surface film; x ray of surface indicated WC

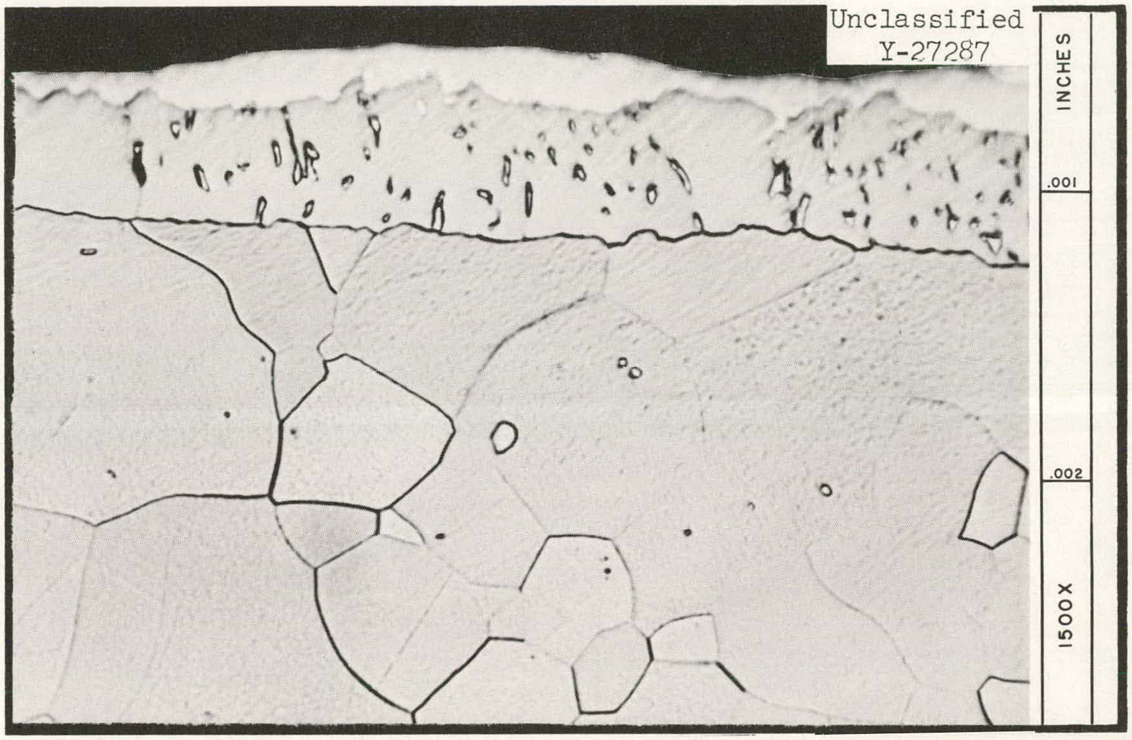

Figure 5. Surface of Molybdenum Specimen Following Exposure to Sodium for 500 Hours at 980°C in an Inconel (80% Ni–14% Cr–6% Fe) Container. Surface layers shown contain nickel, chromium, and molybdenum and have a diamond pyramid hardness of 1200. Etchant: 50% H_2O_2–50% NH_4OH (by volume).

Table 7. Effect of Mass Transfer of Carbon and Nitrogen on Room-Temperature Tensile Properties of Niobium[a] Tested in Sodium in Type 316 Stainless Steel[b] Containers

Temperature (°C)	Time (hours)	Surface Area Ratio of Stainless Steel to Niobium	Change in Concentration in Niobium (ppm)		Room-Temperature Tensile Properties			
					Ultimate Tensile Strength ($lb/inch^2$)		Elongation in 2.5 inch (%)	
			Carbon	Nitrogen	Before Test	After Test	Before Test	After Test
925	1000	0.1	−100	−20				
925	500	6.5	+240	+660	22,800	48,200	17.5	5
925	500	6.5	+420	+1920	22,800	46,200	17.5	11
980	500	20	+790	+860	22,800	50,400	17.5	6

[a] All specimens used in these tests were annealed for 2 hours at 1500°C in vacuum prior to exposure; specimen thickness, 0.040 inch.

[b] 18% Cr–13% Ni–2.5% Mo–1.8% Mn–0.06% C–0.03% N.

ratio of stainless steel to niobium surface area was 6.5 or greater carbon and nitrogen transferred from the stainless steel to the niobium. This caused an increase in ultimate tensile strength and a decrease in ductility of the niobium. Time, temperature, and surface area ratio all affected the amount of interstitial element transfer. When the surface area ratio of the stainless steel to niobium was reduced to 0.1, no significant increase of carbon and nitrogen in the niobium was observed but niobium carbide and niobium nitride were found on the surface of the stainless steel.

Increases in the carbon and nitrogen concentration of niobium found by chemical analyses were verified by metallographic and x-ray examination, which revealed two surface layers on the niobium identified as NbC and Nb_2N (Figure 6). Further studies showed that carbon was confined to the surface layer but that nitrogen had diffused into the metal (Table 8). Tensile tests on specimens with the surface layers removed gave results comparable to the as-exposed samples, indicating that nitrogen contamination in the bulk of the sample rather than brittle surface layers was primarily responsible for the observed changes in tensile properties.

Table 8. Carbon and Nitrogen Concentration of Niobium Specimen[a] Before and After Exposure in Sodium–Type 316 Stainless Steel System for 1000-Hours at 925°C

Specimen Condition	Concentration (ppm) Carbon	 Nitrogen
Before test	90	80
After test	510	2000
After surface layers machined off	150	590

[a] Specimen thickness, 0.040 inch.

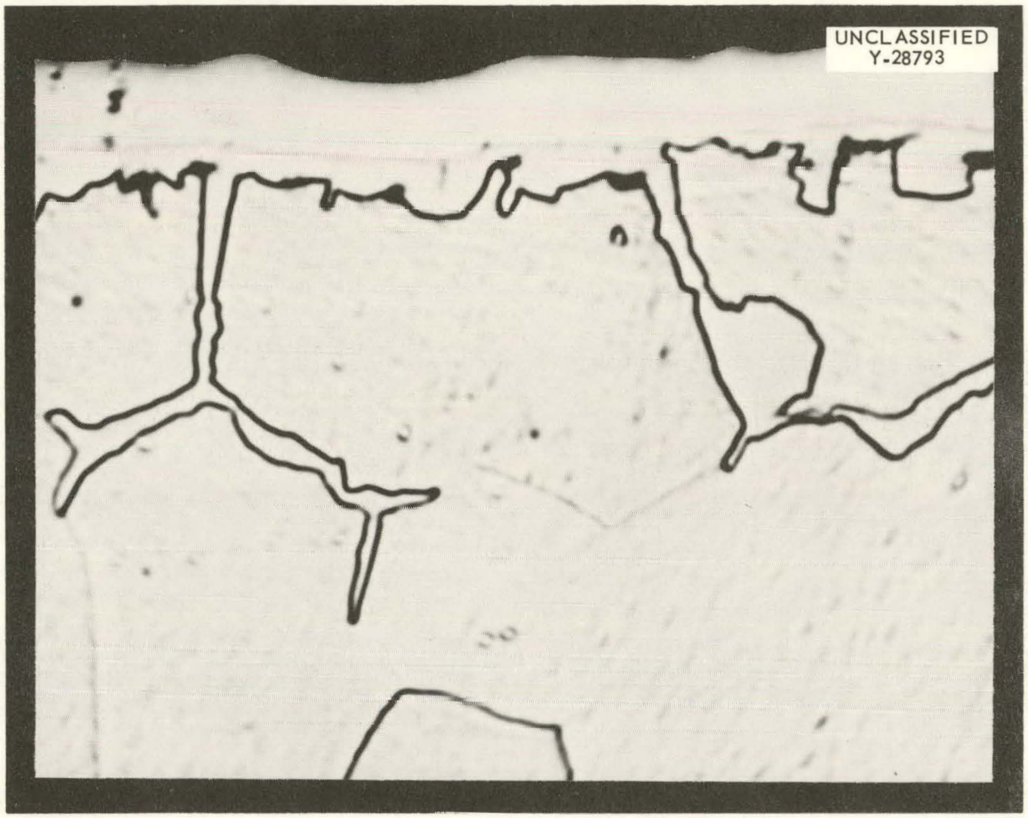

Figure 6. Surface of Niobium Specimen Following Exposure to Sodium at 925°C for 500 Hours in a Type 316 Stainless Steel Capsule. Note the NbC (dark) and Nb_2N (light) layers on the surface. [Etching procedure as described by E. Ence and H. Margolin, "Phases in Titanium Alloys Identified by Cumulative Etching," Journal of Metals 6, 346 (March 1954).] Magnification: 2000X.

Other refractory-metal systems in which similar effects have been noted are (Nb–1% Zr)–K–Haynes alloy No. 25[*],[55–56] (Nb–1% Zr)–K–(Hastelloy X[**]),[57] and (Nb–1% Zr)–Cs–Haynes alloy No. 25.[58]

Temperature-Gradient Mass Transfer

Only a limited number of corrosion tests of refractory metals in contact with flowing nonisothermal alkali metals have been conducted. Although the data are limited, no serious temperature-gradient mass transfer was detected in the systems studied. The results available in the literature are discussed below.

Niobium. – A 300-hour seesaw furnace test[‡] of niobium in contact with lithium at hot- and cold-zone temperatures of 870 and 600°C, respectively, showed no attack or crystal deposition.[59] Although no quantitative results are given, a recent article[60] stated that an alloy of zirconium and niobium had been used to contain lithium for thousands of hours at temperatures up to 1090°C.

In a system with sodium[‡‡] flowing at 30 feet per second, the corrosion rate of niobium at 600°C was found to be less than 1×10^{-4} inch per month in tests of 160-hour duration.[61] These results indicate that temperature-gradient mass transfer of niobium is negligible under these conditions.

A niobium–1% zirconium alloy was used to contain rubidium in a pumped system operating with boiler and cold-zone temperatures of 1000 and 260°C, and a mass flow rate of 340 pounds per hour.[62] At the conclusion of the 500-hour test only a "small amount"[62] of mass-transfer deposit was detected.

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[*] 3% Fe–10% Ni–15% W–20% Cr–bal Co.

[**] 22% Cr–45% Ni–9% Mo–1.5% Co–bal Fe.

[‡] Sealed tube partially filled with liquid metal is tilted in seesaw fashion, causing liquid metal to flow alternately from the hot to the cold end.

[††] Oxygen concentration less than 10 ppm.

Tantalum. — Raines[63] and co-workers found tantalum mass-transfer deposits in the coldest regions (180°C) of flowing-sodium corrosion test loops which had tubular tantalum specimens at 650°C in the heated region. Weight losses of approximately 11 milligrams/cm^2 per month (equivalent to 0.003 inch per year) were observed on the tantalum specimens in the hot regions during an 800-hour test. Oxygen partitioning, which was also observed in this compatibility study, is discussed later in this paper.

Molybdenum. — A series of seesaw tests were conducted on molybdenum in contact with lithium.[64] The test conditions and weight-change results are listed in Table 9. No attack or mass-transfer deposits were detected in any of these experiments.

Molybdenum has been tested in flowing NaK (78% K) systems with respective hot- and cold-zone temperatures of 760 and 95°C for time periods up to 3000 hours and was found to be unattacked.[65]

Carlander[66] reported that molybdenum was unaffected by exposure to rubidium in a 500-hour seesaw test with hot- and cold-zone temperatures of 1040 and 730°C, respectively.

Tungsten. — No dynamic corrosion information was found in the literature.

Impurity Reactions

Liquid-Metal Impurities

The concern here is primarily with those corrosion effects caused by the formation of soluble or nonadherent compounds on the surface of the refractory metal. Of the impurities generally found in alkali metals only the effect of oxygen in sodium or NaK has been studied in detail.

Kelman and co-workers[67] reported that increasing oxygen in NaK caused increased corrosion of niobium, molybdenum, tantalum, and tungsten at 600°C. Carter et al.[68] found that at 590°C molybdenum was not corroded by sodium containing 10-ppm oxygen. In contrast, niobium suffered a weight loss of 1 milligram/cm^2 per day under these conditions. Since the reactions for formation of oxides of these elements should be thermodynamically controlled, it would not be expected (see "Partitioning of Impurities," below, Table 11) that molybdenum or tungsten would pick up oxygen from sodium (or NaK) at these temperatures.

Table 9. Results of Lithium Corrosion Tests on Molybdenum[a] in Seesaw Furnace Test Systems

Furnace tilting rate: 1/2 cycle per minute

Test Number	Hot Zone (°C)	Cold Zone (°C)	Length of Test (hours)	Specimen Weight Change (milligrams/cm^2) Hot Zone	Specimen Weight Change (milligrams/cm^2) Cold Zone
1	930	540	500	−0.06	+0.03
2	980	540	100	−0.02	−0.04
3	980	570	500	−0.06	+0.14
4	1040	540	100	−0.03	−0.05
5	1040	590	150	−0.02	+0.03

[a] Specimens and test capsules: Mo–0.46% Ti, 0.0012% O_2, 0.0006% N_2, 0.030% C.

The effect of oxygen in sodium on the corrosion of niobium has been studied by several investigators,[69–71] and results from the paper of Williams and Heal[70] are given in Table 10. The mechanism of this corrosion process has been discussed by Evans and Thorley,[72] who suggest that the primary corrosion product is niobium oxide, which is removed mechanically by erosion in the flowing sodium. Alternatively, they proposed that once the niobium oxide is formed, nucleation and growth of a complex niobate may take place and that it is this niobate which spalls off and is carried away by the sodium. Data supporting the former hypothesis were reported by Bett,[73] who found Nb_2O_5 on the surface of niobium specimens tested in austenitic stainless steel loops circulating sodium at 600°C.

It is to be noted that results indicating the deleterious effect of oxygen in sodium on the corrosion of niobium have generally been obtained in flowing systems at low temperatures. Refluxing capsule tests of niobium–1% zirconium alloy conducted at 1200°C indicated no increase in corrosion at oxygen concentrations in the sodium up to 300 ppm.[74] Thus it appears that both velocity and temperature are significant variables in this process.

Similar effects of oxygen in sodium on the corrosion of tantalum were found by Raines _et al._,[75] who detected increased corrosion at 690°C of tantalum specimens suspended in a type 316 stainless steel loop when the oxygen in the sodium was increased from less than 10 ppm to 40 ppm.

In static tests at 800°C Litman[76] has observed greater amounts of niobium in potassium as a function of increasing oxygen in the potassium, but no oxide layers or increase of oxygen in niobium were found.

Although impurities in alkali metals have generally been found to adversely affect the corrosion resistance of several metals, it can be seen from the discussion in this section that such effects are by no means universal. Careful attention should be paid to the conditions under which results are obtained and to the variables that could affect them. Some thermodynamic considerations for predicting the extent of impurity transfer are discussed in "Partitioning of Impurities," below.

Table 10. Effect of Oxygen in Sodium on the Corrosion of Niobium

Test conditions

Specimen temperature – 600°C
Velocity – 30 feet/second
Time – 256 hour
System – austenitic stainless steel

Oxygen Control Procedure	Penetration Rate (0.001 inch/month)
Cold-trapped (120°C) (minimum oxygen concentration, 25 ppm)	32.9
Hot-gettered by use of zirconium (oxygen concentration, 5 ppm or less)	0.025

Solid-Metal Impurities

The most severe type of corrosion interaction between refractory and alkali metals appears to occur as a result of the presence of oxygen as an impurity in the solid metal.

Although niobium, tantalum, molybdenum, and tungsten have excellent corrosion resistance to lithium and sodium up to 1000°C in isothermal systems,[77–81] it has been observed that oxygen in either niobium or tantalum can lead to very rapid penetration by lithium over a wide range of temperatures.[82] The corrosion action by lithium is not a dissolutive process but rather one which involves penetration of the metal by lithium and the formation of a "corrosion" phase. This phase has not been identified but is suspected to contain lithium, oxygen, and niobium (tantalum). The corrosion product in niobium has been found in grain boundaries, as shown in Figure 7, and along crystallographic planes, as shown in Figure 8. Major variables affecting the extent of lithium penetration were found to be oxygen concentration and temperature. Time was an insensitive variable in the sense that the maximum depth of corrosion generally occurred in less than 1 hour. Similar effects were

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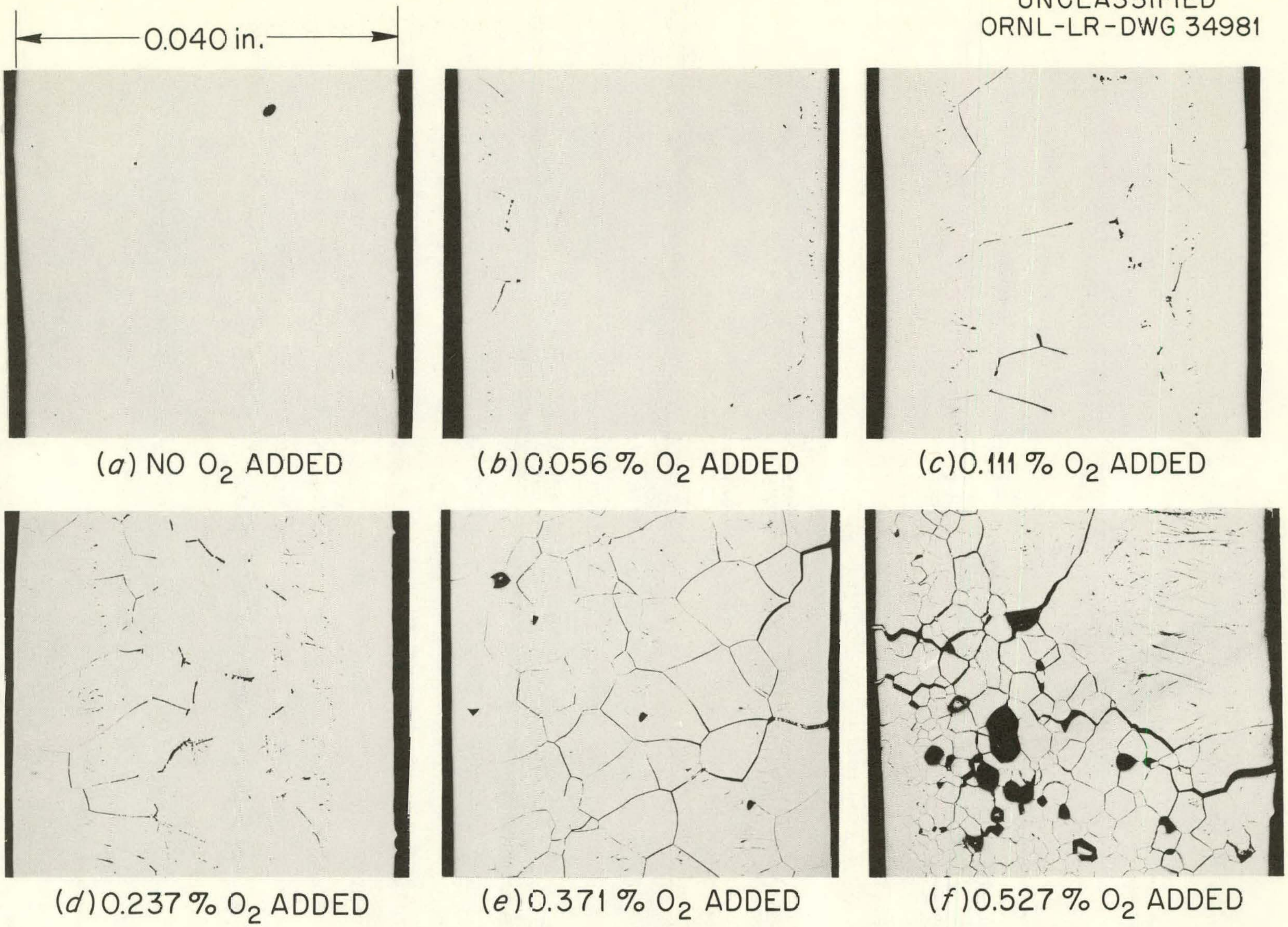

(*a*) NO O_2 ADDED

(*b*) 0.056 % O_2 ADDED

(*c*) 0.111 % O_2 ADDED

(*d*) 0.237 % O_2 ADDED

(*e*) 0.371 % O_2 ADDED

(*f*) 0.527 % O_2 ADDED

Figure 7. Fusion-Weld Zones of Niobium Specimens to Which Varying Amounts of Oxygen Were Added Prior to Welding. Specimens shown in as-polished condition after exposure to lithium. Test conditions: static, 1500°F (816°C), 100 hours.

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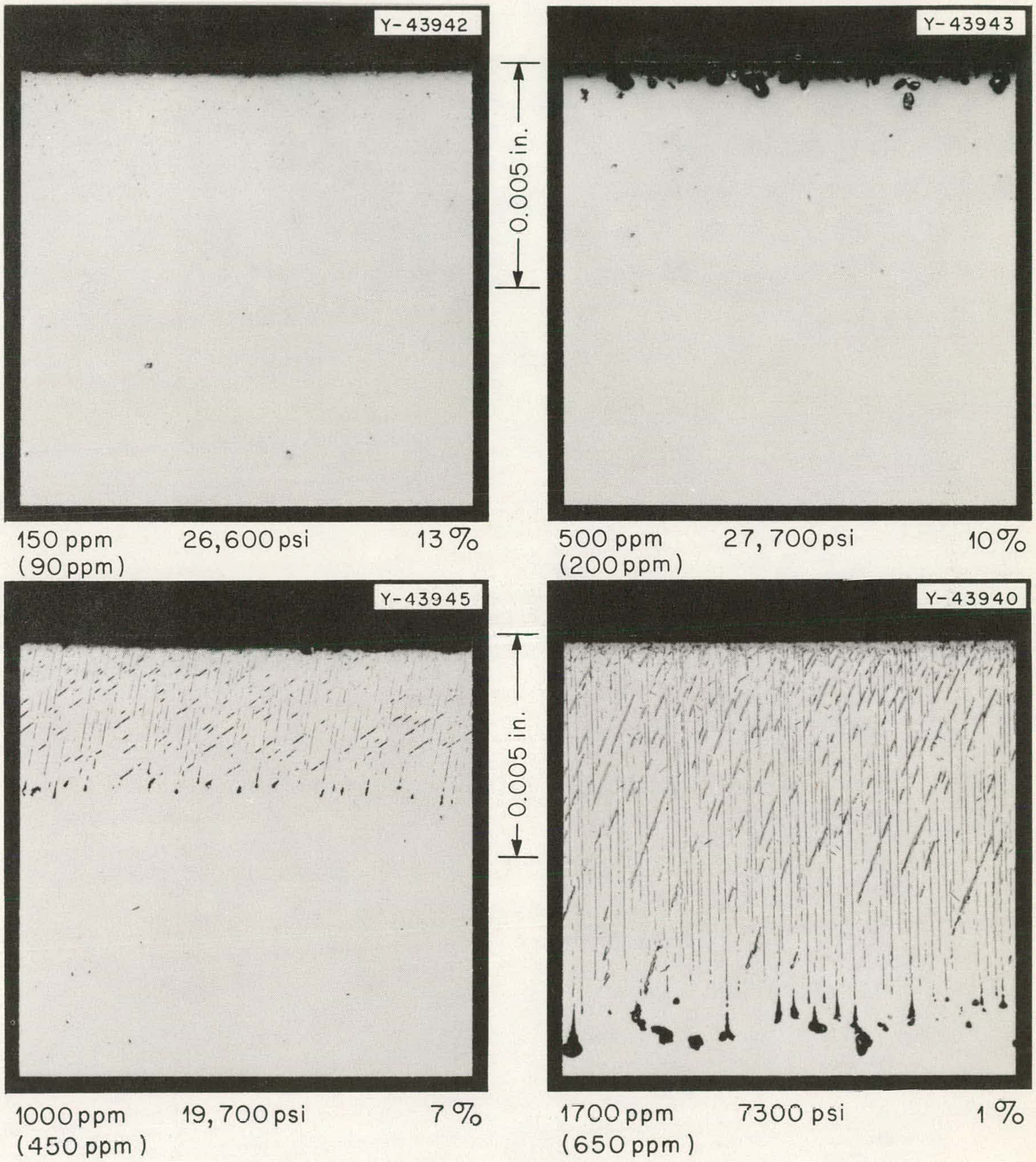

Figure 8. Effect of Initial Oxygen Concentration, 150–1700 ppm, in Niobium on the Depth of Attack by Lithium. Test conditions: 816°C (1500°F) for 100 hours. Following test, the room-temperature tensile strength varied from 26,600 to 7300 psi, the elongation in 2-in. gage length varied from 13 to 1%, and the oxygen concentration varied from 90 to 650 ppm. Etchant: $HF\text{-}HNO_3\text{-}H_2SO_4\text{-}H_2O$.

observed in the tantalum-lithium system, as shown in Figure 9. Although the mechanism of this corrosion process is not well understood, it is proposed that the existence of oxygen-rich areas in grain boundaries or along crystallographic planes may result in lithium corrosion by the formation of a lithium-niobium (tantalum)-oxygen complex in these areas. These areas of high oxygen concentration could occur in niobium or tantalum from the formation of suboxides such as those proposed by Brauer et al.[83] and Pawel et al.[84] Another possible explanation for the proposed existence of submicroscopic inhomogeneities in oxygen distribution is the concentration of oxygen atoms at dislocations. Such concentrations have been associated with etch pit formation[85-87] in niobium and tantalum. It has been suggested[88] that the development of corrosion-resistant niobium systems for the containment of lithium will depend ultimately on the addition to the base metal of an alloying element whose oxide is stable in lithium or at least stable in niobium. This hypothesis has been substantiated by results that have indicated oxygen-contaminated niobium—1% zirconium alloy does not show a similar behavior to unalloyed niobium if the alloy is properly heat-treated prior to exposure to lithium.[89] On the other hand, the addition of vanadium to niobium does not improve the corrosion resistance of niobium, as shown in Figure 10. The standard free energies of formation of oxides of these metals are listed below:

Oxide	$\Delta F^{o}_{725^\circ C}$ (kcal/gram atom of oxygen)
Li_2O	−110
ZrO_2	−108
NbO	−78
VO	−78

A similar corrosion phenomenon in the tantalum-sodium system has been reported by Raines et al.,[90] who found grain-boundary and crystallographic penetration by sodium of arc-cast tantalum containing 390-ppm oxygen at 565°C. However, recent results by the authors indicate that this corrosion problem does not occur in the niobium-potassium system at 800°C. This indicates that oxygen contamination of refractory metals is not a general compatibility problem for all refractory metal—alkali metal systems.

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(*a*) 0.008 % O_2 (*b*) 0.03 % O_2 (*c*) 0.07 % O_2 (*d*) 0.09 % O_2

Figure 9. Effect of Initial Oxygen Concentration of Tantalum on the Depth of Attack by Lithium After 100 hours at 816°C (1500°F). Etchant: HF-HNO_3-H_2SO_4-H_2O.

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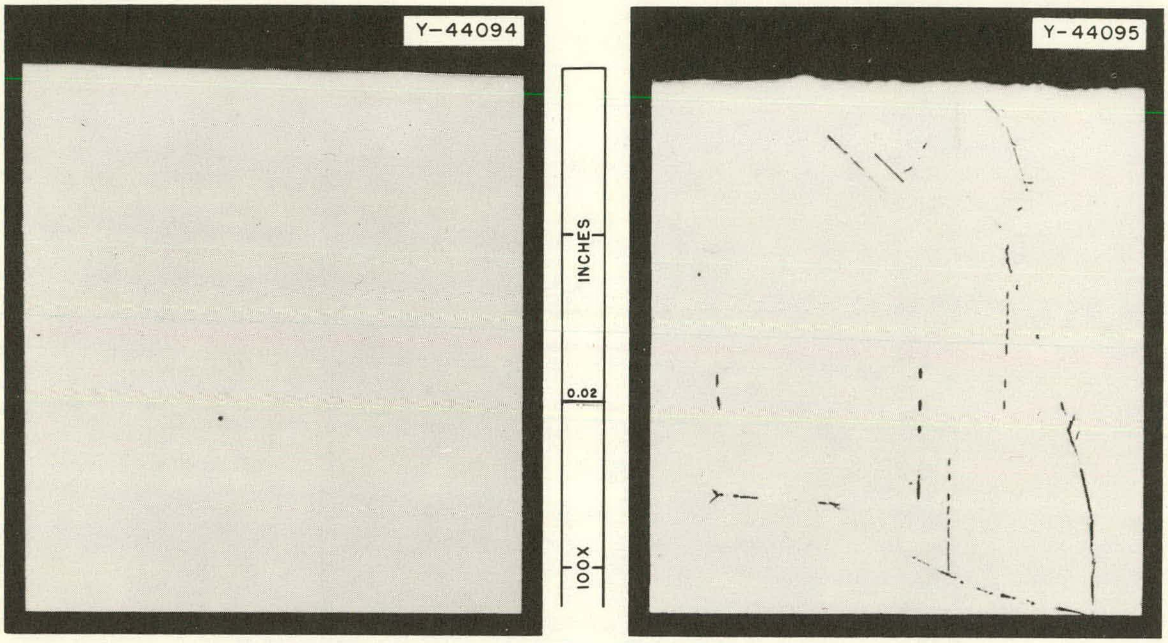
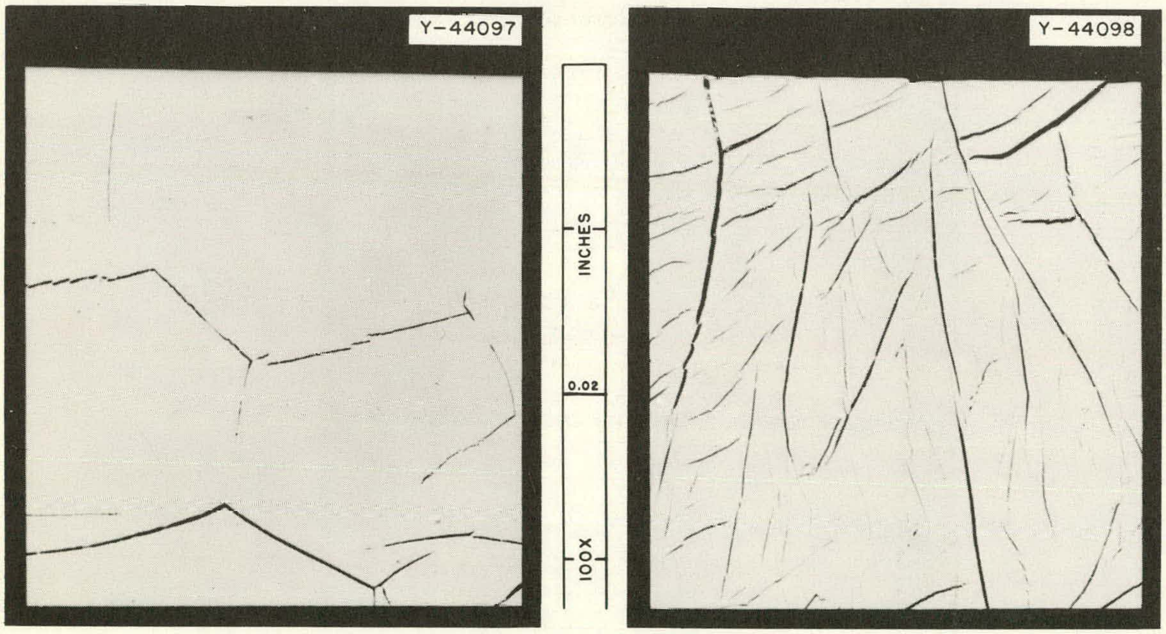


500 ppm O_2

1000 ppm O_2



2000 ppm O_2

4000 ppm O_2

Figure 10. Effect of Oxygen Concentration of Niobium–40% Vanadium Alloy on Its Corrosion Resistance to Lithium. Test conditions: 100 hours, 816°C (1500°F), as-polished.

Partitioning of Impurities

It was shown previously that when an impurity such as oxygen is present in a refractory metal—alkali metal system it should distribute itself between the two immiscible solvents according to the following equation:

$$\frac{C_A}{C_B} = \exp\left[\frac{\Delta F^o_{f(B\ \mathrm{oxide})} - \Delta F^o_{f(A\ \mathrm{oxide})}}{RT}\right] \cdot \frac{(C_A)_s}{(C_B)_s} \quad .$$

It should be noted that the above equation was derived with the aid of several assumptions: (1) immiscibility of refractory and alkali metal, (2) dilute solutions which obey Henry's law, and (3) low solute concentrations such that

$$\frac{N_A}{N_B} = \frac{C_A}{C_B} \ .$$

The equation is valid only when the solute is in solution in both phases, and, in order to use the above equation to calculate κ_T, accurate thermodynamic data must be available for the standard free energies of formation of the oxide phase, which forms at saturation. In addition, the solubility of oxygen in each metal must be known at the temperature of interest. A plot of free energy vs temperatures for these oxides is shown in Figure 11.[91] The data referenced below (see Reference section at end of paper) have been used in this report to estimate the solubility of oxygen in the metals at the temperatures of interest:

Metal	Reference Number
Nb	92
Mo	93
Ta	94
W	95
Li	96
Na	97
K	98

With the above limitations in mind, calculations of κ_T have been made at 500 and 800°C. These data, along with available experimental data, are presented in Table 11.[99–100]

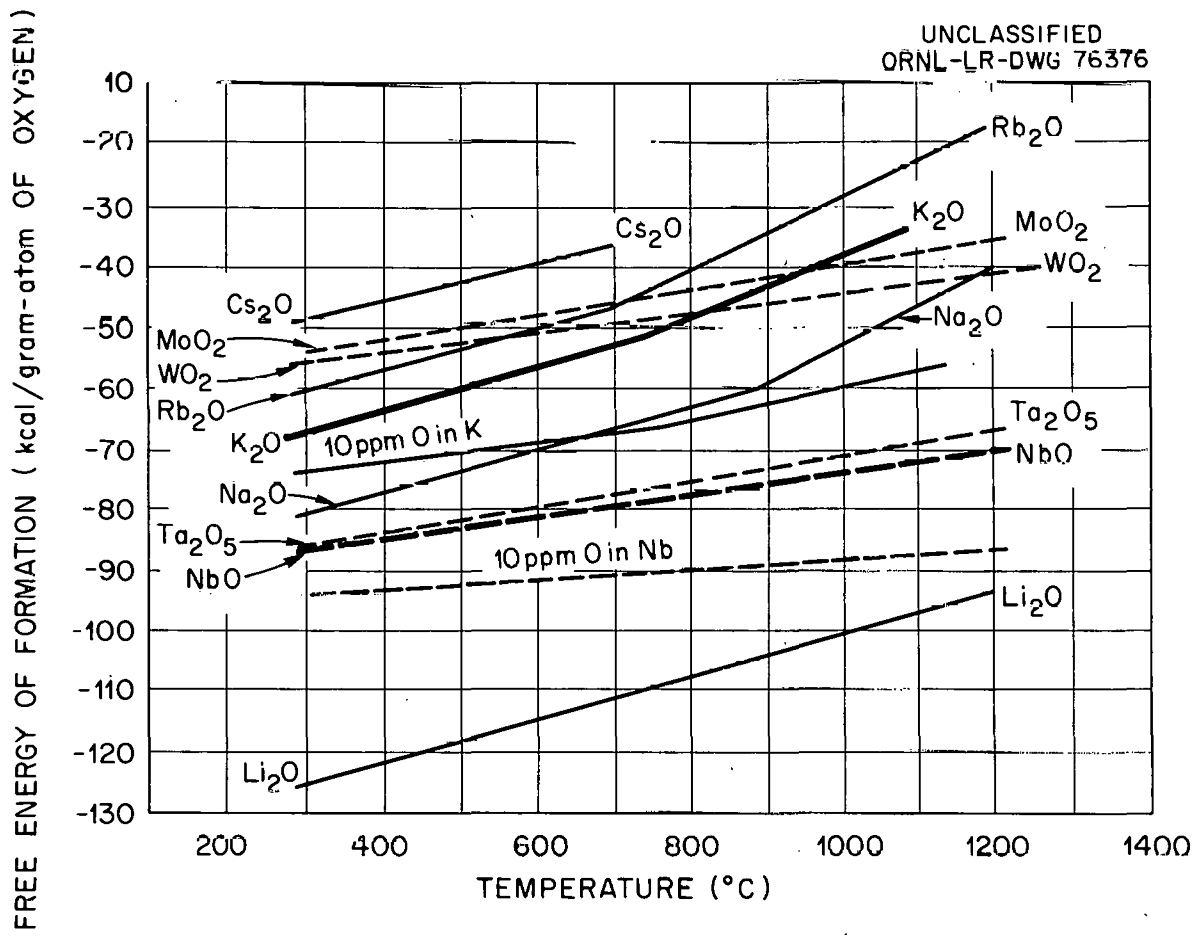


Figure 11. Free Energies of Formation of Oxides of Refractory Metals and Alkali Metals as a Function of Temperature.

Table 11. Calculated and Experimental Values of κ_T for Some Refractory Metal—Oxygen—Alkali Metal Systems

$$\kappa_T = \frac{C_O \text{ in Refractory Metal}}{C_O \text{ in Alkali Metal}}$$

System	Calculated 500°C	Calculated 800°C	Experimental 500°C	Experimental 800°C
Nb-O-Li	5×10^{-11}	1×10^{-7}		
Nb-O-Na	1×10^{3}	4×10^{2}		
Nb-O-K	5×10^{5}	3×10^{4}	0.5–1.2[a]	0.1–0.3[a]
Ta-O-Li	3×10^{-11}	3×10^{-8}		
Ta-O-Na	6×10^{2}	1.5×10^{2}	6–26[b]	2–18[b]
Ta-O-K	3×10^{5}	1×10^{4}		
Mo-O-Li	7×10^{-22}	5×10^{-16}		
Mo-O-Na	1×10^{-8}	2×10^{-6}		
Mo-O-K	7×10^{-6}	1×10^{-4}		
W-O-Li	1×10^{-21}	3×10^{-16}		
W-O-Na	2×10^{-8}	2×10^{-6}		
W-O-K	1×10^{-5}	2×10^{-4}		

[a] See Reference 99 at end of this paper.

[b] See Reference 100 at end of this paper.

Since 800°C is above the melting point of K_2O, extrapolation of solubility data is questionable. It was assumed that the activity of oxygen in potassium could be approximated at this temperature by

$$a = \frac{\text{wt \% oxygen}}{17} ,$$

where 17 is the stoichiometric concentration of oxygen in K_2O.

Any oxygen in molybdenum or tungsten should readily be gettered by these metals. Since both molybdenum and tungsten have been reported to have a very low oxygen solubility at these temperatures, it would not be expected that very much oxygen would be redistributed when these metals are placed in contact with lithium, sodium, or potassium. No experimental quantitative data are yet available, but tests conducted by the authors with molybdenum containers for potassium have generally shown low oxygen in the molybdenum both before and after exposure.

Niobium and tantalum, on the other hand, have appreciably greater oxygen solubilities, and some redistribution does occur. Experimental measurements of κ_T are difficult to obtain because of complications arising from other types of corrosion interactions. For example, the presence of more than 500-ppm oxygen in either niobium or tantalum causes rapid penetration by lithium which results in the formation of a corrosion phase containing oxygen.

Experimental data on the niobium-oxygen-potassium and tantalum-oxygen-sodium systems are shown in Table 11. It has been found that in these systems κ_T is not as large as was calculated. At 800°C, κ_T (calculated) = 3×10^4 for the niobium-oxygen-potassium system, and it can be seen in Figure 11 that the standard free energy of NbO is more negative than that for 10-ppm oxygen in potassium over the temperature range shown. This indicates that niobium should getter oxygen from potassium to a very low concentration level. However, instead of being gettered by niobium or tantalum, potassium and sodium were found to deoxidize niobium and tantalum at 800°C. This type of discrepancy may stem in part from uncertainties in the oxygen analyses of the alkali metals.

No data on oxygen partitioning in rubidium and cesium systems have been reported, because there is a lack of thermodynamic and experimental data. The standard free energies of formation for the oxides of these metals are less negative than that of potassium, which would tend to increase κ_T. However, some preliminary data indicate that oxygen solubilities in rubidium and cesium are higher than in potassium, and this would tend to decrease κ_T.

The effect of partitioning of hydrogen in the niobium-hydrogen-NaK system has been demonstrated by Thorley and Tyzack,[101] who found that hydrogen in NaK was gettered by niobium in the Dounreay Fast Reactor. With a cold-trap temperature of 200°C the hydrogen concentration of the niobium increased from less than 10 ppm to 200 ppm, at which level a bend test showed the material to be brittle. It has also been found[102] that tantalum is hydrided in sodium if the sodium contains hydrogen. Contrary to results in gas phase studies, nitride or oxide film on the tantalum gave no useful protection against hydriding.

With other impurities such as nitrogen and carbon similar effects might also be expected. However, both are generally less soluble than oxygen in refractory and alkali metals and their concentrations are lower. Also, as discussed previously under dissimilar-metal mass-transfer results, carbide and nitrogen layers formed on niobium and tantalum in the range 800–1000°C, and under these circumstances the partitioning equation would not apply.

CONCLUSIONS

The refractory metals and their alloys generally have shown sufficient corrosion resistance to be considered as structural materials for alkali-metal reactors and for power conversion systems designed to operate at temperatures in excess of 1000°C. However, comparatively little quantitative compatibility information is available on specific refractory metal–alkali metal systems under a variety of test conditions. The bulk of such information has been obtained under static isothermal conditions at a maximum temperature of 1200°C. Data in flowing nonisothermal test systems are sparse.

The principal compatibility phenomena are as follows:

Solubility. — The limited data available indicate that niobium, tantalum, molybdenum, and tungsten are all less soluble in alkali metals than are constituents of conventional high-temperature alloys, such as iron, nickel, chromium, and cobalt. Only in lithium at 700°C are solubility data on all four refractory metals available, and molybdenum has been reported to have the lowest solubility.

Dissimilar-Metal Mass Transfer. — Interactions in refractory-metal systems between two or more metals in contact with a common alkali metal have been limited to exposures involving high temperatures and long times. Phase diagrams of the metals under consideration can often be useful guides in predicting interactions of this type. In addition to the transfer of metallic elements, interstitial elements such as oxygen, nitrogen, and carbon also have been observed to transfer to niobium and tantalum from stainless steels or other alloys containing these interstitials.

Temperature-Gradient Mass Transfer. — No serious temperature-gradient mass-transfer effects have been detected in the limited number of nonisothermal tests of refractory metals in contact with flowing alkali metals. The most complete data are available for the molybdenum-lithium system, and no attack or mass-transfer deposits were detected after 500 hours at 980°C and 500°C ΔT.

Impurity Reactions. — The most serious compatibility problems in refractory metal—alkali metal systems appear to occur as a result of impurities such as oxygen, hydrogen, nitrogen, and carbon in the system. Oxygen in alkali metals can cause accelerated corrosion of those refractory metals which form soluble or loosely adherent oxides or complexes more stable than the alkali metal. This effect generally seems to be more serious in systems operated at low temperatures, where diffusion rates are low, and at high velocities, where the corrosion product can be eroded away more easily. Impurities such as oxygen in either niobium or tantalum can lead to rapid penetration by lithium at temperatures from 300 to 1200°C. Although the mechanism of this attack is not well understood, a process involving the formation of a lithium-niobium-oxygen complex has been proposed. The addition of an alloying element whose oxide is more stable than NbO appears to be a solution to this problem.

In some systems no separate corrosion product forms, but the properties of the refractory metal or alkali metal may be altered as a result of the partitioning of an impurity to either the solid or liquid metal. Although thermodynamic calculations lead to the conclusion that tantalum and niobium should getter oxygen from sodium and potassium to a very low level, this was not verified by experiment. Some reasons for this discrepancy may be invalid thermodynamic assumptions, incorrect solubility or standard free energy of formation data, or inaccurate procedures for analyzing oxygen in alkali metals.

RECOMMENDATION

Although many areas of research relating to the compatibility of refractory metals with alkali metals have not been fully investigated, there appears to be a great need for more basic compatibility studies. Solubility experiments conducted to date have generally been limited to the lithium system and often have not taken in account the effect of impurities such as oxygen and nitrogen in the alkali metal.

Because impurities have such an important effect on corrosion behavior, it is very important to develop suitable techniques of analysis for many of the impurities in alkali metals, especially oxygen. Such work must necessarily precede studies to accurately determine the solubility of various impurities in these metals. Then a better understanding of the role of these impurities in causing various corrosion phenomena can be attained.

Temperature-gradient mass transfer is almost certain to occur to some extent in any practical system. Since this is an area that has received particularly little attention, especially systems involving boiling-alkali metals, this problem should be studied in detail before final selection of materials for a particular system is made.

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