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CORROSION RESISTANCE OF METALS AND ALLOYS
TO SODIUM AND LITHIUM

E. E. Hoffman
W. D. Manly

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METALLURGY DIVISION

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E. E. Hoffman and W. D. Manly

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CORROSION RESISTANCE OF METALS AND ALLOYS TO SODIUM AND LITHIUM

E. E. Hoffman

W. D. Manly

The interest in liquid alkali metals – particularly sodium and lithium – in this report is as heat transfer media in various high-temperature nuclear-reactor applications. Because of their very attractive heat transfer properties, use of these liquid metals might also be extended to more conventionally fueled power plants.

In any conventional electricity-generating plant in which water is used as the heat transfer medium, a major difficulty is the high pressures encountered at high operating temperatures. High temperatures lead to increased efficiency of the cycle, but beyond a temperature limit of approximately 1200°F the structural materials used today do not have sufficient strength to withstand the high pressures. Liquid metals, with their high boiling temperatures and excellent heat transfer properties, afford a solution to this pressure problem. However, the metallurgists and corrosion engineers are confronted with the problem of finding materials which have both good strength and good resistance to corrosion in the liquid-metal environments. The attempt to find such materials has necessitated vigorous research to supplement the present liquid-metal technology. The best sources of information covering the various aspects of liquid-metal

(sodium, lithium, and many others) technology are the latest editions of the *Liquid-Metals Handbook*.^{1,2}

Some of the most important properties of sodium and lithium for high-temperature nuclear-reactor applications are listed in Table 1. Several other popular and potential heat transfer fluids are shown for comparison purposes. The advantages and disadvantages of various coolants are considered in relation to their application at temperatures in excess of 1200°F. Properties that are undesirable are underlined. Water is not particularly suitable because of its very low boiling point and its poor thermal conductivity. Sodium and the sodium-potassium alloy (NaK) have properties to which there are no major objections. (Statements concerning the corrosiveness of sodium may be considered as applicable to the sodium-potassium alloys, since differences found to date have been very slight.) The low melting point of NaK is a definite advantage, since the alloy could be maintained in the liquid state without being heated

¹R. N. Lyon (ed.), *Liquid Metals Handbook*, 2d ed., p 5, GPO, Washington, 1952.

²C. B. Jackson (ed.), *Liquid Metals Handbook, Sodium-NaK Supplement*, 3d ed., GPO, Washington, 1955.

TABLE 1. SOME IMPORTANT PROPERTIES* OF HEAT TRANSFER FLUIDS FOR REACTOR APPLICATIONS

	Melting Point (°F)	Boiling Point (°F)	Density at Melting Point (g/cm ³)	Heat Capacity at Melting Point (cal/g·°C)	Thermal Conductivity at Melting Point (cal/sec·cm·°C)	Absorption Cross Section (barns) (10 ⁻²⁴ cm ²)
H ₂ O	32	<u>212</u>	1.0	1.0	<u>0.001</u>	0.6
Na	208	1616	0.92	0.33	0.21	0.45
NaK (56-44 mole %)	66	1518	0.87	0.26	0.06	1.1
Pb	<u>622</u>	3170	<u>10.4</u>	0.04	0.04	0.2
Li	367	2403	0.50	1.0	0.09	<u>65</u>
Hg	-37	<u>675</u>	<u>13.6</u>	0.03	0.02	<u>430</u>

*Undesirable properties are underlined.

while a power plant (nuclear or conventional) is brought to power or is shut down. Lithium has many attractive properties; however, its application in nuclear power plants is limited because of the high-absorption cross section of the Li^6 isotope for thermal neutrons. Such a high-absorption cross section would lead to inefficient utilization of neutrons produced by the fission process. The Li^7 isotope, which comprises 92.5% of naturally occurring lithium, fortunately has a very low absorption cross section (0.033 barn). An isotopic separation of the Li^7 from the Li^6 isotope would be necessary before lithium could be considered as a primary coolant for a nuclear reactor. Lithium has the additional disadvantage of being more corrosive than the other alkali metals. In summary, the outstanding properties of the liquid metals, especially sodium and lithium, are their high thermal conductivities, their high boiling points, and their chemical and thermal stabilities.

Many types of liquid-metal corrosion tests have been and are being performed to determine the most satisfactory container material for a particular set of environmental conditions. As in all tests of this nature, the object is to simulate, as nearly as possible, the actual operating conditions which will prevail in the ultimate use of the material. Each test involves a compromise on one or more of the operating conditions. The liquid-metal corrosion tests discussed here are classified as either static or dynamic, depending on whether or not the molten metal moves with respect to the container material. Static tests conducted under isothermal conditions are easy to perform and usually simple to interpret. The attack suffered by a container material is in almost all cases greater in a dynamic system than in a static system; therefore the purpose of the static test is to screen out those materials which show no promise. The extent of corrosion is evaluated by weight-change data, chemical analysis of the liquid metal, and x-ray and spectrographic examination of the specimen surface, but the greatest importance is given to metallographic examination of the test specimens and the container walls. Because of the chemical activity of sodium and lithium, extreme care must be taken in loading the test containers in order to protect the liquid metals from atmospheric contamination.³ Therefore an inert atmosphere must

³E. E. Hoffman, W. D. Manly, and D. C. Vreeland, *Nucleonics* 11(11), 36-39 (1953).

be maintained over the liquid metal during the loading operation and the test period. The various test systems may be arbitrarily classified as follows:

Static Tests – No movement of liquid metal; no temperature gradients.

Dynamic Tests – Low velocity (2 to 10 fpm).

Seesaw or Tilting Tests – A sealed tube partially filled with a liquid metal and tilted up and down.

Thermal-Convection Loops – A sealed loop filled with a liquid metal and heated in certain sections and cooled in others to cause circulation as a result of changes in the density of the liquid metal.

Dynamic Tests – High velocity (2 to 50 fps) – Flow induced by electromagnetic or mechanical pumps.

The principal types of liquid-metal corrosion are listed below:⁴

1. simple solution,
2. alloying between liquid metal and solid metal,
3. intergranular penetration due to selective removal,
4. impurity reactions,
5. temperature-gradient mass transfer,
6. concentration-gradient transfer or dissimilar-metal transfer.

Solution of the solid-container material in the liquid metal and alloying between the liquid and solid metal could readily be predicted if adequate phase-diagram information were always available. Static-capsule tests are usually sufficient to determine the extent of these reactions (solution or alloying), which are the simplest forms of liquid-metal corrosion. Intergranular penetration of a container material occurs as a result of preferential attack on a constituent of the metal which segregates in the grain boundaries. The two most troublesome forms of liquid-metal corrosion are temperature-gradient mass transfer and dissimilar-metal mass transfer. These corrosion phenomena are very often difficult to observe in a simple capsule test, and in some cases they may be detected only after a large dynamic pump system has been operated for an extended time period.

The mechanism of temperature-gradient mass transfer is illustrated in Fig. 1, and the thermal-convection loop for studying this type of corrosion is shown in Fig. 2. Since the solubility of most

⁴W. D. Manly, *Corrosion* 12, 46-52 (1956).

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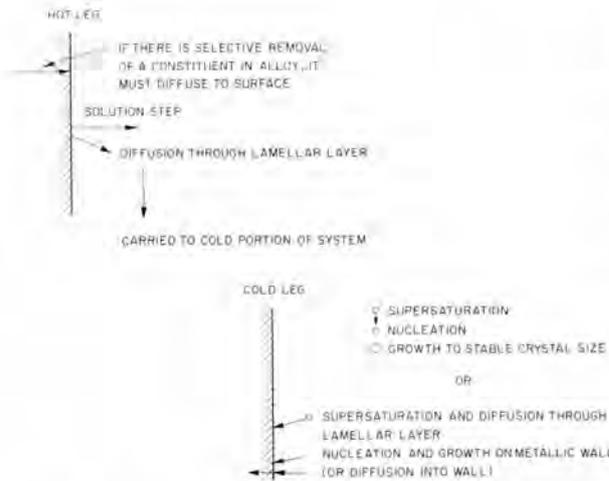


Fig. 1. Temperature-Gradient Mass Transfer.

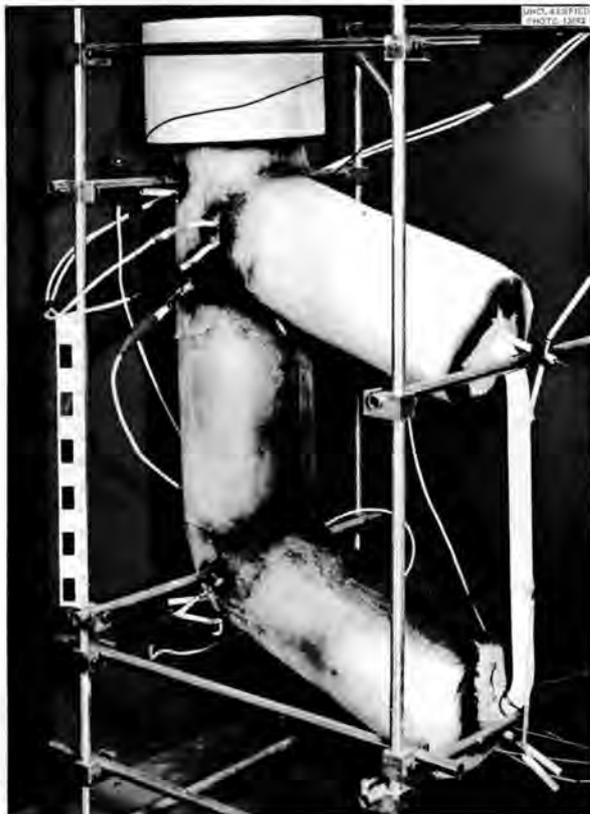


Fig. 2. Thermal-Convection Test Loop in Operation. Bath metal is flowing in a clockwise direction as a result of temperature differences in various sections of the loop.

container materials in a particular liquid metal is temperature-dependent, solution in the hot section and subsequent deposition in a cooler section may occur. The results of this type of corrosion may be seen in Figs. 3 and 4.

Dissimilar-metal transfer or concentration-gradient transfer (Fig. 5) may occur in solid-metal-liquid-metal systems even when no temperature differentials are present. When two or more solid metals are in contact with the same liquid metal, the liquid metal may act as a carrier in transferring atoms of one of the solid metals to the surface of the other solid metal. The effect of such alloying is shown in Fig. 6, where it can be seen that the Vickers hardness number (VHN) is much higher for the nickel-molybdenum alloy than for the molybdenum. Such alloying would, in most cases, have an adverse effect on the mechanical properties of the dissimilar metals and might even cause plugging of small tubes in some cases.

The principal variables affecting liquid-metal corrosion are listed below:

1. temperature,
2. temperature gradient,
3. cyclic temperature fluctuation,
4. surface-area-to-volume ratio,
5. purity of liquid metal,
6. flow velocity or Reynolds number,
7. surface condition of container material,
8. reaction between dissimilar metals in contact with liquid metal,
9. condition of container material (grain-boundary precipitation, second phase, stressed, or annealed).

The relative importance of the numerous variables might change, depending on the liquid metal and the container system. Although it is difficult to generalize, it may be said that, for most liquid-metal-solid-metal systems, these variables are listed in the order of decreasing importance.

The corrosion resistance of some metals and alloys in high-temperature liquid sodium is shown in Fig. 7. For most practical engineering-type applications involving operating temperatures in the range 1000 to 1500°F, some grade of austenitic stainless steel, such as type 347 (18% Cr-8% Ni-balance Fe; Nb stabilized), is the most suitable container material for sodium. Nickel-base alloys such as Inconel (nominal composition, 77% Ni-15% Cr-7% Fe) suffer temperature-gradient mass transfer in dynamic sodium systems above 1400°F. The metal crystals deposited in the cold sections of

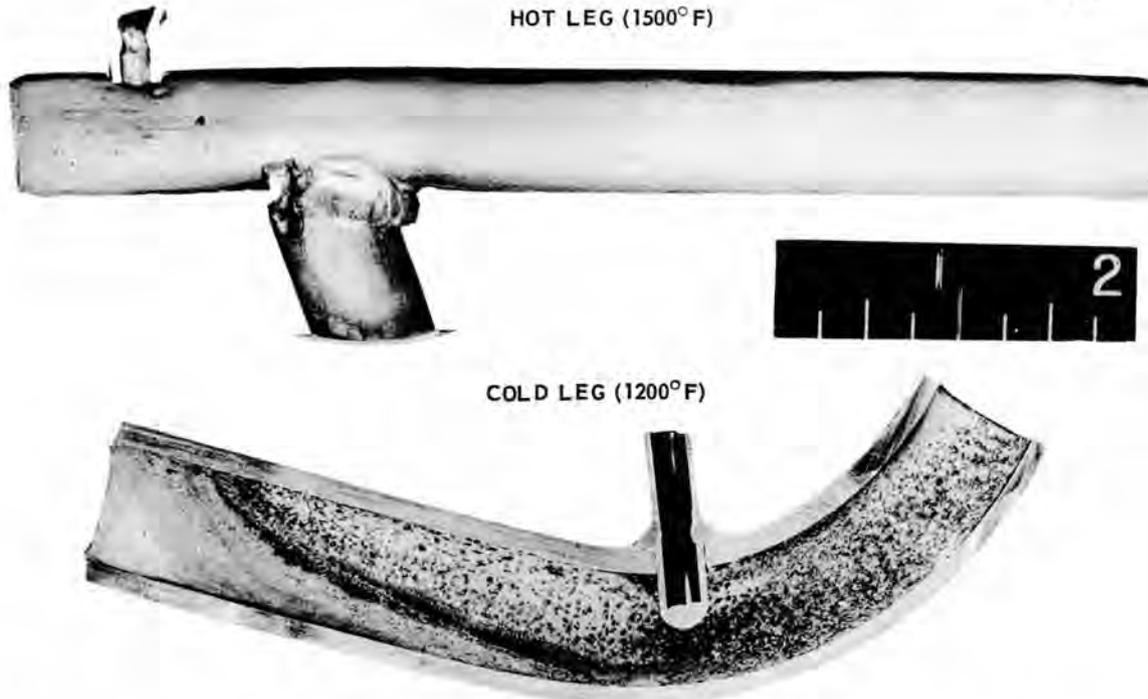


Fig. 3. Hot- and Cold-Leg Sections from Inconel-Sodium Thermal-Convection Loop After 1000-hr Operation. An air blast was directed on the cold leg to increase the temperature gradient.

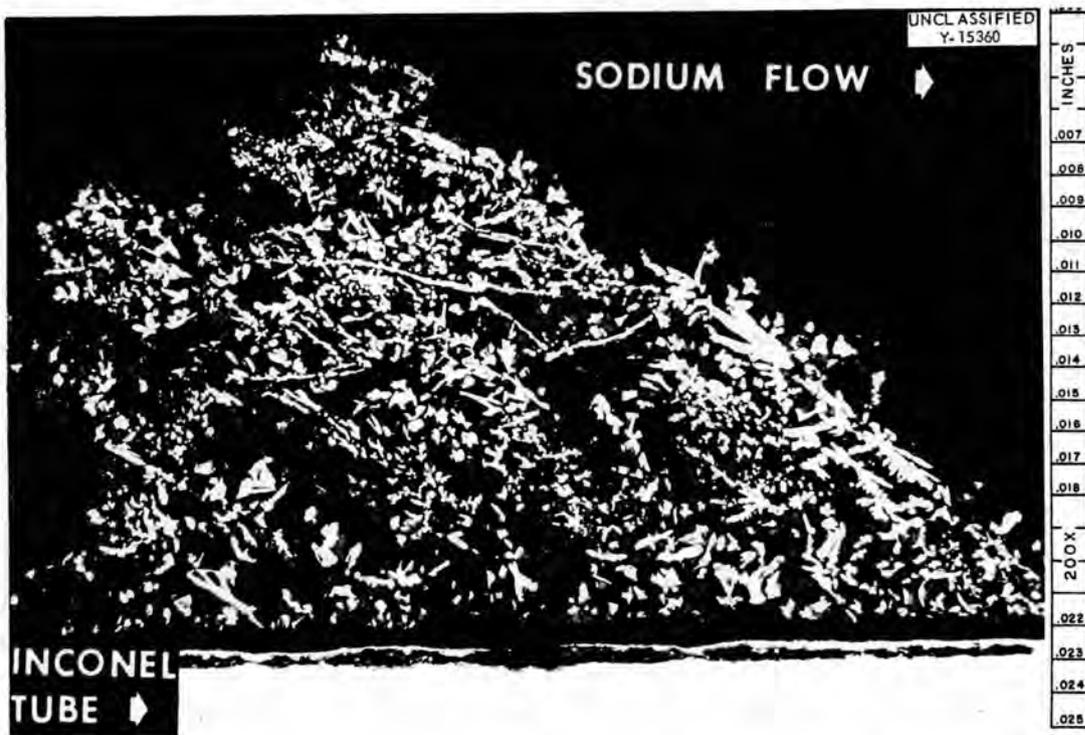


Fig. 4. Cold Section of Inconel-Sodium High-Temperature Dynamic System. The tendency for mass-transfer crystals to grow in the opposite direction to the sodium flow can be noted. 200X. Reduced 15%.

such systems analyze approximately 90% nickel, 8% chromium, and < 0.5% iron, which indicates the preferential transfer of nickel by sodium. The precious metals seem to be quite consistent, in that all have very poor resistance to liquid alkali metals.

Sodium oxide is the most objectionable impurity in sodium insofar as high-temperature heat transfer

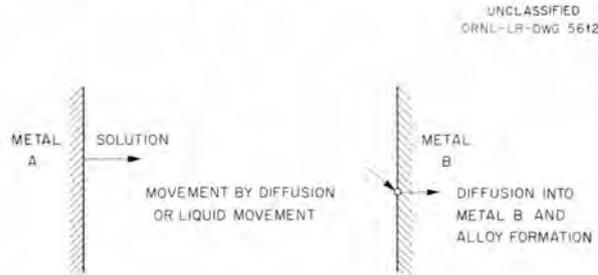


Fig. 5. Dissimilar-Metal Transfer or Concentration-Gradient Transfer.

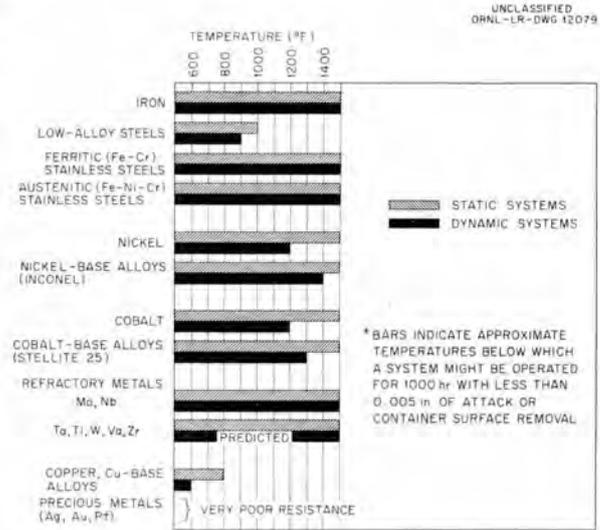


Fig. 7. Corrosion Resistance of Various Metals and Alloys in Sodium.

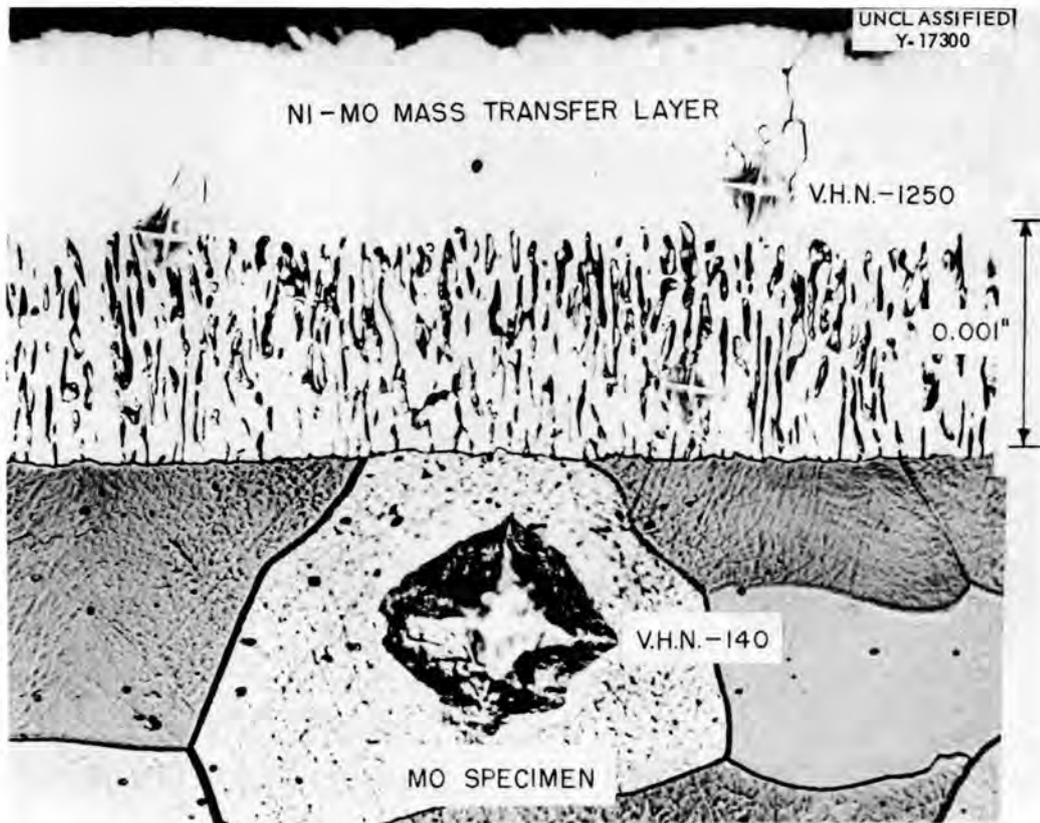


Fig. 6. Alloying of Nickel with Molybdenum Which Occurred During a Static Test at 1830°F for 100 hr of a Molybdenum Specimen in Contact with Sodium in a Nickel Container. Etched with oxalic acid.

systems are concerned. Even though great care is taken to keep sodium free of sodium oxide during its preparation, sodium may easily be contaminated with the oxide, even in a gastight system. Oxides of nickel, iron, and chromium on the walls of a stainless steel system, for example, may be reduced by the sodium to form sodium oxide. This reduction will occur even more readily in the case of lithium, the oxide of which is extremely stable. One of the effects of oxygen in sodium is that in high concentrations it increases the amount of mass transfer observed in the cold sections of nickel-base alloy systems and the austenitic stainless steels.⁵ Dynamic tests have been conducted in

⁵E. G. Brush and R. F. Koenig, p 21-32 in *Nuclear Metallurgy; A Symposium, Special Report Series No. 2*, AIMME, Institute of Metals Division, New York, 1956.

which only distilled sodium has come in contact with the test section (Fig. 8). The distilled sodium was retained for a short period in two traps in the condenser leg of this loop. The traps were held at different temperatures during the experiment, and the cooler trap was examined for mass-transfer crystals following the test. The results of the experiment are shown in Fig. 9. Although the oxygen concentration of the sodium in the test section analyzed less than 25 ppm, some mass transfer still occurred. Lowering the oxygen concentration seems to decrease the rate of mass transfer but does not eliminate it in a nickel-base alloy such as Inconel.

Carburization of container metals is another problem involved in the handling of liquid metals, especially sodium and lithium. Carbon is readily

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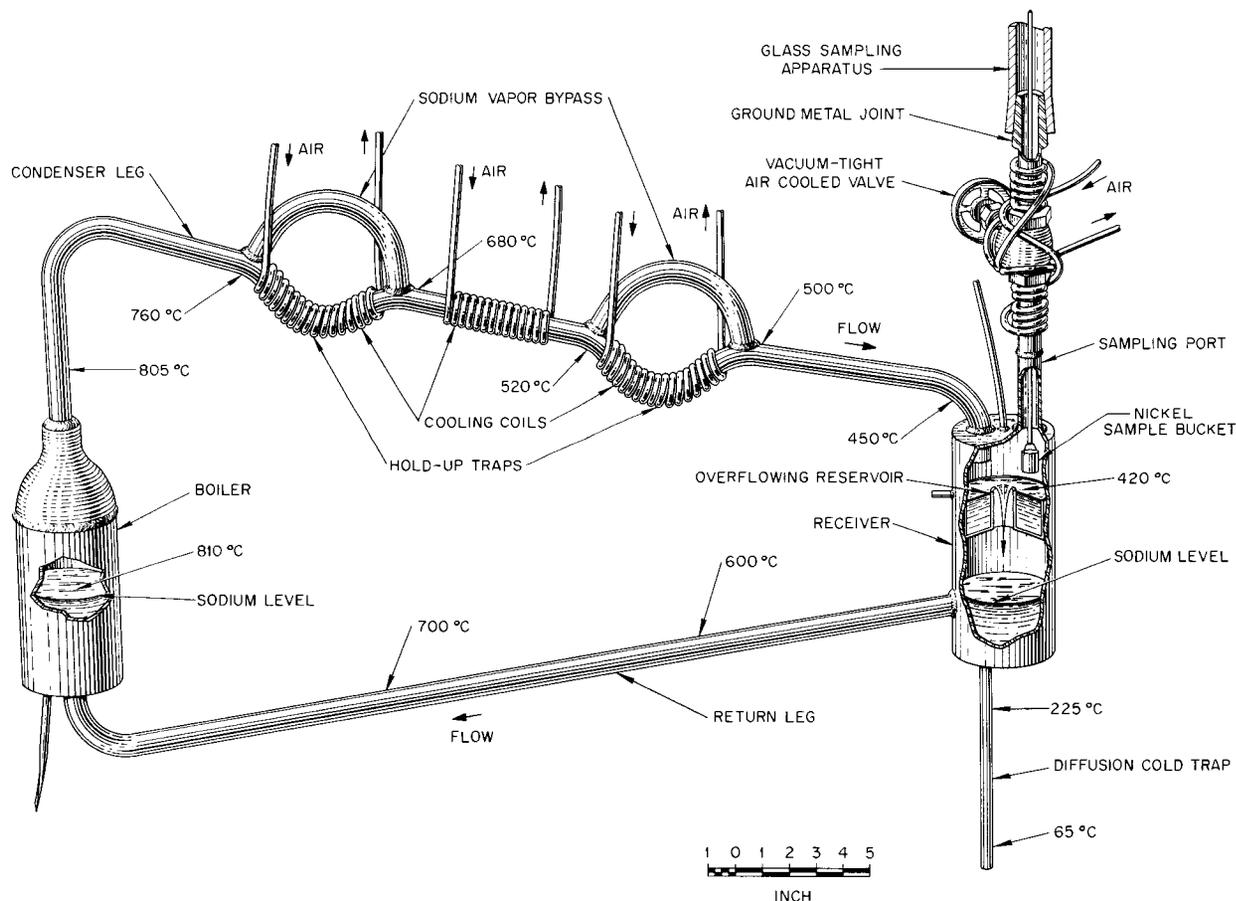


Fig. 8. Inconel-Boiling-Sodium Loop.

transferred between two metals of different carbon contents in contact with sodium, or a monometallic system may be carburized owing to a high carbon concentration in the sodium. An example of the extent to which this carburization may proceed is shown in Fig. 10, a photomicrograph of the wall of a stainless steel capsule following a 100-hr test at 1500°F in which the capsule was in contact with sodium which had been intentionally contaminated with carbon. The walls of the capsule were heavily carburized to a depth of 15 mils. Contamination of sodium by various hydrocarbons may also result in subsequent carburization of metal containers.

The corrosion resistance of various metals and alloys in high-temperature liquid lithium is shown in Fig. 11. Unfortunately, lithium is much more corrosive than sodium. Consequently, it will be impossible to take full advantage of its many attractive heat transfer properties until a satisfactory container material is found. The most corrosion-resistant pure metals in a static isothermal system are molybdenum, niobium, tantalum, tungsten, and iron. Of the commercially available structural materials, no alloys tested to date have had satisfactory corrosion resistance at temperatures above 1400°F for extended time periods in systems where temperature differentials exist. Even though iron has good resistance in static isothermal lithium, iron and iron-base alloys suffer from mass transfer to a serious degree in dynamic systems where thermal gradients exist. The best commercially available structural alloys to use in containing lithium in dynamic systems operating at temperatures below 1100°F are the austenitic grades (Fe-Ni-Cr) and ferritic grades (Fe-Cr) of stainless steels. Figure 12 shows the hot and cold zones of a type 347 stainless steel loop following 3000 hr of operation at the indicated temperatures.

Dissimilar-metal mass transfer can be very serious in lithium systems, especially if one of the metals is nickel or an alloy containing nickel. Figure 13 illustrates how this corrosion process may increase attack in such systems. An austenitic stainless steel specimen containing 8% nickel was attacked to a depth of less than 2 mils when tested in lithium in a stainless steel container. A similar stainless steel specimen tested in an iron container was attacked to a depth of 20 mils. This great

increase in attack was due to transfer of nickel from the specimen to the wall of the iron container.

The corrosion resistance of the refractory-type metals in lithium is characterized by molybdenum (Fig. 14), which has shown excellent resistance in static, isothermal test capsules. Tests must be conducted in dynamic systems with temperature differentials present in order to complete the evaluation of the corrosion resistance of the refractory metals. Many other problems, such as the poor oxidation resistance of molybdenum and niobium, must be solved or circumvented before utilization of these metals is practical. The precious metals have very poor corrosion resistance, even at moderately low temperatures.

The most harmful contaminant found in lithium is lithium nitride. Lithium nitride is formed on the surface of lithium exposed to the atmosphere, and therefore such exposure must always be avoided. The harmful effects of minor additions of this material to lithium may be seen in Fig. 15. The wall of a type 316 stainless steel container was completely penetrated (32 mils), by way of the grain boundaries, when an addition of lithium nitride was made to the lithium test bath. In a standard test with no addition the attack under similar conditions was 2 to 4 mils.

In summary, the austenitic (300 series) stainless steels are the most satisfactory structural materials for containing sodium in systems which are to operate at temperatures below 1500°F. Oxygen is the most troublesome impurity and should be avoided if mass transfer is to be minimized. To date, no structural alloy has been discovered which is satisfactory as a container for lithium in dynamic systems above 1200°F. At temperatures below 1000°F, the stainless steels have good corrosion resistance, but contamination of the lithium with lithium nitride should be avoided.

Acknowledgment

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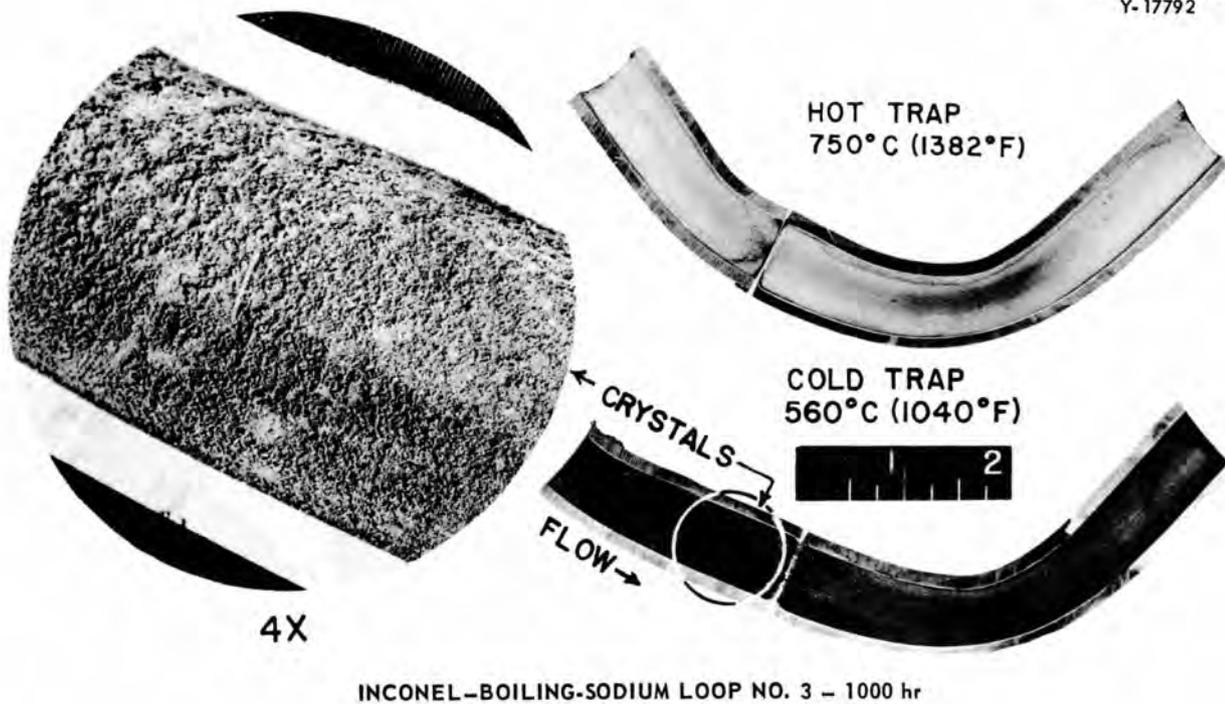


Fig. 9. Sections of Condenser Leg of Boiling-Sodium Loop (see Fig. 8). Mass-transfer crystals can be noted in cold trap.

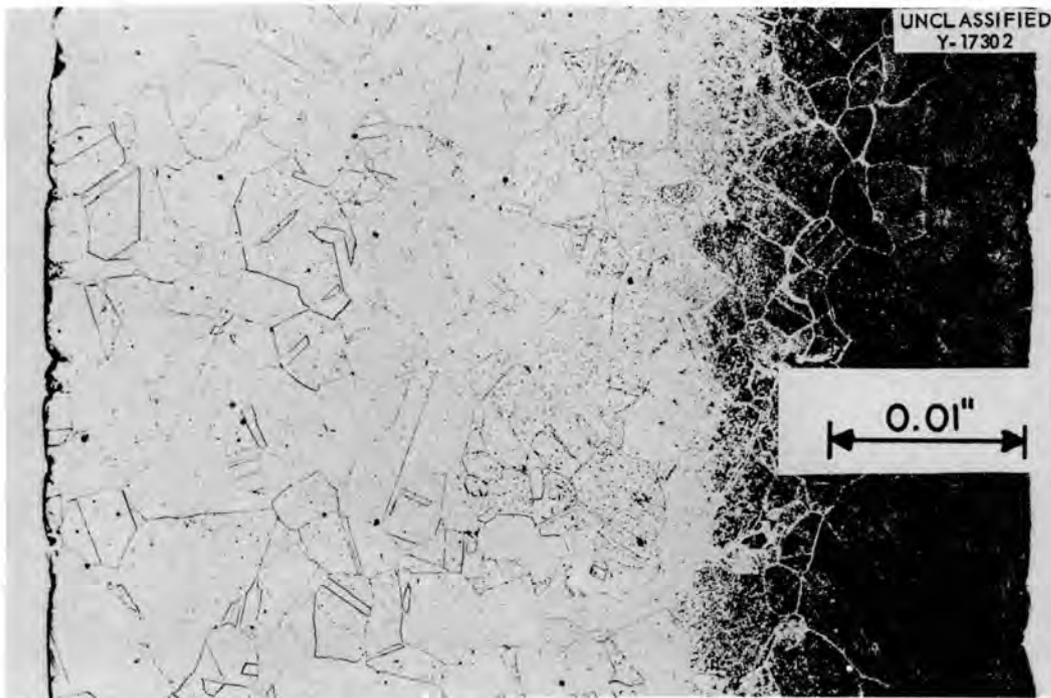
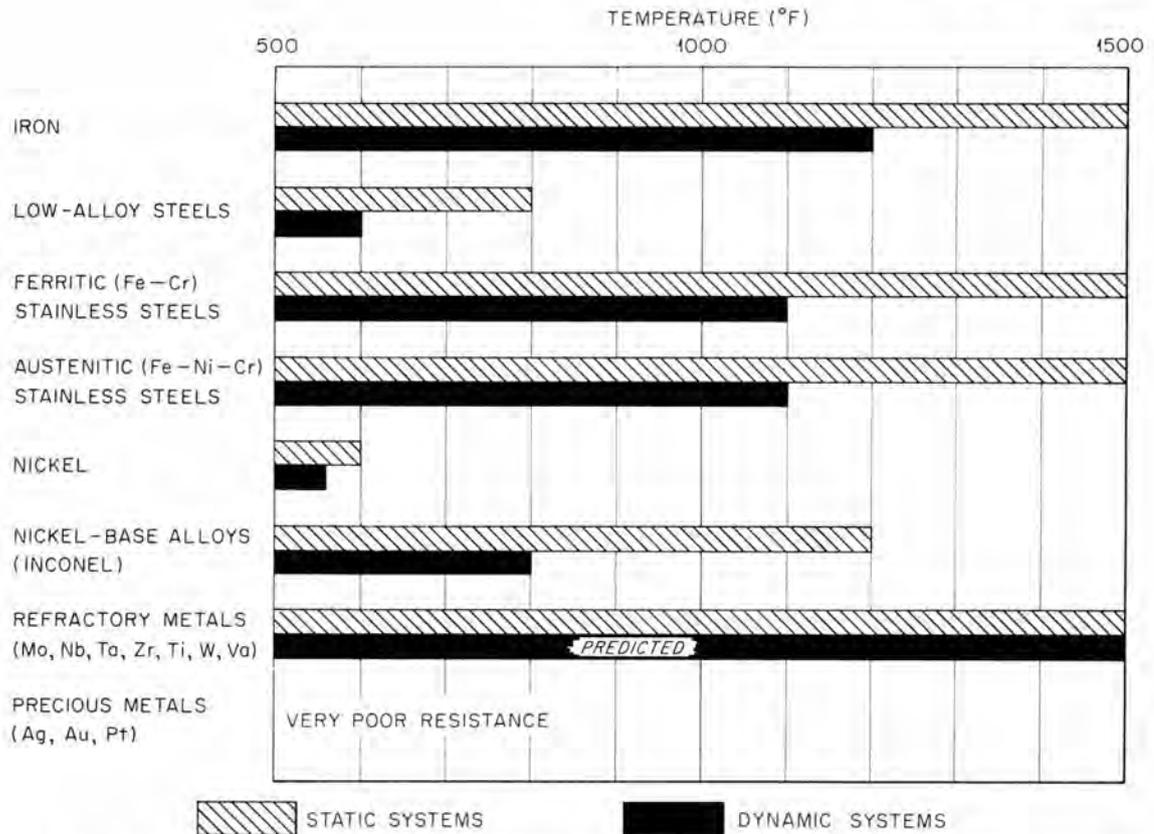


Fig. 10. Effect of Carbon in Type 304 Stainless Steel-Sodium System Held at 1500°F for 100 hr. Specimen was nickel-plated after test in order to preserve edges during metallographic polishing. Heavy carburization of exposed (right) surface of tube can be noted.



BARS INDICATE APPROXIMATE TEMPERATURES BELOW WHICH A SYSTEM MIGHT BE OPERATED FOR 1000 HOURS WITH LESS THAN 0.005 in. OF ATTACK OR CONTAINER SURFACE REMOVAL.

Fig. 11. Corrosion Resistance of Various Metals and Alloys in Lithium.

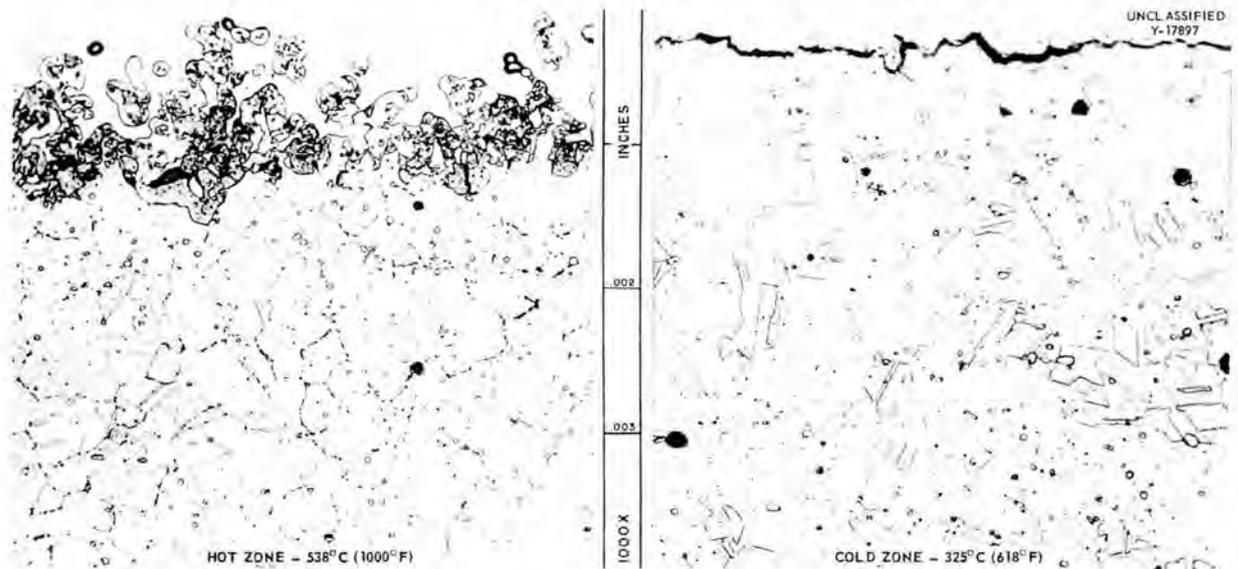


Fig. 12. Sections from Type 347 Stainless Steel Loop in Which Lithium Was Circulated for 3000 hr. 1000X. Reduced 34%.

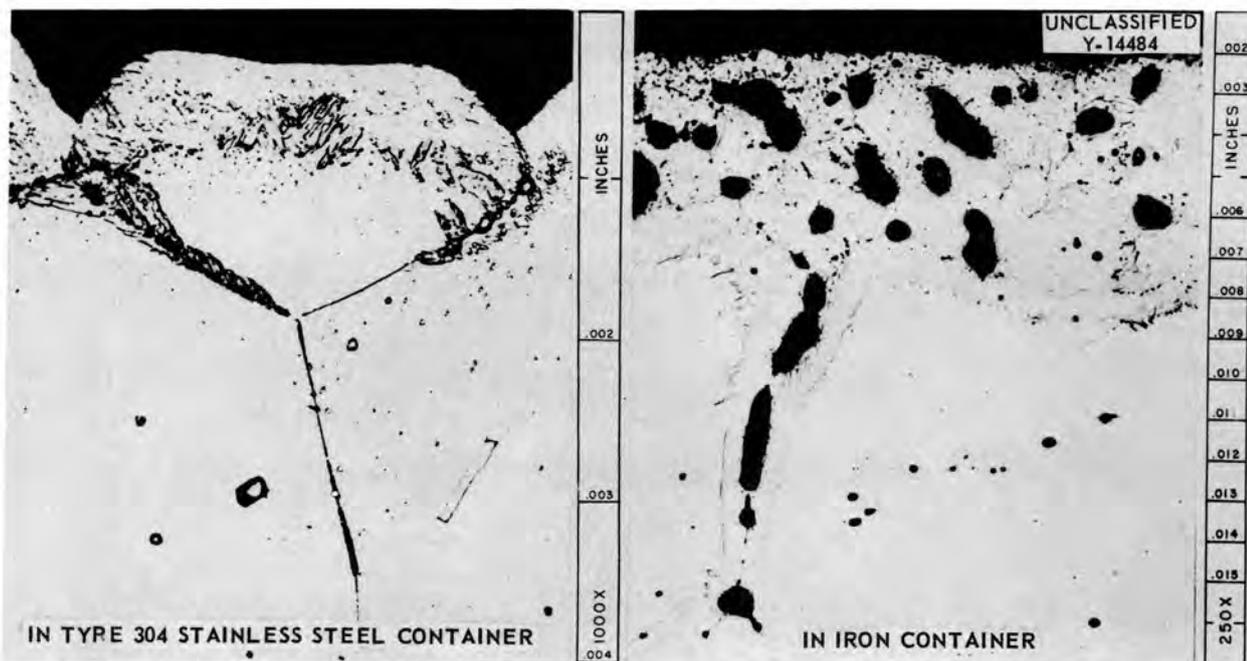


Fig. 13. Phase Change (Austenite to Ferrite) on Exposed Surface of Type 304 Stainless Steel Specimen Tested in Lithium for 400 hr at 1000°C Caused by Preferential Leaching of Nickel. Very heavy attack on the iron container, encountered when dissimilar-metal container was used, can be noted. Etched with glyceria regia.



Fig. 14. Edge of Molybdenum Specimen Following a 100-hr Exposure to Static Lithium at 1500°F. Absence of attack on the surface of the specimen can be noted. Etched with 50% hydrogen peroxide, 50% ammonium hydroxide.

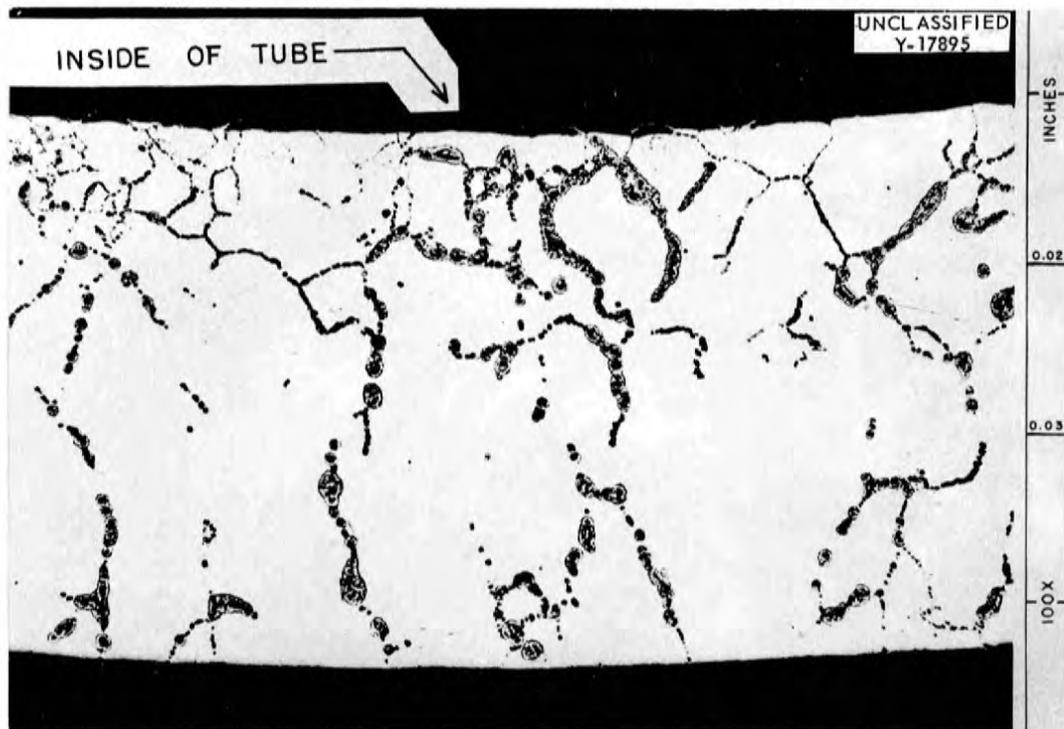


Fig. 15. Type 316 Stainless Steel Tube After a 100-hr Exposure to Lithium (Plus 0.1% Li_3N) at 1600°F.