

UNCLASSIFIED

CENTRAL RESEARCH LIBR.
DOCUMENT COLLECTION



3 4456 0350095 9

ORNL-2055
Metallurgy and Ceramics

cy 5

FUNDAMENTALS OF LIQUID-METAL CORROSION

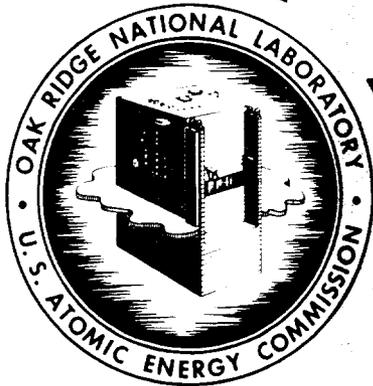
W. D. Manly

CENTRA
DOCL

LIBRARY LOAN ONLY

DO NOT TRANSFER TO ANOTHER PERSON

If you wish someone else to see this document,
send in name with document and the library will
arrange a loan.



OAK RIDGE NATIONAL LABORATORY

OPERATED BY

UNION CARBIDE NUCLEAR COMPANY

A Division of Union Carbide and Carbon Corporation

POST OFFICE BOX 117 OAK RIDGE, TENNESSEE

UNCLASSIFIED

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

ORNL-2055

Contract No. W-7405-eng-26

METALLURGY DIVISION

FUNDAMENTALS OF LIQUID-METAL CORROSION

W. D. Manly

DATE ISSUED

JUL 12 1956

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box P
Oak Ridge, Tennessee

MARTIN MARIE ITA ENERGY SYSTEMS LIBRARIES



UNCLASSIFIED

3 4456 0350095 9

UNCLASSIFIED

ORNL-2055
Metallurgy and Ceramics
TID-4500 (11th ed.)

INTERNAL DISTRIBUTION

- | | |
|--|--|
| 1. C. E. Center | 45. K. Z. Morgan |
| 2. Biology Library | 46. J. A. Lane |
| 3. Health Physics Library | 47. T. A. Lincoln |
| 4-5. Central Research Library | 48. A. S. Householder |
| 6. Reactor Experimental
Engineering Library | 49. C. S. Harrill |
| 7-26. Laboratory Records Department | 50. C. E. Winters |
| 27. Laboratory Records, ORNL R.C. | 51. D. S. Billington |
| 28. A. M. Weinberg | 52. D. W. Cardwell |
| 29. L. B. Emlet (K-25) | 53-75. W. D. Manly |
| 30. J. P. Murray (Y-12) | 76. E. M. King |
| 31. J. A. Swartout | 77. A. J. Miller |
| 32. E. H. Taylor | 78. D. D. Cowen |
| 33. E. D. Shipley | 79. R. A. Charpie |
| 34. M. L. Nelson | 80. M. L. Picklesimer |
| 35. W. H. Jordan | 81. M. J. Skinner |
| 36. C. P. Keim | 82. G. E. Boyd |
| 37. J. H. Frye, Jr. | 83. C. J. McHargue |
| 38. R. S. Livingston | 84. P. M. Reyling |
| 39. R. R. Dickison | 85. G. C. Williams |
| 40. S. C. Lind | 86. N. J. Grant (consultant) |
| 41. F. L. Culler | 87. E. Creutz (consultant) |
| 42. A. H. Snell | 88. T. S. Shevlin (consultant) |
| 43. A. Hollaender | 89. ORNL - Y-12 Technical Library,
Document Reference Section |
| 44. M. T. Kelley | |

EXTERNAL DISTRIBUTION

- 90. R. F. Bacher, California Institute of Technology
- 91. Division of Research and Development, AEC, ORO
- 92-467. Given distribution as shown in TID-4500 under Metallurgy and Ceramics category

DISTRIBUTION PAGE TO BE REMOVED IF REPORT IS GIVEN PUBLIC DISTRIBUTION

UNCLASSIFIED

FUNDAMENTALS OF LIQUID-METAL CORROSION

W. D. Manly

ABSTRACT

The corrosion of structural metals or alloys in liquid metal is for the most part due to the dissolving of the various constituents of the metals or alloys by the liquid metal. The manner in which this dissolution proceeds gives rise to many types of attack, ranging from a simple solution-type attack to a deep intergranular attack with the preferential leaching of one constituent of an alloy. Examples of the many types of corrosion experienced with solid-metal-liquid-metal systems are illustrated. The role of impurities on the corrosion is discussed.

In a static one-metal system the solution step stops when the solubility limit is reached; however, in more complex systems the corrosion of metals can be continued because of removal of the dissolved materials from the liquid metal by a temperature gradient and/or by dissimilar-metal transfer. Thus the transfer of metal from the hot region of a plumbing system and its subsequent deposition in the cold zone, and the transfer of material from one part of the system and its alloying with a metal of different composition in another part of the system will greatly increase the corrosion as compared to the results obtained in static systems. Examples of temperature-gradient mass transfer and dissimilar-metal transfer are reviewed, and factors governing the occurrence of these phenomena are outlined.

Corrosion has been defined by U. R. Evans¹ as follows: "The word *corrosion* denotes destruction of metal by chemical or electrochemical action; a familiar example is the rusting of iron." Thus, corrosion by this definition denotes the transfer of electrons. But this is not usually the case in liquid-metal attack, and, therefore, to define the destruction of a solid metal by a liquid metal as corrosion, this definition must be broadened to allow for the solution or solubility of a solid metal in a liquid metal wherein no transfer of electrons is involved. Liquid-metal corrosion for the most part simply depends on the solution rate and the extent of solubility of the solid metal in the liquid metal. However, many complicating factors can influence the solution rate or the attainment of the solubility limit. The formation of surface intermetallic compounds and of oxide or nitride films are good examples of such factors. Other factors are: impurities in the liquid metals which can increase the solution rate, and temperature gradients and multimetallic systems which can cause an increase

in the amount of attack over that expected to saturate the liquid metal because of the mass transfer of material under the driving force of the temperature gradient or the concentration gradient.

In the short time that interest has existed in the corrosion characteristics of liquid metals, many testing methods have been developed to determine the interaction between liquid metals and solid metals. These methods range from the very simple static capsule test to the expensive and complicated forced-circulation loop tests which carefully reproduce the operating conditions. The tests and the manner in which data are derived from them have been previously described.²

Several types of corrosive attack of solid metals by liquid metals have been observed.³ In this discussion the types of liquid-metal attack will be arranged into the following categories:

1. simple solution,
2. alloying between liquid metal and solid metal,
3. intergranular penetration,
4. impurity reactions,

¹U. R. Evans, "An Outline of Corrosion Mechanisms, Including the Electrochemical Theory," p 3 of *Corrosion Handbook*, H. J. Uhlig, ed, Wiley, New York, N. Y., 1948.

²D. C. Vreeland, E. E. Hoffman, and W. D. Manly, *Nucleonics* **11**, No. 11, 36-39 (1953).

³A. deS. Brasunas, ORNL-1647 (Secret).

of a complex alloy the attack can also be a simple-solution type. An example of this is shown in Fig. 2, which illustrates the corrosion of type 304 low-carbon stainless steel in sodium after 40 hr at 1000°C. Another attack that might be termed simple solution is the decarburizing action of lithium and sodium. Figure 3 illustrates the decarburization of type 430 stainless steel after 40 hr at 1000°C in lithium.

If all the phase diagrams of liquid-metal–solid-metal systems were available, an ascertainment could be made of the depth of attack that would

occur in a static system as a result of simple solution by examining the solubility limit of the solid metal in the liquid metal at the operating temperature. However, there would be no conception of the rate at which the solubility limit was achieved. Thus, in looking at the Fe-Li phase diagram in Fig. 4, it can be seen that the amount of attack of iron by lithium should be quite small in a static, isothermal system; and corrosion tests have proved this. Therefore, in simple-solution type attack the amount of damage the solid metal will receive depends on the ratio of surface area to volume of the system, but the rate at which the attack occurs

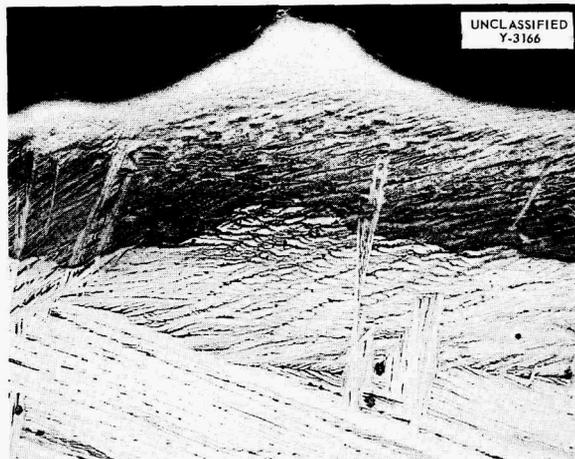


Fig. 1. Even-Surface Removal from Titanium Specimen After 40 hr in Lead at 1000°C. 100X. Reduced 33.5%.

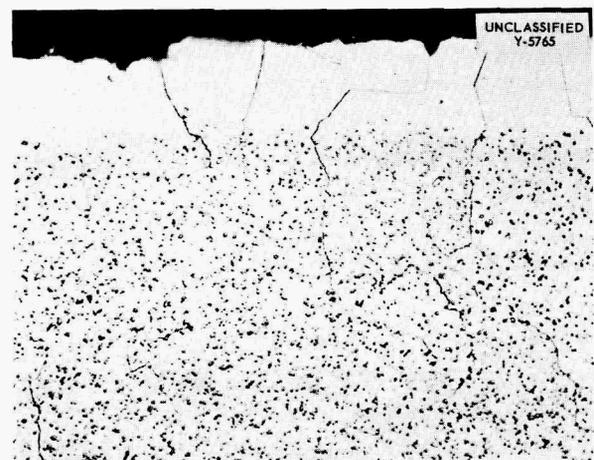


Fig. 3. Decarburization of Type 430 Stainless Steel After 40 hr in Lithium at 1000°C. 750X. Reduced 33%.

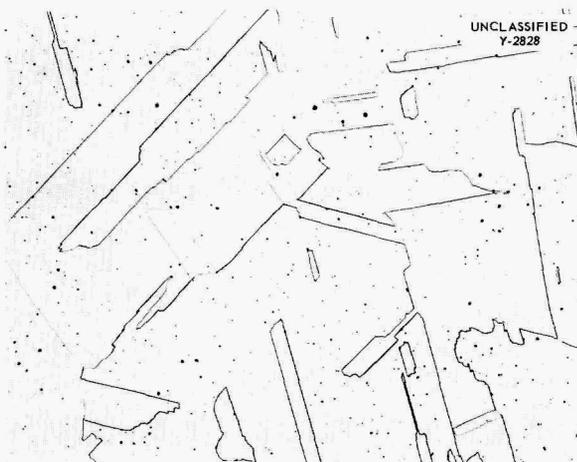


Fig. 2. Attack After 40 hr of Type 304 Low-Carbon Stainless Steel by Sodium at 1000°C. 75X. Reduced 34%.

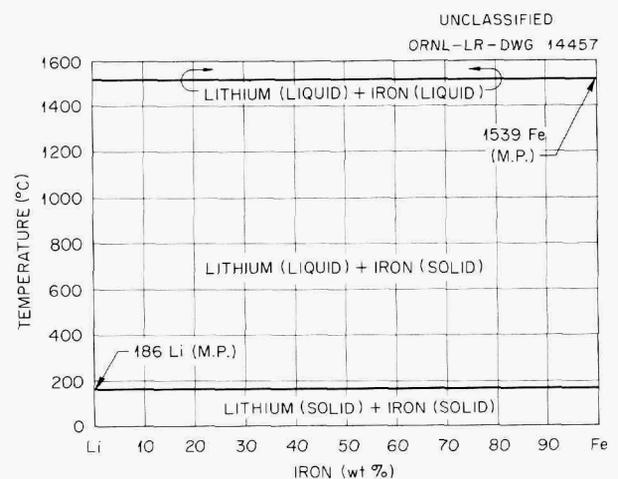


Fig. 4. Fe-Li Phase Diagram.

can be influenced greatly by other variables, such as impurities in the system.

The next type of corrosion to be discussed is the alloying that occurs between liquid metals and solid metals. For this to result, there must be some solubility of the liquid metal in the solid metal. The Ag-Pb phase diagram (Fig. 5) is an example of a system in which the liquid metal is soluble in the solid metal. In some experiments the liquid metal dissolves considerably in the solid metal with the formation of an intermetallic compound. When vanadium is tested for 400 hr in lead at 1000°C, an intermetallic compound is formed between the vanadium and lead, as can be seen in Fig. 6. When type 446 stainless steel is tested in lead at 1000°C, it is found that after 400 hr lead has diffused into the alloy predominantly at the grain boundaries and has formed a compound (Fig. 7). Sodium will penetrate solid copper at the grain boundaries and will form an intermetallic compound, which is considerably harder than the base metal, copper, as illustrated in Fig. 8.

One of the more serious types of corrosion that can occur is the deep intergranular penetration brought about by the removal of one constituent from an alloy. The best example of this is the selective removal of nickel from austenitic stainless steels, and Fig. 9 shows a type 347 stainless steel after 400 hr of testing in lead at 800°C. Other examples of this type of corrosion are given in Figs. 10 and 11, which illustrate the attack on type 304 low-carbon stainless steel after 400 hr

in lead and in lithium, respectively, at 1000°C. A considerable portion of the attack is attributed to the removal of nickel caused by the alloying



Fig. 6. Vanadium (at Left) Tested for 400 hr in Lead at 1000°C. Intermetallic compound formed between the vanadium and lead. 200X. Reduced 14%.

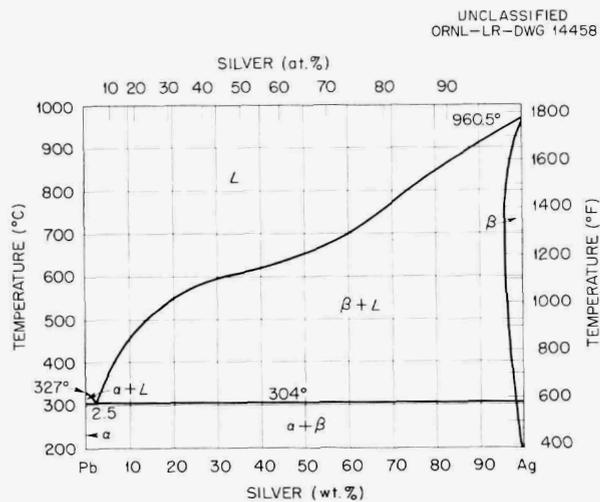


Fig. 5. Ag-Pb Phase Diagram.

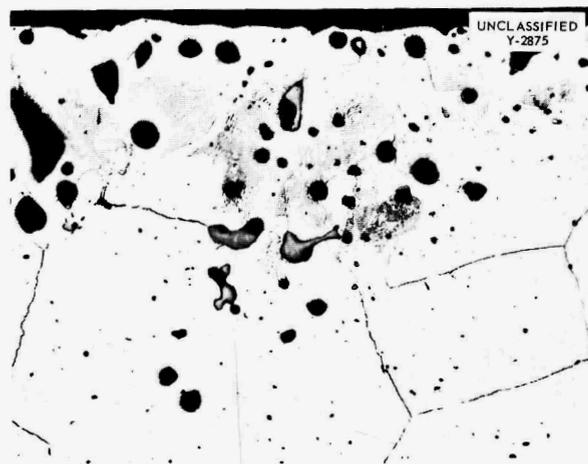


Fig. 7. Type 446 Stainless Steel Tested for 400 hr in Lead at 1000°C. 200X. Reduced 32%.

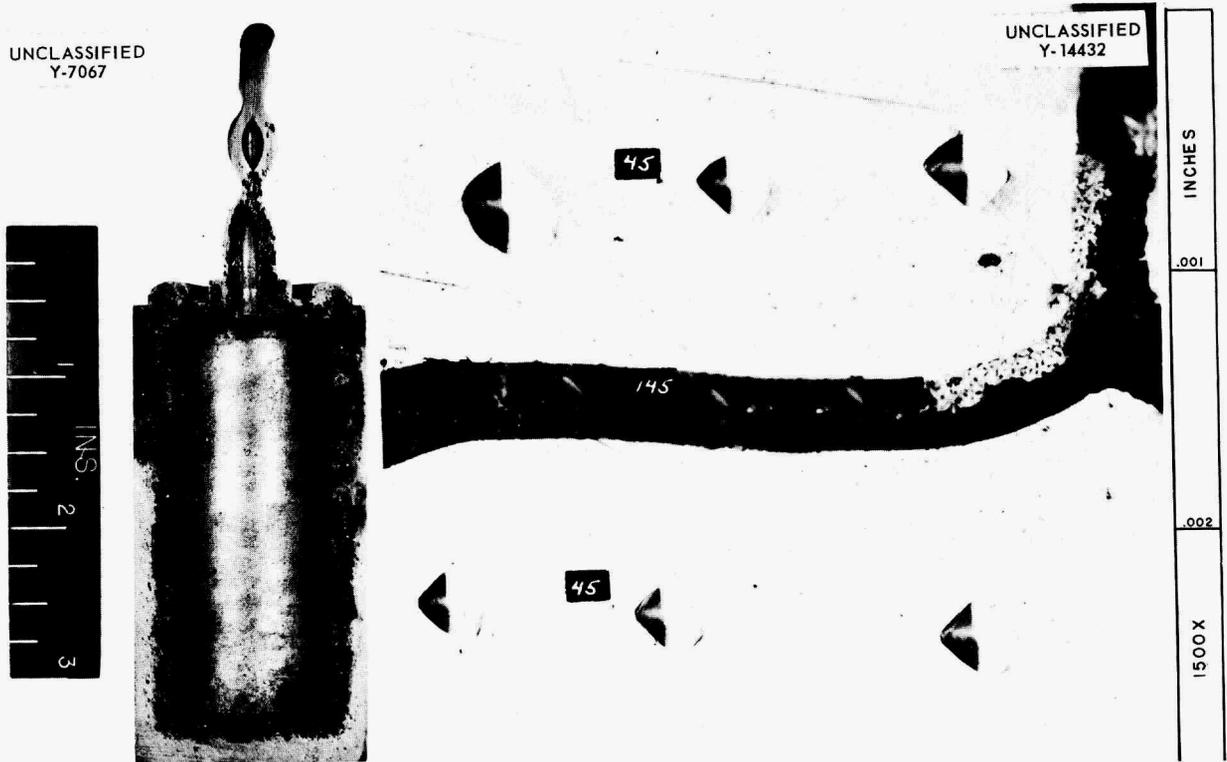


Fig. 8. Copper Capsule-Sodium Test at 1800°F for 100 hr. Sodium penetration into solid copper at the grain boundaries with the resultant formation of an intermetallic compound.

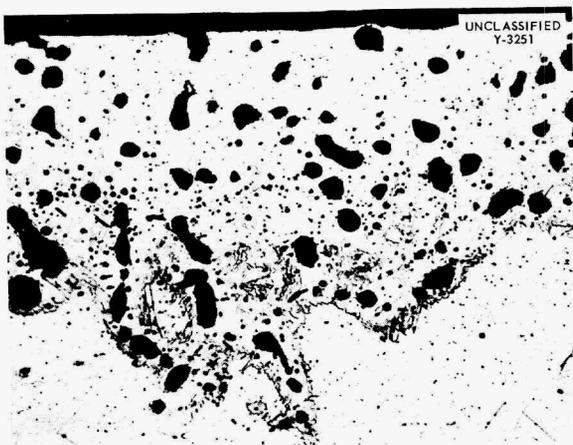


Fig. 9. Selective Removal of Nickel from Type 347 Stainless Steel After 400 hr in Lead at 800°C. 250X. Reduced 35%.

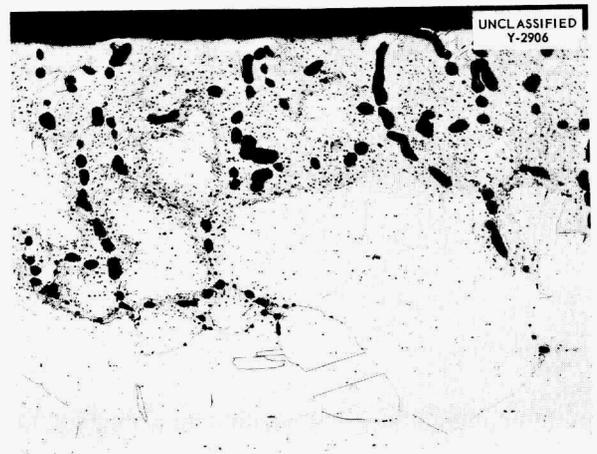


Fig. 10. Type 304 Low-Carbon Stainless Steel After 400 hr in Lead at 1000°C. Removal of nickel from the alloy shown. 100X. Reduced 33%.

of the nickel with the iron container wall, and it is assumed that the attack would have been less if the specimens and containers had been the same material. The selective removal of nickel from a 75% Ni–25% Mo alloy also occurred in a sample from the hot leg of a thermal-convection loop which operated for 200 hr with lead at 800°C and with a 300°C temperature gradient (Fig. 12). In this case the nickel was preferentially removed from the hot zone and deposited in the cold zone of the loop.

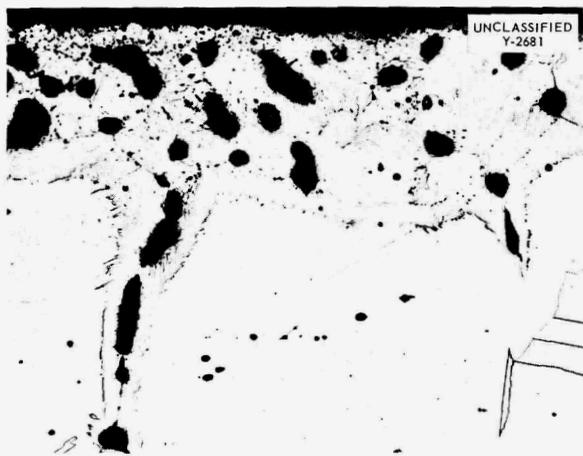


Fig. 11. Type 304 Low-Carbon Stainless Steel After 400 hr in Lithium at 1000°C. Removal of nickel from the alloy illustrated. 250X. Reduced 32.5%.

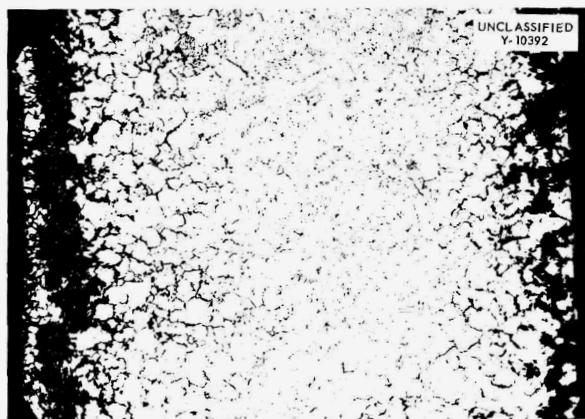


Fig. 12. Hot Leg of a 75% Ni–25% Mo Thermal-Convection Loop Operated for 200 hr with Lead at 800°C and with a Temperature Gradient of 300°C. 150X. Reduced 35%.

In liquid metals, impurities, such as oxygen, nitrogen, and carbon, can have an appreciable effect upon the rate of attack, and in some cases the whole mode of attack can be changed because of the effect of the impurity on the surface tension or because of the reactivity of the impurity. An example is the attack of stainless steels by lithium when nitrogen is the principal contaminant. Figure 13 illustrates the shallow attack produced by pure lithium at 800°C in 100 hr on type 316 stainless steel. However, if the lithium is contaminated with a small quantity of nitrogen, the complete tube wall, comprising 0.035 in., will be penetrated by the lithium during the same type of test. This is due to the nitrogen-contaminated lithium reacting with the carbides that form the grain boundary network, since a test in type 316 stainless steel with lithium that was contaminated with nitrogen resulted in shallow attack when the testing temperature was above the solution temperature of the carbides. The true effect of nitrogen on corrosion by lithium is not understood. High-temperature alloys can be severely carburized by liquid metals, especially sodium and lithium, if the liquid metals have been stored under kerosene or have acquired carbonaceous material from some other source. The carburization, after a long service period, of type 347 stainless steel by sodium contaminated with carbon is shown in Fig. 14. In corrosion by sodium, oxygen impurities can have an appreciable effect on the rate at which the solubility limit is attained. In lead the oxygen contamination, if anything, decreases the rate of corrosion since most



Fig. 13. Very Shallow Attack Produced by Pure Lithium at 800°C in 100 hr on Type 316 Stainless Steel. 250X. Reduced 33%.



Fig. 14. Complete Carburization After Long-Time Service of Type 347 Stainless Steel by Sodium Contaminated with Carbon. 250X. Reduced 32.5%.

of the constituents of high-temperature alloys can reduce the lead oxide and form a film that will act as a diffusion barrier between the solid metal and the liquid.

The most damaging type of liquid-metal corrosion is temperature-gradient mass transfer. The even removal of a slight amount of a container wall will not adversely affect its load-carrying abilities; however, the collection of this material in the colder regions of heat exchanger tubes as dendritic crystals would cause a cessation of flow. An example of mass-transferred material is seen in Fig. 15, which is a plug from a type 446 stainless steel thermal-convection loop that operated 200 hr at 800°C with a temperature gradient of 200°C. These crystals were primarily alpha iron. Another example is the massive mat of mass-transferred material shown in Fig. 16, which is a plug from an Inconel-lead thermal-convection loop that operated for 125 hr at 800°C. In some loop experiments the crystals do not grow from nuclei in the bulk liquid, but mass-transferred material nucleates on the wall; the crystals grow out into the stream as revealed in Fig. 17, a photograph of iron crystals formed on a type 410 stainless steel thermal-convection loop after 40 hr at 1000°C with lithium. The driving force for temperature-gradient mass transfer is the difference in solubility of the dissolved metal in the liquid metal at the temperature extremes of the heat-transfer system. In examining the Cu-Pb phase diagram (Fig. 18), it can be seen that there is considerable solubility of copper in

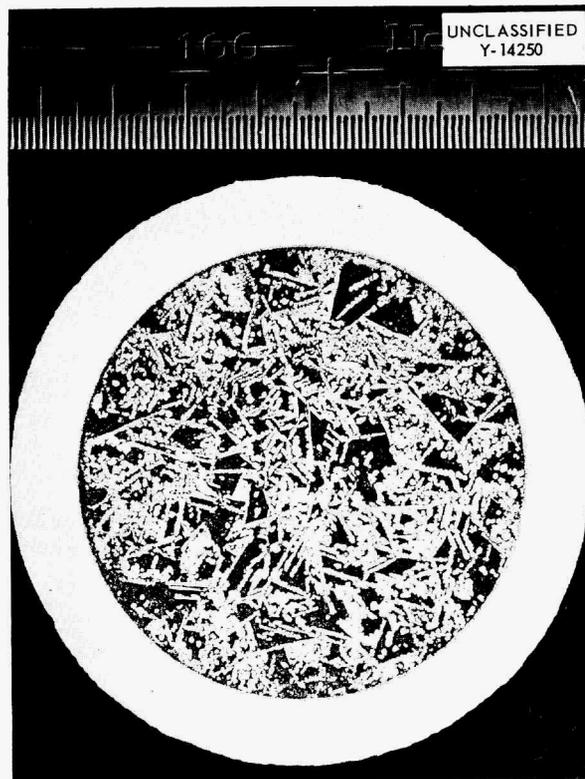


Fig. 15. Plug from a Type 446 Stainless Steel Thermal-Convection Loop That Operated for 200 hr at 800°C with a Temperature Gradient of 200°C. These crystals were primarily alpha iron.

lead at 900°C, whereas at 500°C it is much lower. Thus, by examining the phase diagram, the driving force for this phenomenon can be determined, but no information concerning the rate of the process can be determined.

Figure 19 indicates the various steps in temperature-gradient mass transfer through which metallic atoms must go. If there is selective removal of one element from an alloy, these atoms must diffuse to the surface and then go into solution. The atoms must then diffuse through the lamellar layer into the bulk-liquid stream and are finally carried to the cold portion of the system where supersaturation will occur. A collection of such atoms can accumulate and form a nucleus that will grow to a stable size and then drop from the liquid. On the other hand, the atom may supersaturate close to the wall, diffuse through the lamellar layer, and then nucleate on the metallic wall and form a dendritic crystal, or it may diffuse into the wall. As

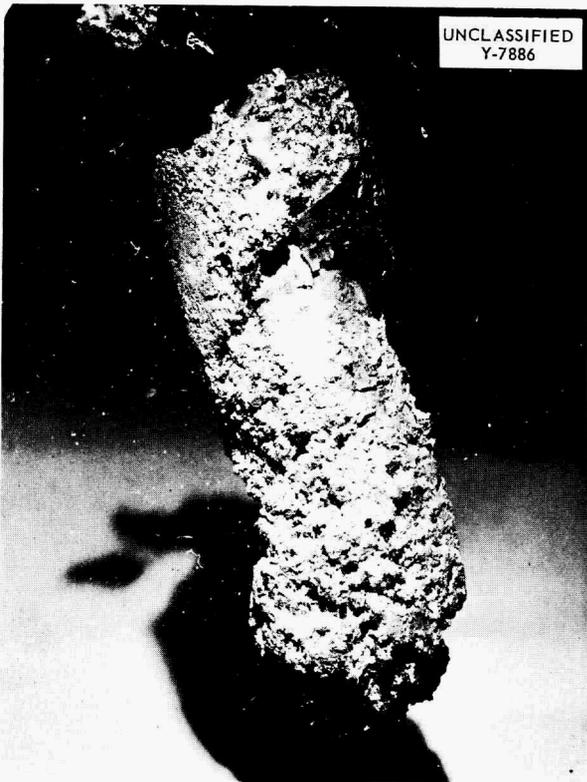


Fig. 16. Plug from an Inconel-Lead Thermal-Convection Loop That Operated for 125 hr at 800°C with a Temperature Gradient of 200°C. 3.5X. Reduced 11%.



Fig. 17. Iron Crystals Formed in a Type 410 Stainless Steel Thermal-Convection Loop After 40 hr Operation with Lithium at 1000°C.

yet, the rate-controlling step in temperature-gradient mass transfer has not been found.

To obtain more data on mass transfer in liquid lead, a series of quartz thermal-convection loops were operated with various alloys and the elements comprising the alloys.⁴ Results of these tests

⁴J. V. Cathcart and W. D. Manly, *A Technique for Corrosion Testing in Liquid Lead*, ORNL-1737 (Aug. 5, 1954).

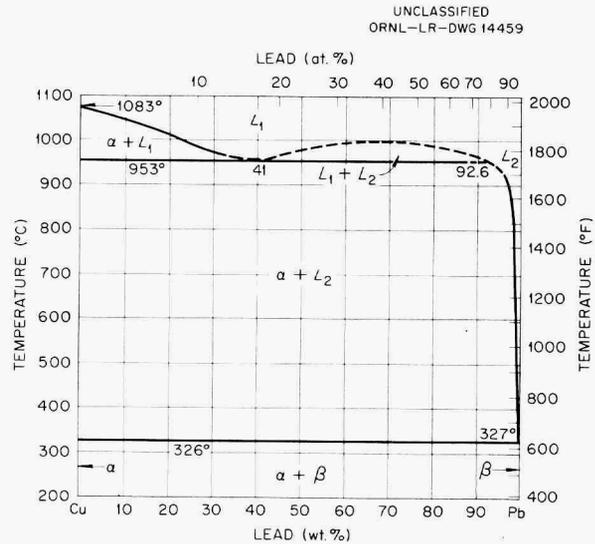


Fig. 18. Cu-Pb Phase Diagram.

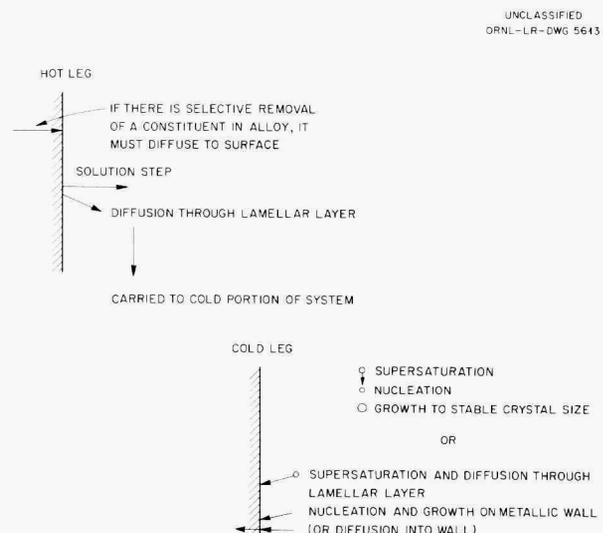


Fig. 19. Various Steps Through Which Metallic Atoms Must Go in Temperature-Gradient Mass Transfer. 200X.

have indicated that the rate-controlling step for mass transfer by lead at the velocities used in the thermal-convection loop takes place in the hot leg and is probably a solution step. For example, it was found that the formation of an intermetallic compound, or other type of diffusion barrier, in the hot zone greatly increases the time that elapses before a plug occurs in the loop.⁵

The last type of liquid-metal corrosion to be discussed is dissimilar-metal mass transfer or concentration-gradient mass transfer. The best example that has been obtained at the Oak Ridge National Laboratory is the interalloying between molybdenum and nickel (Fig. 20). In this case the molybdenum sample was being tested in sodium contained in a nickel crucible, and after 100 hr at 1000°C a sufficient quantity of nickel had transferred through the sodium and deposited and alloyed on the molybdenum surface to produce the Ni-Mo intermetallic compound and solid solution. Another example of this phenomenon resulted in the course of testing silicon with lithium in an iron capsule. Figure 21 shows that all the silicon has gone into solution in the lithium and has been carried to the wall of the iron container where alloying of the iron with the silicon occurred. Dissimilar-metal transfer can cause many misleading results as can be seen in Fig. 22, which illustrates the difference in the depth of corrosion when type 304 stainless steel was tested with lithium in two types of containers. In one case the type 304 stainless steel specimen was placed in a type 304 stainless steel container, and the attack was rather shallow. In the second case the type 304 stainless steel was tested in an iron container, and the attack was much more severe, which was caused by the selective removal of nickel that was transported to the iron wall where it alloyed.

A schematic view of the manner in which dissimilar-metal mass transfer takes place is seen in Fig. 23. In this case atoms of metal A go into solution and move to the surface of metal B either by diffusion and/or by movement of the liquid. When they reach the surface of metal B, they come out of solution, alloy with metal B, and diffuse inward. The driving force for dissimilar-metal transfer is the decrease in the free energy that is achieved through the alloying of the two metals.

⁵J. V. Cathcart and W. D. Manly, *The Mass-Transfer Properties of Various Metals and Alloys in Liquid Lead*, ORNL-2008 (Jan. 10, 1956).

The greater the difference in the chemical potentials of A and of B in the two solid phases, the greater will be the driving force for the occurrence of mass transfer. The rate of mass transfer is dependent on the temperature since an increase in temperature will, of course, increase the diffusion rate in both the liquid and the solid phases. A high solubility of metal A in B, or B in A, or both, will also facilitate mass transfer.

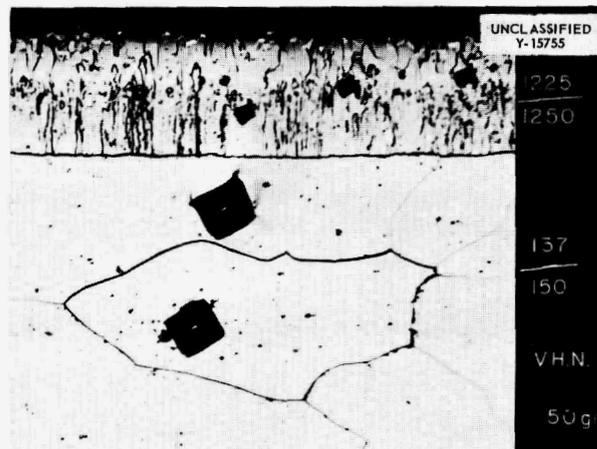
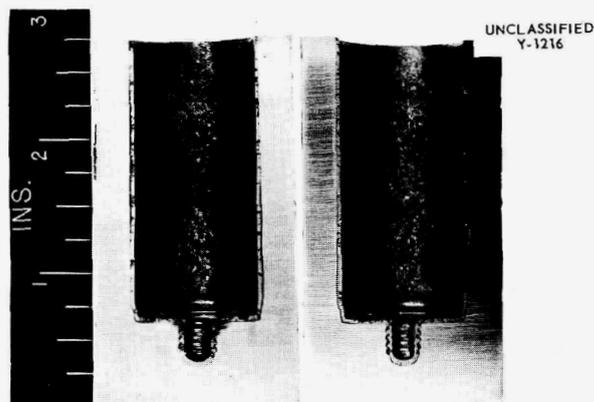


Fig. 20. Interalloying Between Molybdenum and Nickel by Dissimilar Mass Transfer After 100 hr at 1000°C. Vickers hardness impressions (50-g load) indicate relative hardness of the Ni-Mo alloy. 500X. Reduced 32.5%.



IRON CAPSULE WITH LUMP Si IN Li.
ONE OF TRIPLICATE TEST AT 1000°C FOR 4 hr.
APPROX. 25% Si, 75% Li; 14-1L

Fig. 21. Dissimilar Mass Transfer That Occurred Between Silicon and Iron in an Iron Capsule Containing Lump Si in Li Tested at 1000°C for 4 hr.

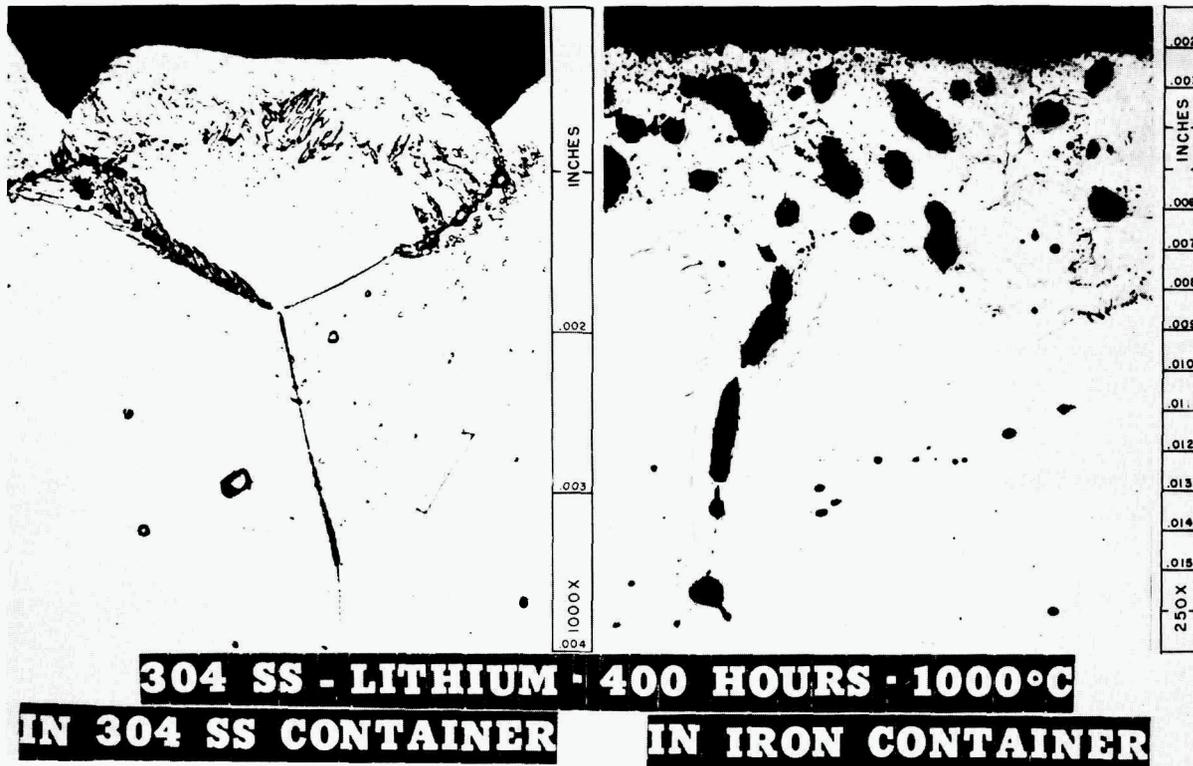


Fig. 22. The Effect of Type of Container on the Corrosion of Type 304 Stainless Steel in Lithium at 1000°C for 400 hr.

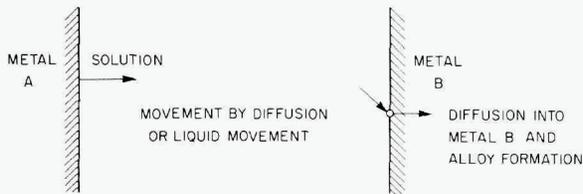


Fig. 23. Schematic View of the Manner in Which Dissimilar-Metal or Concentration-Gradient Mass Transfer Occurs.

CONCLUSIONS

The various types of liquid-metal corrosion have been explained, and examples have been given; the driving forces for the various types of liquid-metal corrosion have been discussed. Liquid-metal corrosion has been described as mainly the solution of the solid metal in the liquid metal. The

rate-controlling step for the various types of liquid-metal corrosion has not been determined. For the successful containment of the liquid metals, the amounts of impurities, such as oxygen, nitrogen, and carbon, should be carefully controlled. Future work in the field of liquid-metal corrosion must be directed toward increasing the understanding of the rate-controlling steps of dissimilar-metal transfer and temperature-gradient mass transfer. When this has been accomplished, corrective measures can then be taken to keep these types of corrosion to a minimum.

ACKNOWLEDGMENTS

The author would like to acknowledge the assistance of J. V. Cathcart, E. E. Hoffman, and other members of the Oak Ridge National Laboratory working in the field of liquid-metal corrosion. The metallographical work used in this paper was performed by a group under the direction of R. J. Gray.