

LIQUID METAL CORROSION CONSIDERATIONS IN ALLOY DEVELOPMENT*

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Abstract

Liquid metal corrosion can be an important consideration in developing alloys for fusion and fast breeder reactors and other applications. Because of the many different forms of liquid metal corrosion (dissolution, alloying, carbon transfer, etc.), alloy optimization based on corrosion resistance depends on a number of factors such as the application temperatures, the particular liquid metal, and the level and nature of impurities in the liquid and solid metals. The present paper reviews the various forms of corrosion by lithium, lead, and sodium and indicates how such corrosion reactions can influence the alloy development process.

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Introduction

The applications of liquid metals in technology are quite varied. Because their excellent heat transfer properties make them attractive candidates for coolants in high power density systems, liquid metals have been used, or are being proposed, as heat transfer fluids in a variety of nuclear and non-nuclear power systems. Examples of such uses include molten sodium for liquid metal fast breeder reactors and central receiver solar stations, and liquid lithium for fusion and space nuclear reactors. Furthermore, since requirements for tritium breeding in deuterium-tritium fusion reactors necessitate the exposure of lithium atoms to fusion neutrons, liquid metal breeding fluids of lithium or Pb-17 at. % Li have been considered for this function while molten lead or bismuth can serve as neutron multipliers to effectively raise the tritium breeding ratio if other types of lithium-containing breeding material are used. Yet another application for liquid metals involves their use as two-phase working fluids in Rankine cycle power conversion devices (potassium) and in heat pipes (potassium, lithium, sodium, NaK). A rather simple utilization of liquid metals that exploits their high thermal conductivities has been the employment of NaK as a static heat sink in automotive and aircraft valves.

Whenever liquid metals are encountered, whether in specific applications or in handling of melts during processing, consideration of the choice of a compatible containment material is required. In some cases, liquid metal corrosion is not important, but for many of the applications cited above, corrosion considerations can play a significant role in choosing the appropriate structural material and operating conditions. Thus, liquid metal corrosion studies in support of aircraft, space, and fast breeder reactor programs and heat pipe technology date back many years. More recently, such research has also been done as part of the fusion energy technology program. In the present paper, we will review our understanding of liquid metal corrosion gained from such studies through a discussion of the principal corrosion reactions and the important parameters that control these processes, particularly with regard to how alloy modification can be used to reduce the deleterious effects of this type of corrosion.

The subject of this paper will be restricted to corrosion phenomena; liquid metal embrittlement factors and environmental effects on mechanical properties will not be considered in developing alloy development principles. Furthermore, the discussion will be limited to corrosion under single-phase (liquid) conditions, which is the primary area of interest for most nuclear and solar applications. The various forms of liquid metal corrosion will first be described and then the influence of alloy composition and microstructure on the underlying corrosion reactions will be discussed.

Forms of Liquid Metal Corrosion

Liquid metal corrosion may manifest itself in a variety of forms. The different types can be broadly classified as

1. dissolution,
2. alloying,
3. intergranular penetration,
4. impurity and interstitial reactions, and
5. mass transfer.

It should be noted that there is overlap of these categories: the various forms of corrosion are not necessarily independent of each other. For example, intergranular penetration can be related to impurity reactions while dissolution is one step in the mass transfer process. However, such a classification scheme is adequate for the purposes of this paper; it establishes a base on which to discuss the corrosion reactions of importance to alloy development.

Dissolution

This form of liquid metal corrosion is the most obvious — the simple solution of the atoms of the containment material in the liquid metal. It is governed by the elemental solubilities in the liquid metal and the kinetics of the dissolution reaction(s). Simple dissolution is the principal form of corrosion that occurs in isothermal, single alloy, static systems of liquid metals containing very low levels of impurities in both the alloy and melt.

Alloying

In this case, reactions between atoms of the liquid metal and those of the structural alloy occur such that a stable product forms without the participation of impurity or interstitial elements. This is not a common form of liquid metal corrosion (particularly with the alkali metals) and will not be discussed further in this paper. Alloying reactions, however, can be used to inhibit corrosion by adding an element to the liquid metal that will react with the containment material to form a corrosion resistant layer. Examples of this can be found in lithium and lead systems (1).

Intergranular penetration

Under certain impurity and/or microstructural conditions, localized attack of grain boundaries can occur upon exposure to a liquid metal (see, for example, Figure 1). The tendency for this type of corrosion can generally be related to the instability of grain boundary precipitates relative to the liquid metal or a susceptible band of altered composition near grain boundaries.



Figure 1 — Polished cross-section of type 316 stainless steel exposed to nitrogen contaminated lithium for 2000 h at 700°C (from reference 2).

Impurity and interstitial reactions

Examples of such reactions include the decarburization of steel in sodium or lithium and the oxidation of steel in sodium or lead of high oxygen activity. In many cases when the principal elements of the containment material have low solubilities in liquid metals (for example, refractory metals in sodium and lithium), reactions involving light elements such as oxygen, carbon, and nitrogen dominate the corrosion process.

Mass transfer

In this form of corrosion, there is a net movement of material in response to a gradient in temperature or composition across a liquid metal system. Thermal gradient mass transfer is shown schematically in Figure 2. Since the liquid metal is the means by which the material is transported, the dissolution and deposition reactions are of prime concern. In cases where liquid metals are used under nonisothermal conditions, nonuniform deposition of material in the cold zone of the circuit can be a more severe problem than dissolution in the hot region due to flow restrictions and, in nuclear applications, excessive radiation levels outside the core caused by radionuclide deposition. Concentration gradient mass transfer can occur in the absence of a thermal gradient or add to the severity of the mass transport problem in nonisothermal systems due to elemental activity differences across the liquid metal arising from the simultaneous exposure of containment materials of different composition. An example of concentration gradient mass transfer would be carbon transfer from a steel to a refractory metal in a bimetallic liquid metal system.

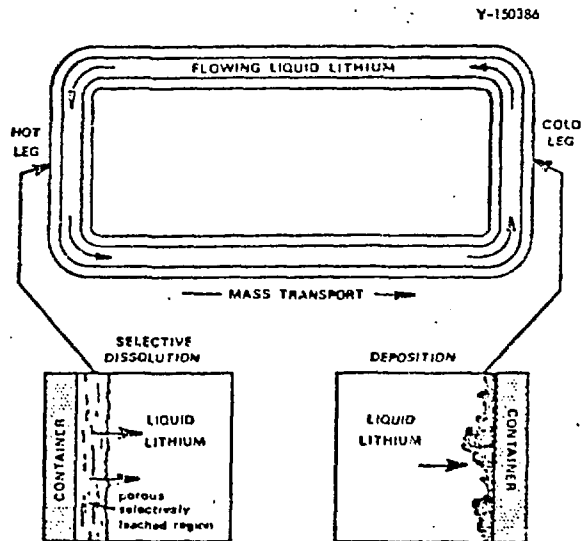
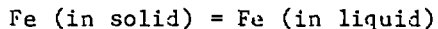


Figure 2 — Schematic representation of thermal gradient mass transfer in a lithium-austenitic stainless steel system (from reference 3).

Corrosion Reactions - Influence of Alloy Composition and Microstructure

Direct dissolution reactions

Direct dissolution reactions are those that involve the simple solution of an element from the containment material in the liquid metal in the absence of any impurity effects. An example of this reaction would be

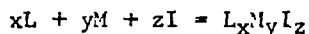


This type of reaction is governed by the solubility of the particular element of the solid in the liquid metal and the kinetics of the dissolution process. For pure metals, a straightforward approach to the selection of a containment material would therefore be to use an element that has a very low solubility in the liquid metal. For example, refractory metals have low solubilities in sodium, lithium, and lead and are essentially inert to these molten metals aside from some impurity-induced effects (see below). For the more practical situation where an alloy is required, it is sometimes possible to develop a dissolution-resistant alloy based on reducing or eliminating an element that exhibits a high solubility in the liquid metal of interest and increasing the relative enrichment in elements that have lower solubilities. Such behavior has been found in sodium, lead, and lithium systems, where nickel exhibits significant solubilities: decreasing the concentration of nickel in Fe-Cr-Ni alloys decreased the extent of dissolution of these alloys (4-6). An alternative to reducing an "active" elemental concentration in an alloy is to reduce its activity. It has been shown that a high nickel alloy can have a significantly lower dissolution rate in lead than alloys with lower nickel concentrations if the former material consists of an intermetallic compound (7).

It should be noted that while alloy development can often be guided by solubilities in the liquid metal, this "rule of thumb" can have exceptions. Indeed, as in many other processes, the kinetics of the dissolution (or deposition) reaction may control the overall rate of weight loss such that solubility does not determine the ultimate amount of dissolution, particularly for short-time exposures and for nonisothermal conditions in which deposition is simultaneously occurring.

Corrosion product formation

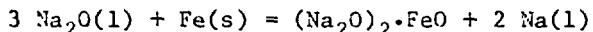
Corrosion product formation is one type of what was classified as an interstitial or impurity reaction. The general form of such a reaction is



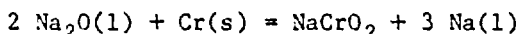
where L is the chemical symbol for a liquid metal atom, M is one for the containment alloy, and I represents an interstitial or impurity atom in the solid or liquid ($x, y, z > 0$). The $L_xM_yI_z$ corrosion product that forms may be soluble or insoluble in the liquid metal. If soluble, the effect of the "I" atom could be to cause higher measured weight losses and result in an apparently higher solubility of M in L. (This is a frequent cause of erroneous solubility measurements.) Furthermore, if a soluble corrosion

product forms at selected sites on the surface, localized attack will be observed. If the corrosion product is insoluble, then a surface layer will develop. However, this does not necessarily mean that it can be directly observed: the product may dissolve during the process of removing the residual liquid metal from the exposed containment alloy.

A good example of the importance of impurity or interstitial reactions that form corrosion products can be found in the sodium-steel-oxygen system. It is thought that the reaction

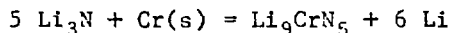


increases the apparent solubility of iron in sodium at higher oxygen activities while the interaction of oxygen, sodium, and chromium can lead to the formation of a corrosion product film



This second reaction is one of primary importance in sodium corrosion of chromium-containing steels. It can be controlled by reduction of the oxygen concentration of the sodium to less than about 3 wt ppm and/or by composition modification of the alloy, that is, by reducing the chromium concentration of the steel.

An example of such corrosion product reactions can also be found in lithium-steel systems, where nitrogen has been observed to increase corrosion (2,8,9). In particular, the reaction



has been observed (10) and this corrosion product has been found to be localized at grain boundaries of exposed steels (11,12). In addition, nitrogen is thought to increase the dissolution of nickel in molten lithium (10) and is effective at increasing corrosion whether it is in the lithium or in the steel (12,13). Therefore, reducing the nickel, chromium, and nitrogen concentrations of steels exposed to lithium could improve their corrosion resistance.

A final example of a corrosion product reaction that can occur in a liquid-metal system is that of oxidation of a metal or alloy exposed to molten lead. In some cases, this reaction may actually be beneficial by providing a protective barrier against the highly aggressive lead (6). [Pure lead is more corrosive toward ferrous alloys than pure lithium or sodium (1,4,6)]. However, this surface product will form and then heal only when the oxygen activity of the melt is maintained at a high level or when oxide formers such as aluminum or silicon have been added to the containment alloy to promote this form of protection (6). Therefore, alloy development considerations based on the oxidation reaction in lead-steel systems would favor the use of alloying additions that are strong oxide formers to help protect the steel from dissolution.

Impurity transfer

The second general type of impurity or interstitial reaction is that of elemental transfer. Such a reaction is of crucial importance for oxygen-metal-lithium systems since lithium is such a strong sink for oxygen. In fact, despite their low solubilities in lithium, niobium and tantalum can be severely attacked when exposed to lithium if the oxygen activity of these metals is not minimized. Their oxides are rapidly attacked with concomitant transfer of the oxygen into the molten lithium. The result is localized penetration along grain boundaries and selected crystallographic planes (14,15). This form of corrosion can be eliminated, however, by minimizing the oxygen concentration of these refractory metals and by using alloying additions that form oxides that are not reduced by lithium (1-2 at. % Zr in Nb and Hf in Ta) (14).

Another important example of impurity transfer is that of decarburization/carburization. Carbon transfer to or from the liquid metal can cause decarburization of Fe-Cr-Mo steels (particularly lower chromium steels) and carburization of refractory metals and higher chromium alloys. There have been many studies of such reactions for sodium-steel systems (see, for example, references 16-18) while less work has been done in the area of lithium-steel carbon transfer (18,19). However, the same type of considerations apply in both cases and as an example, results from two lithium studies (19,20) will be briefly discussed. The equilibrium partitioning of the carbon between the Fe-Cr-Mo steel and the lithium can be described as (19)

$$\frac{C_{C(s)}}{C_{C(Li)}} = (a_{Cr})^{x/y} \frac{C_{C(s)}^0}{C_{C(Li)}^0} \exp \frac{\Delta F_{\frac{1}{2}Li_2C_2}^0}{RT} \exp \frac{-\Delta F_{1/yCr_xC_y}^0}{RT}$$

where

$$\begin{aligned} C_{C(s)}, C_{C(Li)} &= \text{concentration of carbon in the steel and lithium,} \\ &\quad \text{respectively,} \\ a_{Cr} &= \text{chromium activity of the steel,} \\ C_{C(s)}^0, C_{C(Li)}^0 &= \text{solubilities of carbon in the steel and lithium,} \\ &\quad \text{respectively,} \\ \Delta F^0 &= \text{free energies of formation of the indicated} \\ &\quad \text{compounds,} \end{aligned}$$

and x, y are defined by the stoichiometry of the chromium carbide. This equation indicates that to decrease the tendency for decarburization of an alloy [i.e., to increase the "partitioning coefficient," $C_{C(s)}/C_{C(Li)}$], the chromium activity of the alloy must be increased or the free energy of formation of the matrix carbide must be lowered (made more negative) by alloy manipulation to form a more stable carbide. Experiments in lithium and sodium have shown these factors indeed have the desired effect. Tempering of Fe-Cr-Mo steels to yield more stable starting carbides can significantly reduce decarburization by these two liquid metals (16,18,19). Furthermore, alloying additions such as niobium form very stable carbides and can dramatically reduce decarburization (20). (With very unstable microstructures, the carbides are rapidly dissolved (20) in a manner similar to that described above for oxygen-containing refractory metals in lithium.)

In addition, as shown by the above partitioning equation, increasing the chromium level of a steel effectively decreases the tendency for carbon loss in sodium (18) and lithium (19). With higher chromium steels (for example, (austenitic stainless steels), carburization can then become a problem at higher temperatures.

Based on thermodynamic predictions and experimental results, it is apparent that carbon transfer in sodium and lithium systems containing steels can be minimized by optimizing chromium levels and increasing the stability of the carbide precipitate structure by proper heat treatment and/or addition of carbide stabilizers.

Mass transfer

Alloy modification may also affect mass transfer. In a trivial sense, concentration gradient mass transfer may be eliminated by not using more than one alloy composition in contact with the same liquid metal. Otherwise, the principal way to decrease mass transfer via alloy development is to reduce the amount of dissolution, corrosion product formation, and impurity transfer by the ways already discussed above.

Another method to affect mass transfer is to control deposition. This can be done by tailoring the temperature distribution around a loop, but, with respect to alloy considerations, the effects that can be influenced are rather special cases. For example, if the liquid metal has to flow through a magnetic field, as it would in certain designs of magnetic fusion reactors, preferential deposition of magnetic elements can occur. A reduction in the amount of material available for magnetic trapping (Fe, Ni, Co) may then be necessary. In another case, preferential deposition of chromium was observed in some lithium systems during the early stages of mass transfer (21) and was sufficiently severe to cause plugging in one instance. Reducing the amount of starting chromium in the containment material would decrease this tendency. Finally, lowering the nitrogen content of some alloys may eliminate some deposits in the cold regions of lithium loops — nitrogen may have played an intermediary role in the chromium deposition described above (21) and some HfN deposits were observed (as the only mass transfer products) in the cold zones of two Ta-10 W-0.8 Hf (wt %) lithium loops (22).

Alloy Development Example: Fe-Cr-Mo Steels Exposed to Lithium

A specific example of how liquid metal corrosion considerations can influence development of Fe-Cr-Mo steels for lithium service will be briefly described. For these steels, the possible reactions with chromium are of prime importance. As discussed above, carbon transfer in liquid metal systems can be controlled by increasing the chromium concentration and/or stabilizing the microstructure. A concentration of about 8 to 10 wt % Cr in Fe-Cr-Mo alloys would result in a minimization of carburization-decarburization at 500°C. However, such a chromium concentration is not optimal from the viewpoint of direct dissolution, deposition, and nitrogen-induced corrosion reactions, which are minimized by reducing the chromium activity of the alloy (for a fixed nitrogen concentration). Alloy development based on liquid lithium corrosion considerations would therefore result in a lower chromium steel (for example, Fe-2 1/4 Cr-1 Mo steel) that has been stabilized by use of alloying additions such as niobium or vanadium to minimize decarburization. Furthermore, such a steel should be produced so

that certain minor elements are minimized. For example, elements that dissolve readily in lithium, such as nickel and manganese, should be maintained at low levels; concentrations of 1 wt % could lead to significant mass transfer (23). In addition, the nitrogen level of the steel should be as low as possible to avoid the corrosion reactions involving nitrogen.

Summary

The variety of forms of liquid metal corrosion and the number of possible containment materials makes the consideration of every possible reaction impossible. Rather, selected cases were examined in the present paper to show what type of factors have to be considered in alloy selection for liquid metal containment and how alloy development can be used to minimize particular types of liquid metal corrosion reactions. A general summary of the types of the most common corrosion reactions and their consequences for alloy development is given in Table I, which also includes specific examples in each category from among those discussed in the text. Since two or more concurrent corrosion reactions are possible in a liquid metal system, consideration of all the applicable alloy development consequences may lead, in some cases, to opposite alloy strategies. (For example, chromium in Fe-Cr-Mo steel-lithium systems should be minimized on the basis of mass transfer, while a higher chromium is preferred for minimizing carbon transfer.) In such instances, optimization of concentrations and/or microstructures would be necessary.

Table I. Consequences for Alloy Development Based on Liquid Metal Corrosion Reactions

Corrosion reaction	Consequence for alloy development	Example
Direct dissolution	Lower activity of key elements	Reduce Ni in Li, Pb systems
Corrosion product formation	(1) Lower activity of reacting elements (2) In case of protective layer, add elements to promote formation	(1) Reduce Cr, N, and Ni in Li systems (2) Add Al or Si to steel exposed to Pb
Impurity and interstitial transfer	(1) Increase (or add) elements to decrease transfer tendency (2) Minimize element being transferred	(1) Increase Cr in steels; add Zr to Nb exposed to Li (2) Reduce O in Nb and Ta exposed to Li
Mass transfer	(1) Reduce extent of other corrosion reactions (2) Reduce concentration of elements that tend to deposit nonuniformly in cold zone (3) Reduce amount of material available for magnetic trapping (magnetic devices only)	(1) See above (2) Reduce Cr in Li systems (3) Ni and Fe in Pb or Li fusion systems

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