

1966

Effect of oxygen content on the liquid metal corrosion of molybdenum

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**SMITH, Dale LeRoy, 1938-
EFFECT OF OXYGEN CONTENT ON THE LIQUID
METAL CORROSION OF MOLYBDENUM.**

**Iowa State University of Science and Technology
Ph.D., 1966
Engineering, metallurgy**

University Microfilms, Inc., Ann Arbor, Michigan

**EFFECT OF OXYGEN CONTENT
ON THE LIQUID METAL CORROSION OF MOLYBDENUM**

by

Dale LeRoy Smith

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

Major Subject: Nuclear Engineering

Approved:

Signature was redacted for privacy.

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**Iowa State University
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Ames, Iowa**

1966

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INTRODUCTION

The advent of nuclear power has created considerable interest in the development of liquid metal technology. Because of their advantageous properties, liquid metals have been proposed for several uses in the nuclear reactor industry. Probably the most important use of liquid metals to date has been as a reactor coolant to remove heat from the reactors. Other possible uses which have been considered for liquid metals include molten metal reactor fuels, molten metal fuel carriers, and high temperature reprocessing of reactor fuels.

Materials technology, which has been a limiting factor in the growth of the nuclear industry, has also limited the use of liquid metals. The containment or corrosion problem is perhaps the most important problem which has been encountered in the development of liquid metals. Much of the first work concerned with the containment problem of liquid metals involved the phenomenological approach which concentrated on categorizing certain metals and alloys as to whether they would contain a particular liquid metal for a specified time at a given temperature. In general, the refractory metals have been shown to have the greatest resistance to attack for most liquid metals. Investigations have also been undertaken to determine the type of interaction, such as solution of the solid container or intergranular penetration, which occurs between a liquid metal and a solid metal.

Recently, due to significant disagreement in the corrosion results of various investigators, it has been concluded that impurities in the

systems may have considerable effect on the corrosion results. Thus, two investigators testing the same liquid metal-solid metal system could get very different results if the impurity content of the two systems varied. The ideal approach to this problem would be to eliminate all impurities by using ultra high purity materials. This approach, although it has been used, is far from being the most practical. The limited knowledge of the effect of the impurities on liquid metal corrosion and the mechanisms by which they interact is responsible for the use of the expensive high purity material approach to the corrosion problem.

The impurities generally considered to be of importance are the interstitial impurities oxygen, nitrogen, hydrogen and carbon. Since oxygen and nitrogen are present in large quantities in the atmosphere and are frequently present to some extent in many metals, these impurities are of particular concern. The removal of oxygen and nitrogen from the metals being used and the subsequent protection of the metals from the atmosphere is often quite difficult and expensive; therefore, it is desirable to know which systems are affected by the impurities and whether or not the impurities can be inactivated without being removed.

Since the most important use of liquid metals to date has been as reactor coolants and the alkali metals appear to be superior for this purpose, most of the investigations on impurity effects have been on systems containing the highly active alkali metals. Only a few particular systems have been studied in detail and this type of corrosion phenomenon is not yet well understood. A better understanding of the impurity interactions will be derived from a study of the less active low melting metals.

OBJECT OF THIS INVESTIGATION

The purpose of this investigation is to further the understanding of the effects of interstitial impurities on the liquid metal corrosion of refractory metals by testing the effect of oxygen on the corrosion of molybdenum by four low melting metals. Since the majority of the work done in this area has been with the highly active alkali metals, a study of some of the less active low melting metals is desirable.

The various mechanisms by which oxygen may interact will be discussed and the results of the experimental tests will be explained in terms of these mechanisms. The conclusions of this investigation will better enable one to predict the types of systems in which the effect of oxygen and other interstitial impurities may be of importance and the systems in which the effect of the impurities might be expected to be negligible.

CORROSION BY LIQUID METALS

Liquid metal corrosion may briefly be defined as any interaction which takes place between a solid and a metal in the molten state. A weight loss or weight gain of the solid metal usually accompanies the interaction. In this report the solid will be assumed to be a metal. These interactions which occur between liquid and solid metals have been subjected to numerous investigations in recent years and have been categorized by several investigators (4,5,33,37,43,47).

Corrosion Mechanisms

In general, liquid metal corrosion can be classified as a combination of one or more of the following types of interactions:

- A. Dissolution of solid metal in liquid metal.
- B. Alloying between solid metal and liquid metal.
- C. Intergranular penetration of solid metal by liquid metal.
- D. Concentration gradient mass transfer.
- E. Temperature gradient mass transfer.
- F. Impurity reactions.

If alloys are used as either the solid metal or the liquid metal, the corrosion mechanism may be somewhat more complicated; however, the same types of attack generally apply.

Dissolutive attack

Dissolution of the solid metal in the liquid metal occurs when the chemical potential of the solid metal in the pure state differs from the chemical potential of the solid metal in solution with the liquid metal.

The solid metal will dissolve in the liquid metal until an equilibrium exists between the chemical potential of the solid metal in the two phases. A general idea of the amount of dissolutive attack which will occur in a system can be obtained from the phase diagram of the two components.

The rate of dissolution has been studied in considerable detail (23, 33, 63) and appears to be limited by the reaction rate at the solid-liquid interface and by the diffusion rate of the solute away from the interface. The dissolution rate has also been found to be affected by high energy regions such as grain boundaries and twinned regions.

Alloying

In some systems an intermetallic compound of the solid metal and the liquid metal forms at the interface. The compound formation has been observed (3, 8) in several systems containing molten uranium alloys. The corrosion rate is limited by the diffusion rate of either the solid metal or liquid metal through the boundary layer. As the thickness of the boundary layer increases, the rate of corrosion generally decreases. Cracking or eroding of this boundary layer will, of course, affect the rate of attack.

Intergranular penetration

Dissolution along grain boundaries and inward diffusion of liquid metals along the solid metal grain boundaries have both often been classed as grain boundary penetration. For this report, the preferential dissolution along boundaries will be classified as dissolution attack and the inward diffusion along grain boundaries will be classified as intergranular penetration. Results of tests with liquid metals contained

in solid metal capsules have indicated that the liquid metals have diffused through the solid metal walls leaving the capsules completely empty (6,60).

Temperature gradient mass transfer

Temperature gradient mass transfer is more likely to occur in a circulating liquid metal system but may also occur in a static system if there is a temperature differential in the system. The driving force for this type of mass transfer is the temperature differential and the fact that the solubility of the solid metal in the liquid metal is temperature dependent (36). The interaction is usually of the simple dissolution type at some hot point of the system and a precipitation of the solute at a cold point in the system. Simple dissolution of the solid metal occurs to the extent of its solubility at the hot point and, since the solubility is generally less at a lower temperature, some of the solute precipitates out at the low temperature section. Although the dissolution process at the high temperature is of concern, it is generally the precipitation at the low temperature which creates the problem.

Concentration gradient mass transfer

A three component system, which many investigators (4,9,17,18,20,55) have used because of economy, may support mass transfer caused by a concentration gradient in the system. This type of mass transfer typically occurs by dissolution of a solid metal by a liquid metal followed by a second interaction between dissolved metal with another solid metal to form a compound. The liquid metal simply acts as a carrier for the one solid metal. Considerable transfer may occur even though the solubility

of the solid metal in the liquid metal is quite small. This type of transfer does not require a dynamic system or a temperature gradient but may occur in a static, isothermal system.

Impurity reactions

Additional interactions may occur if impurities are present in either the solid metal or the liquid metal. The interstitial impurities oxygen, nitrogen, carbon, and hydrogen, with oxygen appearing to be the most important, have been found to affect the corrosion rate in some systems (21,34,42,51). Experimental data on liquid metal corrosion by the alkali metals have shown that impurity oxygen has a significant effect on the corrosion rate. In some cases the oxygen content of the alkali metals appears to be controlling (51), while in other systems the oxygen content of the solid metal appears to be the rate controlling factor (21,42). Although experimental data have shown that interstitial impurities may affect corrosion rates considerably, the phenomena are not well understood at this time. The mechanisms of interactions and theories advanced on impurity effects will be discussed in more detail later.

Systems for Investigation

Since the data available concerning the effect of interstitial impurities on liquid metal corrosion is almost entirely limited to the alkali metals, an investigation of the low melting "heavy" metals would contribute significantly to a better understanding of this corrosion process.

The effect of interstitial impurities can more accurately be determined if the other types of corrosion can be eliminated or at least kept

to a minimum. As described earlier, the dissolution of the solid metal by the liquid metal is dependent on the solubility of the solid metal in the liquid metal. Very low solubilities of molybdenum in lead, cadmium, tin, and zinc make these systems attractive for this investigation. Table 1 compares available data on the solubilities of molybdenum in the four low melting metals with that for three of the alkali metals. The references from which the data were obtained are also listed. The solubility of tin was calculated from the corrosion results of this investigation.

Table 1. Solubility data for molybdenum in liquid metals

Liquid Metal	Temperature °C	Solubility ppm	Reference
Lead	871	0.5	(53)
	1016	0.5	(53)
	1200	23	(2)
Cadmium	603	12	(12)
Tin	800	1000 ^a	
Zinc	750	200	(20)
	730.5	213	(43)
	664.3	216	(43)
	593.3	213	(43)
	550.4	225	(43)
	527.1	145	(43)
	502.4	122	(43)
	450.7	63.6	(43)
422.2	31.4	(43)	
Potassium	1000	3	(44)
Sodium	900	low	(51)
Lithium	727	21	(40)
	944	1175	(40)

^aValue was calculated from corrosion results of this investigation.

Although the literature is somewhat meager in the area of compound formation between molybdenum and the four low melting metals, there apparently is little problem in the temperature range being considered here. Hansen (31) reported that up to twenty weight percent molybdenum has been dissolved in boiling lead; however, elemental molybdenum precipitated from the melt at very high temperatures. Hansen also reported no alloying between cadmium and molybdenum. Sargent (59) reported that molybdenum-tin alloys could not be obtained by reduction of the metal oxides with carbon; however, Brown (7) has recently published some crystal structure data for a compound of the composition $\text{MoSn}_{1.5}$. Koster and Schmid (39) report that molybdenum and zinc do not alloy up to 1350°C . With the exception of tin there should be no intermetallic compound formation at the liquid-solid interface if high purity materials are used.

Mass transfer, both temperature gradient and concentration gradient, should not contribute to the corrosion in static tests using small capsules to contain the liquid metal. Only a two-component system is required if the capsule is also used as the corrosion specimen.

From the foregoing analysis, it appears that the systems of lead, cadmium, tin, and zinc in molybdenum should be satisfactory for determining the effect of impurity oxygen on the liquid metal corrosion of refractory metals. By using high purity materials, a significant amount of any corrosion should involve the oxygen in the interaction.

Impurity Reactions

The impurity reactions are probably the least understood of the various types of corrosion mechanisms. This is undoubtedly due to the fact

that very little experimental data is available and until recently it was not known that interstitial impurities had a significant effect on liquid metal corrosion. Much of the corrosion data available does not include the impurity content of the system, and the difficulty encountered in determining the oxygen content for some systems leaves doubt as to the accuracy of some of the measurements which have been made.

Any one of several mechanisms may be postulated to explain the interactions and corrosion which are caused by the presence of oxygen in the system. These include the resultant effects caused by the redistribution of oxygen between the liquid metal and the solid metal, any effect on the amount of corrosion due to a change in the solubility of the solid metal in the liquid metal caused by the presence of oxygen in the system, and any effect on corrosion caused by the oxidation of the solid metal wall and subsequent erosion or solution of the oxide. The net effect on the corrosion may be due to a combination of these mechanisms.

Partitioning of oxygen

The comparison of the curves of free energy of formation versus temperature for the simple oxides has been used as a measure of the distribution of oxygen between a solid and a liquid metal. For many systems this method gives a fairly good indication of the net direction of oxygen redistribution to attain equilibrium conditions; however, the assumptions made in this derivation are not valid. Thermodynamically this approach assumes that the two solutions (i.e. oxygen in solid and oxygen in liquid) are in equilibrium when the activity of oxygen in

each solution is the same. This relationship, assuming that oxygen distributes itself between the two solutions according to the ratio of the solubility limits for each solution, can then be derived (10). In the linear Henry's Law region of the activity (a) versus atom fraction (N) curve, the following relation can be written, where k is the slope.

$$a = kN \quad (1)$$

Since the activity is unity at the solubility limit, the constant k in Equation 1 may be expressed as

$$k = \frac{1}{N_{s.l.}} \quad (2)$$

where $N_{s.l.}$ is the atom fraction at the solubility limit. Therefore, the activity at any composition obtained from Equations 1 and 2 is

$$a = \frac{N_{soln}}{N_{s.l.}} \quad (3)$$

where N_{soln} is the atom fraction of oxygen in solution. If, as previously assumed, the activity of oxygen in each solution is equal, the oxygen distributes itself according to the ratio of the solubility limits.

$$\frac{N_{1soln}}{N_{soln}} = \frac{N_{1s.l.}}{N_{s.l.}} \quad (4)$$

This relationship is not generally valid since it requires that a different standard state be assumed for each solution, namely the oxygen

saturated solution composition. Only in the cases where two oxygen saturated solutions can exist in equilibrium with each other without differing in oxygen atom fraction from that of the binary systems of each of the two solvents with oxygen, can the activities be set equal. This relationship, although not completely valid, is sometimes used because of its simplicity or because of lack of data required for more sophisticated calculations.

A more rigorous derivation may be obtained by equating the partial molal free energies or chemical potentials (10) rather than the activities for two solutions in equilibrium. If the two metals are completely immiscible in each other when in physical contact, and both contain oxygen in solution, then the partial molal free energy of oxygen in each metal is the same when the system is in equilibrium. Therefore,

$$\bar{F}_l = F_l^\circ + RT \ln a_l \quad (5)$$

where \bar{F}_l is the partial molal free energy of oxygen per gram atom in the liquid metal, F_l° is the free energy per gram atom of oxygen in some reference state, and a_l is the activity of oxygen in the liquid metal. Similarly the partial molal free energy of oxygen per gram atom in the solid metal can be written as

$$\bar{F}_s = F_s^\circ + RT \ln a_s \quad (6)$$

Considering the limitations previously discussed, the partial molal free energy of oxygen is equal in both the solid and liquid metal when the system is in equilibrium. Therefore,

$$\bar{F}_l = \bar{F}_s \quad (7)$$

and

$$F_l^\circ - F_s^\circ = RT \ln \frac{a_s}{a_l} \quad (8)$$

The most practical reference state is that in which oxygen in solution with the solid or liquid metal is in equilibrium with their respective oxides. The free energies of the reference state, F_l° and F_s° may, therefore, be replaced by $\Delta F_f^\circ(\text{L oxide})$ and $\Delta F_f^\circ(\text{S oxide})$ which are the standard free energies of formation of the oxides of the liquid and solid metal respectively. The ratio of the activities is then given by

$$\frac{a_s}{a_l} = \exp \left[\frac{\Delta F_f^\circ(\text{L oxide}) - \Delta F_f^\circ(\text{S oxide})}{RT} \right] \quad (9)$$

If dilute solutions are involved such that Henry's Law is valid, the development of Equations 1, 2, and 3 may be used to relate activity to atom fraction. Substitution of Equation 3 into Equation 9 gives

$$\frac{N_s}{N_l} = \frac{N_{s.l.}}{N_{l.s.l.}} \exp \left[\frac{\Delta F_f^\circ(\text{L oxide}) - \Delta F_f^\circ(\text{S oxide})}{RT} \right] \quad (10)$$

The distribution coefficient of oxygen in the solid and liquid metal may be denoted by D , where

$$D = \frac{N_s}{N_l} \quad (11)$$

Several investigators (32,42,43) have used similar treatments to calculate the distribution of oxygen in liquid metal-solid metal systems. This derivation is somewhat more rigorous than the first one which assumed equal activities at equilibrium; however, this derivation has several limitations for practical applications and should be considered only with these limitations and assumptions in mind.

1. The solid metal and the liquid metal are assumed to be completely immiscible. The solubility data shown on page 8 indicate that this assumption is quite good for the systems being considered in this investigation. Several other refractory metal-low melting metal systems also show very low solubilities.

2. The oxide which is used for the reference state must be the one which is in equilibrium with the solution phase at the test conditions. Since some oxides decompose at relatively low temperatures, care must be taken in determining the stable oxide phase at higher temperatures. The limited data for some of the metal-oxide systems create some problems in this area.

3. Any solubility between the liquid oxide and the solid metal or the solid oxide and the liquid metal will limit the accuracy of the expression derived. The standard states used in the derivation considered only a metal-oxygen solution in equilibrium with its oxide. The presence of a second metal or oxide would undoubtedly affect the equilibrium state of the original metal solution and the oxide.

4. The formation of complex oxides such as molybdates, or polyoxides of the liquid and solid metal oxides, would also affect

the standard state equilibrium conditions. An additional problem is encountered due to the liquid state of the one metal. The knowledge of the bonding and the actual form of a polyoxide or even a simple oxide when contained in a liquid metal is very limited.

The distribution coefficients for oxygen in three alkali metal-molybdenum systems and the four low melting metal-molybdenum systems under investigation here have been calculated using Equations 10 and 11. The calculated distribution coefficient for each system is listed in Table 2 along with the standard state oxides and the values used in the calculations. The values for the free energy of formation of the oxides were obtained from a compilation report by Chiotti and Shoemaker (15) and are shown graphically in Figure 1. The solubility of oxygen in several of the low melting metals is not well known at the temperatures of interest; therefore, some error may be involved since extrapolated values have been used for some of the calculations. However, the order of magnitude of the distribution coefficient should be representative of the system. The reference from which the solubility data was obtained is given in parentheses in Table 2 following the value used for the solubility in the calculation. Due to the lack of data for cadmium, tin, and zinc, the solubility values used for these systems correspond to experimental results obtained in this investigation.

The distribution coefficients which are greater than one indicate a higher atom fraction of oxygen in molybdenum than in the liquid metal, and the coefficients which are less than one indicate a higher atom fraction of oxygen in the liquid metal than in molybdenum when the system is in equilibrium. The liquid metal systems with a very low distribution

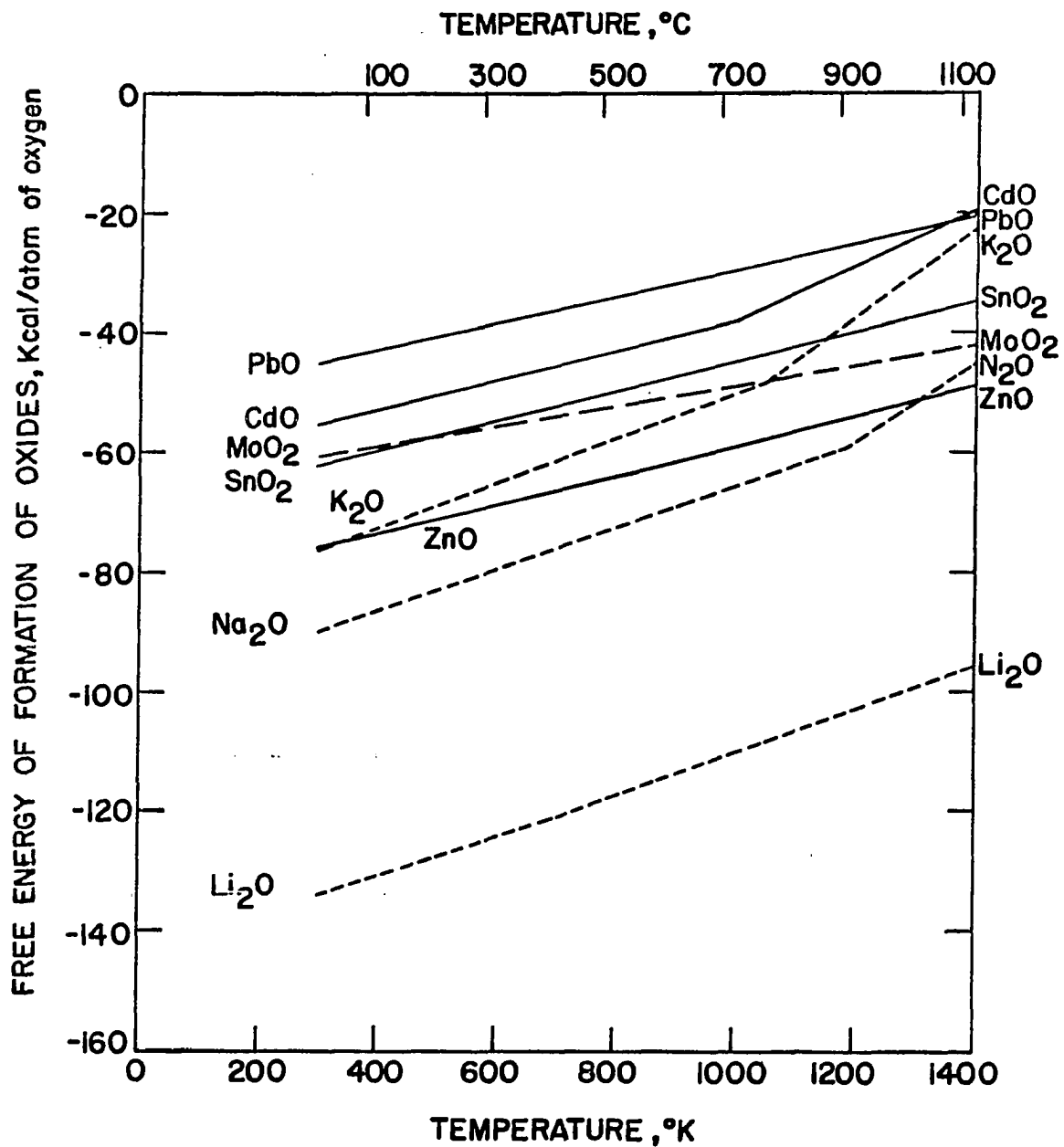


Figure 1. Free energy of formation for several metal oxides

coefficient, such as lithium, therefore, would be expected to have a high affinity for any oxygen in the molybdenum.

Table 2. Calculated distribution coefficients for oxygen in several liquid metal-molybdenum systems

Liquid Metal	Standard State Oxide	Temperature °C	$-\Delta F_f^\circ(\text{oxide})^a$ Kcal/atom of oxygen	Solubility ^b of Oxygen atom percent	Distribution Coefficient D
Lead	PbO	800	27.5	0.16 (30)	1.6×10^3
Cadmium	CdO	700	38.2	0.045 ^c	1.4×10^2
Tin	SnO ₂	800	42.6	0.22 ^c	9.4×10^{-1}
Zinc	ZnO	700	59.7	0.086 ^c	1.0×10^{-3}
Potassium	K ₂ O	700	51.0	8.4 (63)	9.7×10^{-4}
Sodium	Na ₂ O	700	66.4	0.36 (63)	7.7×10^{-6}
Lithium	Li ₂ O	700	111.0	0.18 (33)	1.3×10^{-15}
	MoO ₂	700	49.0	0.023(24)	
	MoO ₂	800	47.2	0.024(24)	

^aValues obtained from Chiotti and Shoemaker (15).

^bReferences from which data was obtained are given in parentheses.

^cData obtained from this investigation.

The distribution coefficient for the lead-molybdenum system at 800°C indicates a condition of equilibrium for oxygen when the molybdenum contains 40 parts per million oxygen and the lead contains much less than one part per million oxygen by weight. Therefore, any significant

amount of oxygen in the lead would be expected to be attracted by the molybdenum based on this theory. Since the 40 parts per million oxygen content of the molybdenum is near the solubility limit, an increase in oxygen content of the molybdenum cannot be predicted by this theory.

The distribution coefficient for oxygen in the cadmium-molybdenum system at 700°C indicates that equilibrium conditions for the oxygen exist when the cadmium contains slightly less than one part per million oxygen if the molybdenum contains 40 parts per million. This indicates that very high purity cadmium would be required to attract oxygen from the molybdenum. Since the calculations are not considered highly accurate, the possibility of some redistribution of oxygen to high purity cadmium cannot be eliminated. As for the lead-molybdenum system, this theory cannot predict a net exchange of oxygen to the molybdenum since the derivation is not valid in the region above the solubility limit for oxygen.

The calculations indicate that the affinity of tin for oxygen is almost identical to that of molybdenum and that equilibrium conditions exist when the oxygen contents of both metals are practically equal.

The zinc appears to be much more active than molybdenum and might be expected to attract oxygen from the molybdenum; however, molybdenum does not readily give up oxygen below its solubility limit.

The importance of the equilibrium oxygen distribution lies in the fact that any transfer of oxygen is likely to be accompanied by an effect on the corrosion of the molybdenum. Any oxygen in the grain boundaries of molybdenum may attract highly active liquid metals and promote intergranular penetration. Impurity oxygen in the molybdenum might also tend to block diffusion of liquid metals along grain boundaries.

Effect of oxygen on solubility

Systems which exhibit simple dissolutive attack of the solid metal by the liquid metal may also be affected by the presence of oxygen. The corrosion rate for these systems is generally quite high until the limit of solubility of the solid metal in the liquid metal is reached, at which time the corrosion ceases. The presence of any impurity in the system is likely to affect the solubility limit for the solid metal and thus change the composition at which the corrosion essentially stops. Any change in the solubility of the solid metal in the liquid metal due to the presence of oxygen is likely to be caused by the solubility of the solid metal oxide since little change in the solubility of the solid metal is expected to be caused by the presence of the liquid metal oxide (48). However, Weeks (62) has stated that more often than not, the solid metal oxide is insoluble in the liquid metal. Probably any important effect of corrosion due to a change in the solubility of solid metal would be in systems in which temperature gradient or concentration gradient mass transfer can occur, since these two mechanisms are strongly dependent on the solubility limit of the solid metal. The corrosion rates for these mechanisms may be altered considerably by a small change in the solubility limit.

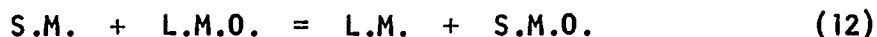
Oxide formation

Oxide formation may affect the liquid metal corrosion by forming complex oxides such as molybdates, by forming oxides having a low melting or sublimation temperature, or by forming low melting point eutectic mixtures between the liquid metal oxide and the solid metal

oxide. The formation of oxides is particularly important for the systems under consideration in this investigation due to the relatively low solubility of oxygen in the metals being considered and the fact that one of the oxides of molybdenum (MoO_3) has a particularly low melting temperature and a high vapor pressure.

Two of the liquid metals being considered in this investigation, lead and cadmium, form molybdates which are complex oxides with the form PbMoO_4 and CdMoO_4 . Although very little data are available for these molybdates, some increase in the solubility of molybdenum in liquid lead or cadmium would be expected if these complex oxides were formed.

The formation of a solid metal oxide, by exchange of oxygen from a liquid metal oxide in a liquid metal, may be expressed by



The formation of a solid metal oxide would be expected to increase the rate of corrosion since oxide surface layers do not normally adhere strongly to the metal surface on which they form. Therefore, they would be expected to erode more easily than a metal surface. If the solid metal oxide formed happens to have a low melting point, it is likely to melt at the test temperatures and thus cause increased corrosion.

Molybdenum is particularly susceptible to increased corrosion due to the formation of a low melting oxide. The melting temperature of MoO_3 is listed as 795°C ; however, its vapor pressure is very high at this temperature and it is believed to sublime below the melting temperature. The formation of molybdenum trioxide is believed to be a two-step process which includes the oxidation of the dioxide.



The formation of low melting point eutectic mixtures between the liquid metal oxide and the solid metal oxide might also be expected to contribute to increased corrosion. The two oxides, like many binary metal systems, may combine in proper proportions to form a lower melting polyoxide which could be molten at the test temperature, thus creating a non-adhering surface layer. A MoO_3 - MoO_2 eutectic with a melting point of 778°C has been reported by Rathenau and Meijering (57). Additions of chromium, nickel, and iron oxides to these molybdenum oxides have been reported to lower the melting temperature to 705°C . Mixtures of MoO_3 with some metal oxides and molybdates have been reported to have melting temperatures in the neighborhood of 500°C . It is obvious that extensive formation of MoO_3 could have a very detrimental effect on the liquid metal corrosion resistance of molybdenum.

The understanding of polyoxides is complicated by the fact that their exact form or even the form of simple liquid metal oxides in the liquid metals is not definitely known. It is generally believed that they probably dissociate in the liquid metal which then frees the oxygen to interact with the solid metal again. This cycling effect has been used to explain gross effects of oxygen on the liquid metal corrosion detected in some systems (10,48).

Summary

It is apparent that there is much to learn in the area of the effects of interstitial impurities on liquid metal corrosion. The previous paragraphs have discussed several mechanisms which may be used to explain the experimental results. Much more data are required before a complete understanding of this type of corrosion can be attained and a knowledge of which systems are affected significantly by interstitial impurities. The experimental work conducted in this investigation was designed to contribute to this much needed information.

SCOPE OF THIS INVESTIGATION

Although a better understanding of the effect of interstitial impurities on the liquid metal corrosion of the refractory metals is the goal of this research, the scope of the experimental work is limited to one refractory metal and one impurity element. The four low melting metals; lead, cadmium, tin, and zinc; with varying oxygen contents were statically tested in molybdenum corrosion capsules. The initial oxygen content of the liquid metals was the important variable being considered and most other variables, such as duration and temperature of the tests, were generally held constant for each system.

Each of the four systems is deserving of a separate investigation; however, it was believed that more benefit would be derived by studying several systems. The systems studied were chosen so that some of the liquid metals were less active and some more active toward oxygen than the refractory metal. Since the effect of oxygen was to be determined, systems were also chosen in which the other mechanisms of corrosion were expected to be a minimum.

REVIEW OF THE LITERATURE

Several investigators have published corrosion data on the systems considered in this report and on related systems; however, it is difficult to correlate the data of the various investigators due to the many variables which may be considered.

Several methods of corrosion testing are in common use and each has its advantages and disadvantages. The three-component system consisting of small test specimens exposed to a liquid metal contained in an "inert" container has an advantage from an economic standpoint. Problems associated with this method include finding a truly "inert" container and the fact that mass transfer, such as that described by Covington and Woolf (18) for systems in bismuth, lead, and tin, may occur and complicate the analysis. It is sometimes possible to use the same material for both specimen and container which will eliminate the third component and, therefore, the concentration gradient mass transfer problem.

As will be described in more detail later, the method chosen for this investigation uses the container as the specimen. This method has an advantage in that it more nearly resembles the ultimate use of the material, which would be as a container for the liquid metal. The dynamic test is also used to simulate more closely the conditions of a flowing liquid metal. The final test in many cases is the actual construction of a circulating liquid metal loop with a temperature gradient in the loop to simulate conditions in a nuclear reactor.

Considering only the static test with a two-component system still leaves many variables to be determined by the individual investigator. The

period of the test, the test temperature, the geometry of the specimens (e.g. surface to volume ratio of the components), and the purity of the materials may all vary with the investigator. The method of determination of impurities also varies with the investigator as do the impurity elements which are analyzed. Until recently the interstitial impurity content of the component materials was not determined and thus the effect was not considered. It is now believed that the presence of oxygen or nitrogen in some tests were responsible for the significant variation in results obtained. Accurate determination of the oxygen content of some of the liquid metals is quite difficult. Neutron activation analysis has become valuable for some low melting metals; however, interference patterns cause difficulty for others. Several new methods for oxygen determination have been devised; however, the accuracy of some of these methods is still questionable.

Published Results

Since many of the results published do not give interstitial impurity contents, it was necessary to conduct experimental work to obtain the desired data. The available data on the corrosion of the refractory metal, molybdenum, by various liquid metals will be compared with the data of this investigation.

Lead

Several investigators have published results of corrosion tests with molybdenum and liquid lead. Both static and dynamic corrosion data have been reported. Climax Molybdenum Company (49) reports that molybdenum has good resistance to attack by liquid lead up to 2190°F (1200°C).

investigators at Martin Company (55) report that molybdenum specimens exposed to liquid lead for 500 hours at 1500°F (816.6°C) are left in good condition. A specimen weight loss of 0.0216 gram was measured for the molybdenum coupons. These tests were made using lead purified with a new PbO reducer unit to show the effect of low oxygen on the corrosion of molybdenum by lead.

Studies at Stanford University have been reported by Parkman and Shepard (54). Static corrosion tests with molybdenum exposed to lead at 1800°F (982°C) for 250 hours indicate no apparent attack; however, there was wetting of the molybdenum wall. Stress-rupture tests of molybdenum specimens in a lead bath indicate a satisfactory degree of resistance of molybdenum to liquid lead at 1500°F (815.5°C). A slight darkening of the molybdenum microstructure was noted near the edge after exposure for 2463 hours; however, this was not considered serious. The stress-rupture tests in lead compared favorably with similar tests conducted in a helium atmosphere.

Stress-rupture tests conducted by Grassi et al. (27) at the University of California showed no visible attack of molybdenum by lead after 500 hours at 1400°F (760°C) to 2000°F (1093°C). The stress-rupture tests exposed to lead gave results comparable to similar tests conducted in a helium atmosphere.

Static tests on molybdenum specimens contained in Vycor capsules and exposed to a 1000°C lead bath contained in a Type 302 stainless steel bomb were reported by Wilkinson et al. (64). The molybdenum specimens were exposed for ten days before removal from the lead bath and cleaning with HCl. Results indicated a relatively high dissolution rate of 8.6

mils per month and the presence of a scale on the molybdenum surface. It was believed that some sort of oxidation reaction had occurred with the oxygen from the Vycor capsule.

Static corrosion tests conducted at Oak Ridge National Laboratory were reported by Brasunas (4). Molybdenum coupons were exposed to high purity (99.994%) lead contained in iron capsules. Results after exposure for 40 hours at 1000°C indicated a thin film formation and the presence of iron in the molybdenum. The iron apparently deposited on the surface by mass transfer and then diffused into the molybdenum. Neither iron nor molybdenum was detected in the lead bath analysis. Results of two-component tests were reported after exposure of molybdenum to liquid lead for 100 hours at 1000°C. A thin surface film was noted on the molybdenum and ten parts per million molybdenum were detected in the lead bath.

Dynamic corrosion tests at Oak Ridge National Laboratory by Cathcart et al. (1) indicated excellent corrosion resistance of molybdenum to liquid lead. Molybdenum specimens exposed to circulating lead in a quartz thermal convection loop showed no mass transfer, slight corrosion, and little if any intergranular penetration after 473 hours with a hot zone temperature of 800°C and a cold zone temperature of 450°C. Later tests (9) also indicated that molybdenum has a high degree of resistance to mass transfer by 800°C lead. These conclusions were drawn after a 500-hour exposure to lead flowing at one foot-per-minute in a quartz loop.

Cadmium

Very little data are available on the corrosion of molybdenum by liquid cadmium. This is probably due to the fact that cadmium is not

particularly corrosive and, therefore, can be contained satisfactorily in less expensive and more easily fabricated materials.

The solubility of molybdenum in liquid cadmium is reported by Martin and Wach (12) to be only 0.0012 weight percent. Therefore, very little dissolutive attack of molybdenum by liquid cadmium would be expected.

In a compilation report for the Climax Molybdenum Company, Nair and Briggs (49) have indicated that if aluminum is present in the system, isothermal mass transfer of aluminum onto molybdenum occurs in cadmium at 930°F (499°C).

Tin

In a compilation report, Nair and Briggs (49) indicated the corrosion resistance of molybdenum to liquid tin to be satisfactory at 660°F (349°C), fair at 1165°F (630°C), and poor above 1525°F (830°C). Results listed indicated pronounced solution and severe corrosion in static tests after 338 hours at 1830°F (1110°C) and severe corrosion after two-hour static tests at 2730°F (1500°C).

Static corrosion tests at Argonne National Laboratory (11) indicated a ten-fifteen micron penetration of molybdenum by liquid tin after 26 hours at 1000°C.

Lance and Kemeny (40), at Westinghouse Research Laboratories, published results of static corrosion tests conducted with $\frac{1}{2}$ in. O.D. by 0.040 in. wall by 1 in. long molybdenum crucibles filled with 30-mesh reagent-quality tin. Tests were carried out in a Vycor vacuum cell at 10^{-5} torr. Slight local corrosion (0.00002 mil per hour) with some mass transfer was observed on molybdenum after exposure to liquid tin for 96

hours at 630°C. Water-line attack, severe corrosion (0.000135 mil per hour), and mass transfer resulted from exposure for 74 hours at 830°C.

Static corrosion tests performed by Coultres (17) were among the few in which the oxygen content of the system was reported. These tests were conducted with 2 in. by 0.025 in. by 0.060 in. molybdenum specimens exposed to 99.9 percent liquid tin. Vacuum-tight Vycor capsules were used to contain the tin for the 1800°F (982°C) tests. The oxygen content of the tin was less than 0.001 percent. Results of the 1800°F (982°C) tests indicated pronounced solution of molybdenum in tin after 338 hours. Analysis of the tin showed the presence of 0.0620 grams (1.69 percent) of molybdenum. Higher temperature tests were conducted in alumina capsules, which were not vacuum tight, and the oxygen content of the tin was subject to question. Results after exposure for one hour at 3150°F (1731°C) indicated marked solubility of molybdenum in tin (0.01 gram or 0.7 percent) and the presence of dendritic precipitate of molybdenum in the tin. Similar results (0.11 gram or 0.10 percent) were also noted after 2.5 hours at 3000°F (1649°C).

Zinc

The compilation report (49) also included the results of several investigators on the corrosion of molybdenum by zinc. The corrosion resistance was listed as fairly good at 825°F (440°C) since a weight loss of only 3.2 percent was noted after 50 hours exposure. Fair resistance was indicated at 930°F (500°C) after a weight loss of 12.7 grams per square meter per day was noted for a 138.5 hour test. A 12 percent weight loss was reported after exposure for 50 hours at 1290°F (700°C).

Corrosion studies by DeKany et al. (20) were conducted at Argonne National Laboratory. Molybdenum coupons ($\frac{1}{2}$ by 1 by $\frac{1}{8}$ in.) were exposed to liquid zinc contained in tantalum capsules. After exposure for 100 hours at 750°C , metallographic analysis indicated mild corrosion through dissolution which was confirmed by the presence of molybdenum in zinc to the extent of its solubility (0.02 weight percent). Dynamic tests by Nelson et al. (13) were conducted with a rocker furnace. Molybdenum capsules prepared by powder metallurgy were exposed to zinc at 850°C . Gross intergranular corrosion had occurred after 100 hours with complete disintegration of the sample after 300 hours.

Summary of the Literature

The many variables which are determined by the individual investigator are very well illustrated by the literature just reviewed. Test temperatures ranged from 825°F (440°C) to 3150°F (1731°C) with exposure times varying from one hour to 500 hours. Both dynamic and static tests were run on two- and three-component systems.

Since the oxygen content was determined for only a few of the tests, it was necessary to run a complete set of corrosion tests to obtain the desired data. The results of the various investigators have been included for a rough comparison with the data of this investigation when possible.

EXPERIMENTAL PROCEDURE

The major problem confronted in performing the corrosion tests was the attainment of materials with the desired impurity content. An attempt was made to test the four low melting metals with oxygen contents of 0, 100, 1000, and 10,000 parts per million oxygen. Of course it was impossible to eliminate the oxygen completely; however, the low oxygen samples generally contained less than ten parts per million oxygen. The solubility of oxygen in the metals created another problem in attaining the desired oxygen levels. Generally tests were made at or near the limit of oxygen solubility in the metals. The high oxygen levels were attained only by the addition of specific amounts of oxides of the respective metals.

Materials

High purity materials were used in all of the corrosion tests in order to minimize the effect which any impurity material might have on the corrosion. Care was taken to remove all surface films from the metals before encapsulation to ensure high purity samples.

Molybdenum

The molybdenum used in this investigation was 99.95 percent pure molybdenum obtained from the Fansteel Metallurgical Corporation. The capsules were constructed from 3/4 in. O.D. by 0.050 in. wall extruded tubing and 0.050 in. sheet for end caps. The following mechanical properties of this lot were tested under Fansteel Quality Control Program and are given in Table 3. Since hardness data were not given by the

supplier, tests were run at the Ames Laboratory using a Tukon type hardness tester.

Table 3. Mechanical properties of molybdenum

Temper	Fully stress relieved
Ultimate tensile strength (transverse)	128,000 psi
Elongation, 2" gage lengths (transverse)	11%
Hardness, DPH (1000 kg)	205 ^a

^aAmes Laboratory data (DLS-088).

A typical chemical analysis (percent by weight) was also given by the supplier. Analysis of the interstitial impurities was made at the Ames Laboratory and the results are compared with the values of the supplier in Table 4.

Lead

The lead used for this investigation was obtained from two sources. The low (<10 ppm) oxygen tests were made using high purity (99.999%) lead obtained from the Cominco Company in one inch square billet form. Cylindrical slugs were turned on a lathe to fit inside the molybdenum capsules and to remove any impurity surface films and thus ensure high purity samples.

The higher oxygen levels were attained using reagent grade, granulated (20 mesh) lead obtained from the Baker Chemical Company. Samples containing 26 parts per million oxygen were obtained by oxidizing the

granulated lead with pure oxygen for two hours at a temperature of 300°C. The granulated lead was then melted by heating at a temperature of 600°C for fifteen minutes in a graphite crucible and then air cooling to room temperature. This oxygen level compares favorably with the solubility of oxygen in lead given by Hansen (31). Higher oxygen concentrations were not attainable by this method.

Table 4. Chemical analysis of molybdenum

Element	Suppliers Analysis ppm	Ames Laboratory ^a Analysis ppm
Oxygen	50	53±5 ^a
Carbon	30	
Nitrogen	10	<4 ^a
Hydrogen	5	<2 ^a
Silicon	50	
Calcium	10	
Chromium	10	
Iron	10	
Magnesium	10	
Nickel	10	
Tungsten	100	
Silver	10	
Copper	10	

^aVacuum fusion analysis.

The very high oxygen (1,000 and 10,000 ppm) concentrations were obtained by combining specified amounts of analytical reagent grade Pb_3O_4 , obtained from the Mallinkrodt Chemical Works, with the granulated lead. The metal in these samples was placed in the capsules in granulated form.

The amount of lead placed in each sample was 55 grams which filled the capsule approximately half full of liquid metal. The various lead samples were analyzed for common impurity elements. The analysis is given in Table 5 for both the ingot and granulated lead.

Table 5. Chemical analysis of lead

Element	Ingot Lead ppm	Granulated Lead ppm
Sn		
Sb	<10	<10
Fe	6	4
Ni	2	2

Cadmium

The cadmium used for the tests was high purity (99.9%) 3/8 inch diameter sticks obtained from the Baker Chemical Company. The cadmium samples were analyzed for the common impurity elements found in cadmium. The Ames Laboratory analysis is compared in Table 6 with the analysis provided by the supplier.

The cadmium sticks, which were turned on a lathe to remove any impurity film, were used for the very low oxygen content samples. Oxygen additions were made by adding specified amounts of reagent grade cadmium oxide (CdO), obtained from the Fisher Scientific Company, to the pure cadmium. The samples were premelted for fifteen minutes at a temperature of 1000°C and water quenched to room temperature before being analyzed for oxygen. Although no recent data were found on the solubility of oxygen in cadmium, only 64 parts per million oxygen were found in the cadmium after the addition of oxide equivalent to 1000 parts per million oxygen. It is assumed, therefore, that the solubility of oxygen in cadmium is of this order.

Table 6. Chemical analysis of cadmium

Element	Suppliers Analysis ppm	Ames Laboratory Analysis ppm
Cu	<10	10
Fe	<10	1
Pb	<100	27
Zn	<500	21

As in the case of lead, the higher oxygen levels were attained by adding specified amounts of oxide directly to the capsule. Each sample contained 38 grams of cadmium.

Tin

The tin used for the corrosion tests was also obtained from two sources. The low oxygen (<10 ppm) tests were made using high purity (99.999%) tin obtained from the Cominco Company in bar form. Cylindrical samples were turned on a lathe to remove any surface film on the ingot.

The higher oxygen levels were attained using reagent grade granulated (20 mesh) tin obtained from the Baker Chemical Company. The oxygen level was changed by oxidizing the granulated tin with pure oxygen at a temperature of 200°C for varying periods of time. The granulated tin was then melted by heating at a temperature of 500°C for fifteen minutes in graphite crucibles and then air cooling to room temperature.

Each tin sample contained 32 grams of tin in the form of a cylindrical slug similar to that shown in Figure 2. The analysis made at the Ames Laboratory for the common impurities in tin is given in Table 7 for both the ingot and the granulated tin.

Table 7. Ames Laboratory analysis for tin

Element	Ingot Tin ppm	Granulated Tin ppm
Pb	35	45
Fe	28	33

Zinc

The zinc used for the low (<10 ppm) oxygen samples was also supplied by the Cominco Company. The one-half inch diameter rod ingots had a

listed purity of 99.999 percent. The rod was turned on a lathe to remove any surface impurity before placing it in the molybdenum capsule.

The higher oxygen samples were made from reagent grade granulated (20 mesh) zinc supplied by the Baker Chemical Company. The oxygen content was varied by oxidizing the granulated zinc with pure oxygen at a temperature of 400°C. The granulated zinc was then melted into 5/8 inch diameter ingots by heating in graphite crucibles at a temperature of 700°C for fifteen minutes under an argon atmosphere, and then air cooling to room temperature. The maximum oxygen content attained by this oxygenation process was 211 parts per million.

The very high oxygen content samples were obtained by combining specific amounts of reagent grade zinc oxide (ZnO), obtained from Matheson, Coleman & Bell, with the granulated zinc. In these samples the zinc was placed in the molybdenum capsules in granulated form.

Each corrosion sample contained 32 grams of zinc which filled the molybdenum capsule half full of liquid zinc. Both the ingot and the granulated metal were analyzed for the common impurities found in zinc. The results are given in Table 8.

Table 8. Ames Laboratory analysis of zinc.

Element	Ingot Zinc ppm	Granulated Zinc ppm
Pb	9	30
Fe	16	29

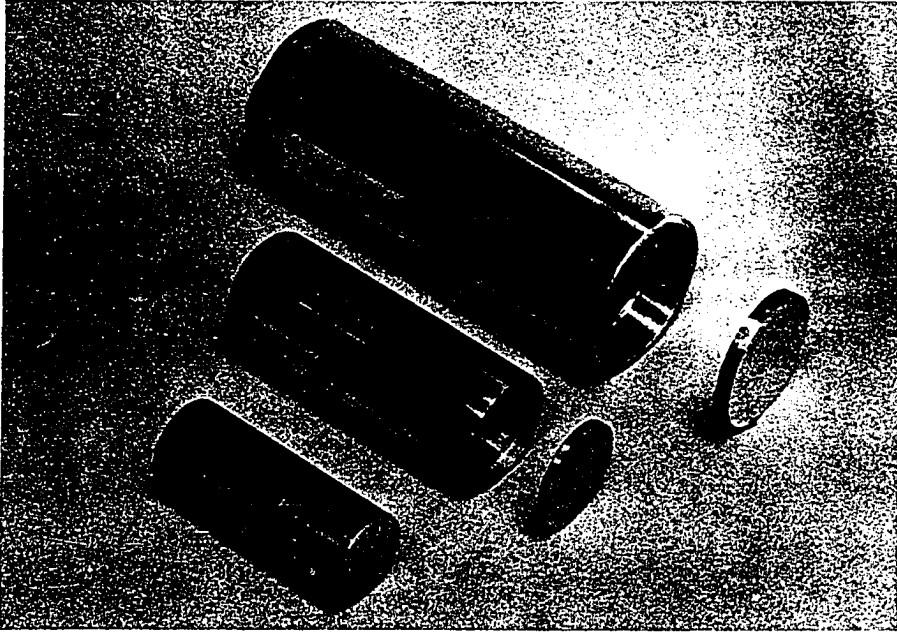


Figure 2. Lead slug with molybdenum capsule and Inconel shield

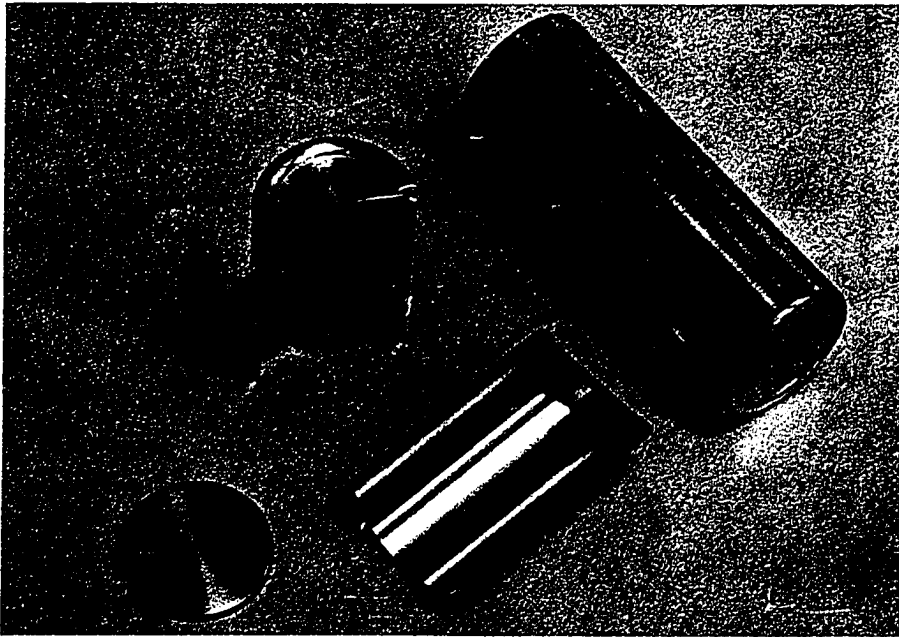


Figure 3. Molybdenum capsule showing weld, cap, and inside surface

Corrosion Test

As discussed previously in this report, the static corrosion test was decided upon for this investigation. The molybdenum capsules, half filled with molten metal, were placed in a constant temperature furnace for a designated period of time before air cooling the samples to room temperature.

Most of the corrosion samples were prepared using cylindrical slugs similar to the lead slug shown in Figure 2. The cylinders were turned on a lathe from ingots obtained from the suppliers or from ingots melted from the granulated metal. In each case the slug was turned on a lathe just prior to welding in the capsules in order to remove any surface films and to ensure high-purity samples. The cylinders were approximately one-half inch in diameter and contained enough metal to fill the capsules half full when in the molten state. Since the high oxygen levels (1,000 and 10,000 ppm oxygen) were not attainable in homogeneous ingot form, the usual procedure was to mix granulated metal with a specified amount of the respective metal oxide and put this mixture directly into the capsule. At all oxygen levels the weight of the metal was held constant for each metal. In a few cases for comparison, the same oxygen level was tested in both the slug and granular form.

The corrosion capsules were prepared from $3/4$ inch extruded molybdenum tubing with a 0.050 inch wall. The tubing was cut into two-inch long capsules. Since the inside of the tubing was quite rough due to the extrusion process, the inside surface was turned on a lathe to give a smooth clean surface and a wall thickness of 0.035 inch. Each end of the

two-inch capsule was turned out further to give a wall thickness of 0.025 in. for a depth of 0.075 in. from each end. This created a ledge on which the end caps rested for welding. The end caps were cut from 0.050 inch molybdenum sheet and were turned on a lathe to form a cylindrical disk 0.690 in. in diameter and 0.050 in. thick. The end cap was fuse welded into the end of the tube with an electron beam welder. Figure 3 is a photograph showing the tube, cap, weld, and cleaned inside surface of a molybdenum capsule.

All of the electron beam welding took place in a vacuum chamber under a vacuum of 10^{-4} torr. Thus, most of the atmospheric gases were removed from the capsule before the top was sealed. This welding procedure produced a sub-atmospheric pressure inside the molybdenum capsules even at the corrosion test temperature, and in most of the systems the metal vapor was the major constituent of the vapor phase in the capsule.

Since molybdenum oxidizes rapidly at the test temperatures, it was necessary to provide a shield to protect the molybdenum from the atmosphere. Due to the high oxidation resistance of Inconel at the temperatures under consideration, it was chosen as the shield material for the molybdenum. Compatibility tests at a temperature of 1000°C indicated no reaction between molybdenum and Inconel in contact for several hundred hours. The Inconel shields were constructed from $3/4$ inch schedule 40 Inconel-600 pipe, and $1/8$ inch thick cylindrical disks for end caps. The Inconel shields were constructed similar to the molybdenum capsules with the end caps electron beam welded. The electron beam weld produced a vacuum of approximately 10^{-4} torr between the molybdenum capsule and the

Inconel shield which was sufficient to protect the molybdenum from oxidation. Figure 4 is a photograph of a test specimen illustrating the relative size of the components and how they fit together.

After the molybdenum capsules were welded in the Inconel shields, the samples were placed in preheated electrical resistance muffle furnaces for the corrosion tests. Figure 5 is a photograph of the furnace bank used for the corrosion tests. The furnace temperatures were measured by chromel-alumel thermocouples placed inside the furnaces and each temperature was recorded on a six-point Bristol strip chart recorder. The furnace temperatures were controlled by individual powerstats which controlled the power input to each furnace. A constant voltage transformer was used to eliminate the normal voltage fluctuations and supply the electrical power to the variable powerstats. This method of furnace control was preferred over the standard on-off type of control since it eliminated the cyclic temperature fluctuation of ± 5 or 10 degrees. Any variations in temperature were probably within the accuracy of the measuring system and they were gradual over a period of hours and not like the frequent cycling of an on-off controller. In some systems it is believed that constant temperature cycling has a considerable effect on corrosion rates (43).

Corrosion Test Evaluation

Several methods of analysis were used to evaluate the type of corrosion and the corrosion products of each specimen. These include fast neutron activation analysis for oxygen in the low melting metals, vacuum fusion analysis for the oxygen content of the molybdenum, analytical

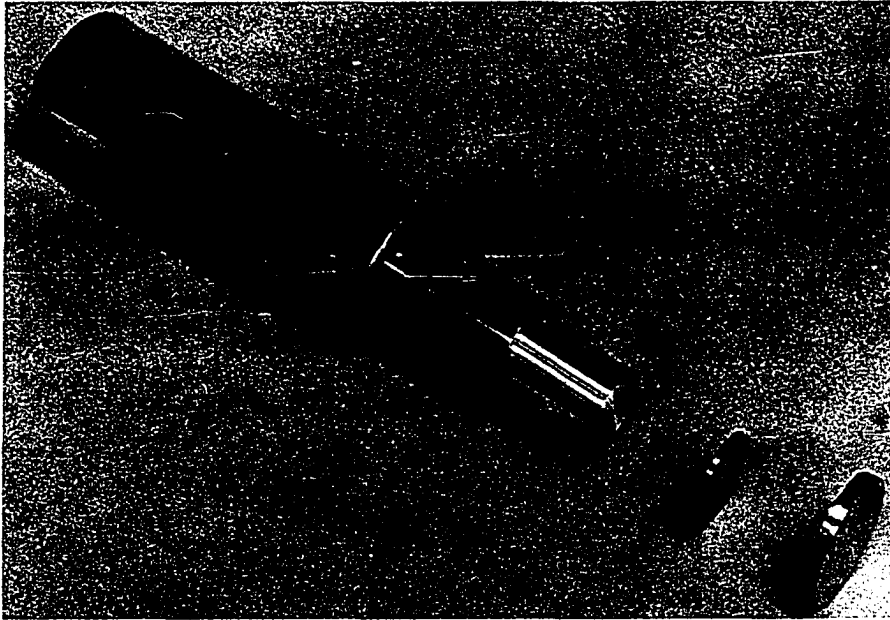


Figure 4. Expanded sample illustrating how tin slug, molybdenum capsule, and Inconel shield fit together

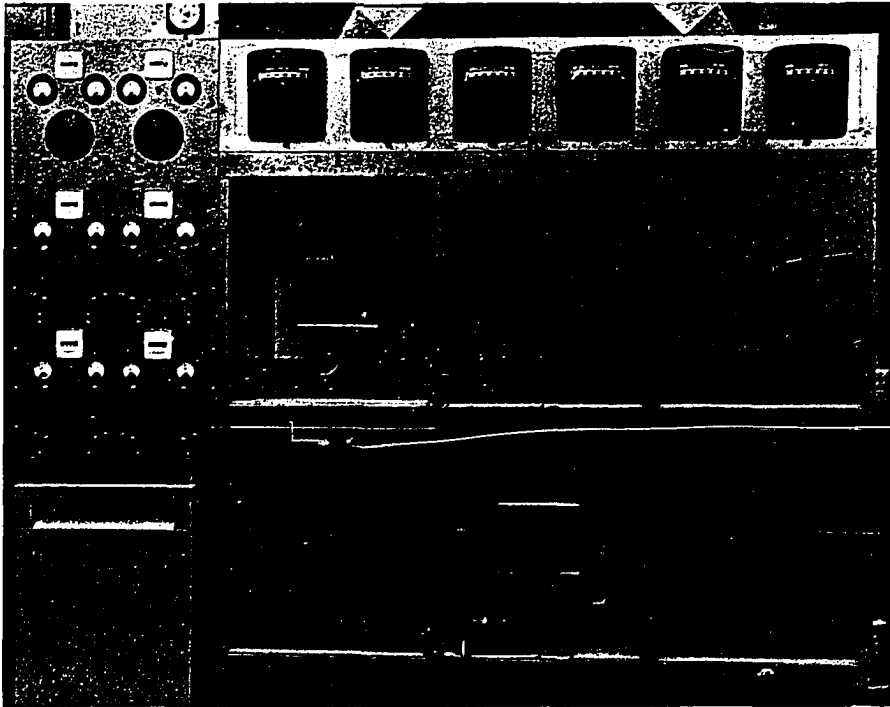


Figure 5. Furnace bank showing control panel and constant voltage transformer

analysis for molybdenum in the low melting metals, spectrographic analysis for any lead, cadmium, tin, or zinc in the molybdenum, and metallographic and visual analysis to determine the amount and type of corrosion. The combined results of all of these analyses were considered in drawing conclusions to the corrosion specimens.

Neutron activation analysis

The oxygen content of the liquid metals was determined both before and after the corrosion test by the fast neutron activation technique. The analysis was performed by the radiochemistry group using a 14 Mev neutron generator with a deuterium-tritium reaction. This method of analysis is further discussed and described by Clark and Stensland (16).

Vacuum fusion analysis

The oxygen content of the molybdenum was determined both before and after corrosion testing by the vacuum fusion technique. Samples were prepared and analyzed from both the liquid and vapor regions of the molybdenum capsules. Since both the inside and outside surface layers of the molybdenum capsules were removed mechanically, the results indicate the bulk oxygen content.

Spectrographic analysis

Specimens similar to those used for vacuum fusion analysis were also prepared for spectrographic analysis to determine the content of lead, cadmium, tin, or zinc in the molybdenum. This test was primarily concerned with the zinc tests where it was observed that the zinc diffused rapidly through the molybdenum wall and interacted with the Inconel shields.

Analytical analysis

Samples of the metal remaining in the capsules after the corrosion test were analyzed for molybdenum content. The sample was taken from the bulk metal at a distance from the molybdenum wall. The purpose of this test was to determine the amount of molybdenum in solution as a function of oxygen content.

X-ray analysis

In a few cases, x-ray analysis was used in an attempt to identify some of the phases. This analysis was limited mainly to residues in the zinc tests and boundary layer phases noted in some of the high oxygen samples.

Visual analysis

Simple visual inspection of the samples after sectioning and during preparation of the samples for analysis was particularly informative as a qualitative analysis. Such information noted visually was the presence of any residues, the presence of any condensate on the walls of the vapor region, and the appearance of the molybdenum wall. The difficulty encountered in removing the soft metal from the molybdenum wall gave a qualitative measure of the corrosion. In some cases the soft metal actually fell out of the capsule while in others it was extremely difficult to remove the soft metal from the molybdenum.

Metallographic analysis

Probably the most informative single analysis is metallography. Sections of the corrosion specimens were polished and etched for

microscopic examination. Portions of the low melting metals were etched to detect any precipitates of oxides, molybdates, or intermetallic compounds present in the liquid metals. The molybdenum wall adjacent to both the liquid and vapor region was etched to detect any changes in grain structure or any grain boundary penetration by the liquid metals. The formation of any boundary layer compounds or any solution attack of the molybdenum wall could also be detected.

RESULTS AND DISCUSSION

The results of the corrosion tests for each of the four liquid metals tested are discussed individually in the following paragraphs and are summarized in Tables 9 through 13. Photomicrographs of the molybdenum-liquid metal interface and the molybdenum grain structure are also included. The lead and cadmium generally showed very little attack of molybdenum while tin indicated moderate attack and zinc diffused rapidly through the molybdenum wall.

Corrosion by Lead

Very little attack of molybdenum by liquid lead was noted in any of the tests run. The lead tests were run at a temperature of 800°C for periods of 300 or 1000 hours. The results of the various corrosion tests with lead contained in molybdenum are summarized in Table 9.

The lowest oxygen content samples (6 ppm) were the only samples which indicated a significant amount of molybdenum in solution with the lead. Two samples agreed very well with a molybdenum content of about 70 parts per million in the lead after a 300 hour test at 800°C. The maximum molybdenum detected in any of the other tests was only 3.8 parts per million.

The post-test oxygen content of the lead was found to be very low for all cases. Even when 10,000 parts per million oxygen were placed in the capsule in the form of lead oxide, the oxygen content of the lead was found to be only 5 ± 3 parts per million. No significant change in the oxygen level of the molybdenum wall was detected and no lead was detected in the molybdenum for any of the samples tested.

Table 9. Results of 800°C lead-molybdenum corrosion tests

Sample No.	Duration of Test hours	Form of Lead	Oxygen in Lead Pretest ppm	Oxygen in Lead Post-test ppm	Molybdenum in Lead ppm	Remarks
127	300	slug	6	5 ± 3	74.2	Slight penetration (<1 mil) of molybdenum wall by lead indicated by darkening of the molybdenum structure near the surface. Some solution attack is also indicated by the change in the surface finish of molybdenum. Lead adhered strongly to capsule wall. No attack on vapor wall.
128	300	slug	6	2 ± 2	61.4	
165	300	slug	26	3 ± 2	0.4	No detectable interaction. Molybdenum surface of both liquid and vapor region was unchanged. Lead adhered strongly to the capsule wall.
166	300	slug	26	2 ± 2	2.3	
045	1000	granulated	30	6 ± 3	2.6	Darkening of molybdenum wall near surface appears to be penetration by lead (<1 mil).
172	300	granulated plus oxide	1000	3 ± 2	3.8	Brittle boundary layer (<1 mil) of lead molybdate formed on vapor wall. Similar layer also noted between molybdenum and liquid lead. Localized attack (10% of 35 mil wall) noted at several spots of vapor wall. Remainder of vapor wall and all of liquid wall showed little attack. Lead was easily removed from molybdenum wall.
173	300	granulated plus oxide	10,000	5 ± 3	2.5	Brittle boundary layer (1 mil) of lead molybdate noted on vapor wall. Similar boundary layer also covered liquid wall. Slight attack (<1 mil) of molybdenum wall. Localized attack (25% of 35 mil wall) noted in vapor region. Lead was easily removed from molybdenum wall.

No detectable attack was noted for the tests containing 26 parts per million oxygen. This oxygen level is the same order of magnitude as the solubility limit for oxygen in lead at the test temperature. The regular waviness of the molybdenum surface, which was due to the lathe finish and is illustrated in Figure 6, indicates no interaction between the lead and molybdenum. The vapor wall also showed the regular waviness and was still shiny indicating no interaction with the vapor. However, the lead adhered very strongly to the molybdenum wall and was difficult to remove for analysis.

A small amount of attack of molybdenum by the high purity (6 ppm oxygen) lead is apparent since a significant amount of molybdenum was detected in the lead. It was impossible to identify any molybdenum in the lead by metallography due to the presence of a considerable amount of sanding grit imbedded in the soft lead. The sanding grit shows up in the lead phase of Figure 6. Also, the molybdenum surface did not show the regular waviness which was present in the previous case. A slight penetration (<1 mil) of the molybdenum wall by the high purity lead was also indicated by a darkening effect on the molybdenum structure near the surface. This darkening effect is illustrated in Figure 7. Figure 8 illustrates the absence of the regular waviness of the molybdenum surface which indicates the occurrence of some solution attack of the molybdenum. Difficulty was also encountered in removing the lead from the capsule. No interaction was noted on the vapor wall.

One test with granulated lead containing 30 parts per million oxygen was carried out for 1000 hours. A slight darkening of the molybdenum

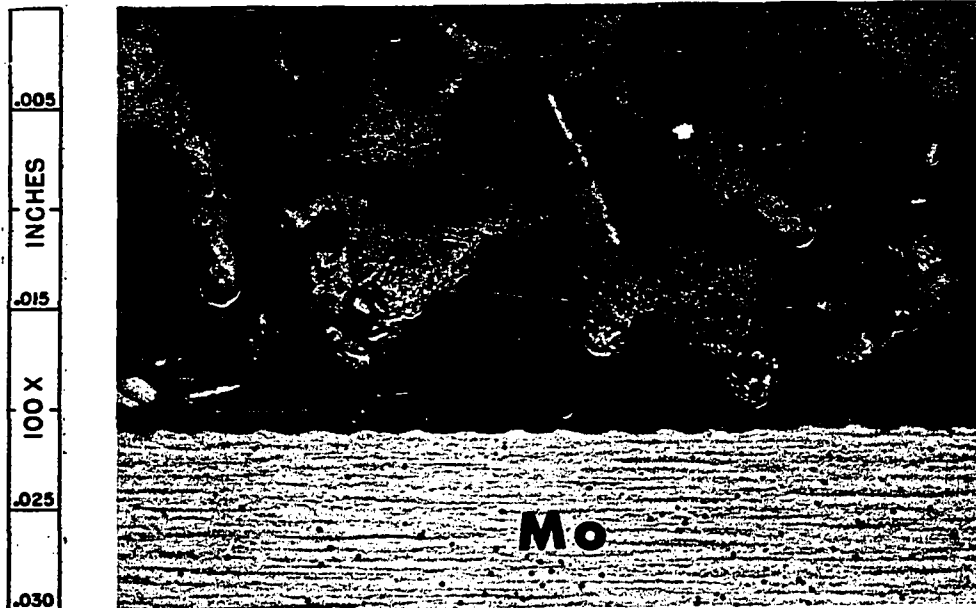


Figure 6. Lead-molybdenum interface after testing for 300 hours at 700°C using lead initially containing 26 parts per million oxygen. Sample Number 166 (100X)

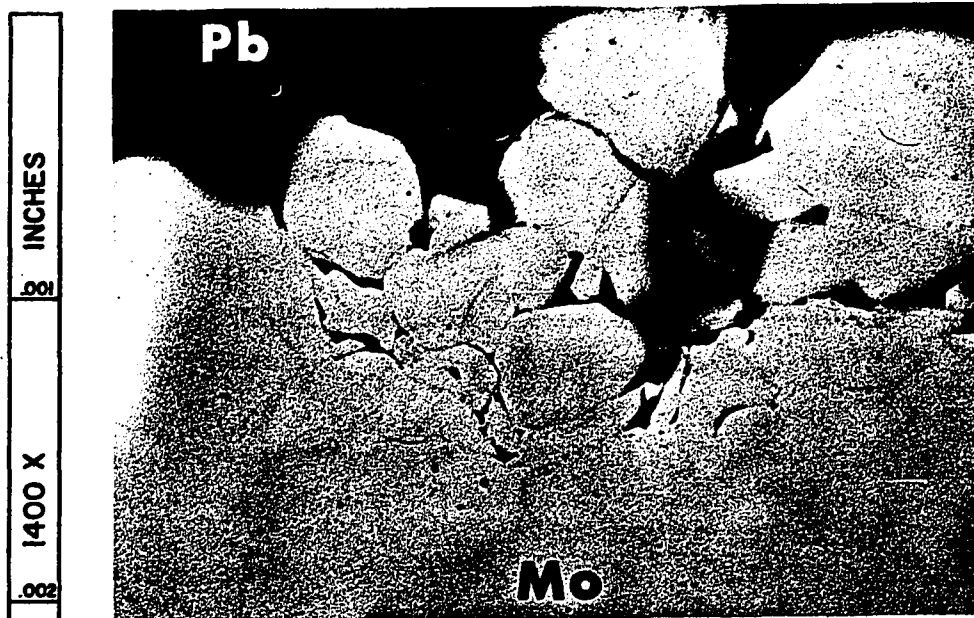


Figure 7. Lead-molybdenum interface after testing for 300 hours at 700°C using lead initially containing six parts per million oxygen. Sample Number 128 (1400X)

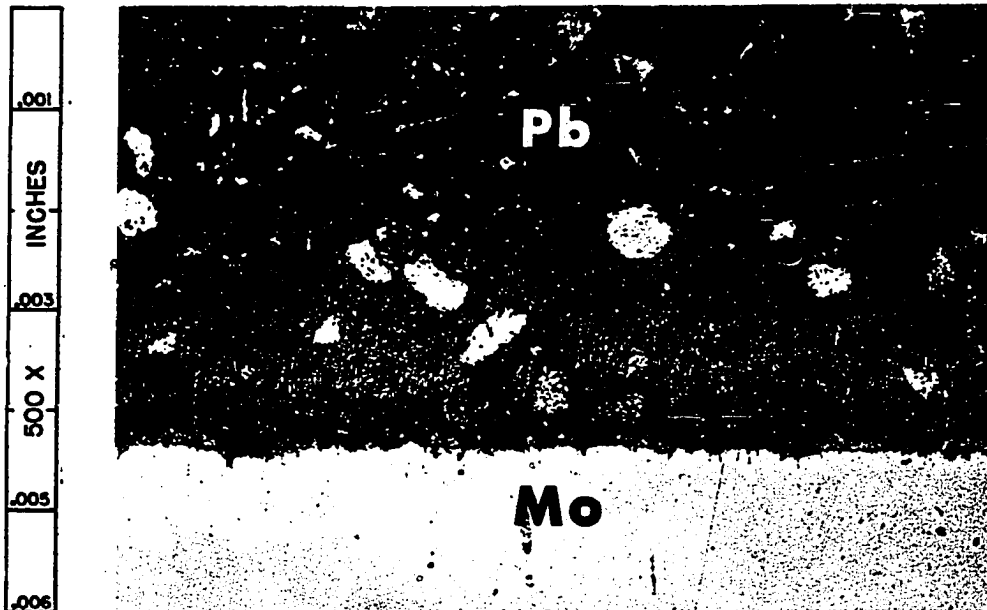


Figure 8. Lead-molybdenum interface after testing for 300 hours at 700°C using lead initially containing six parts per million oxygen. Sample Number 128 (500X)

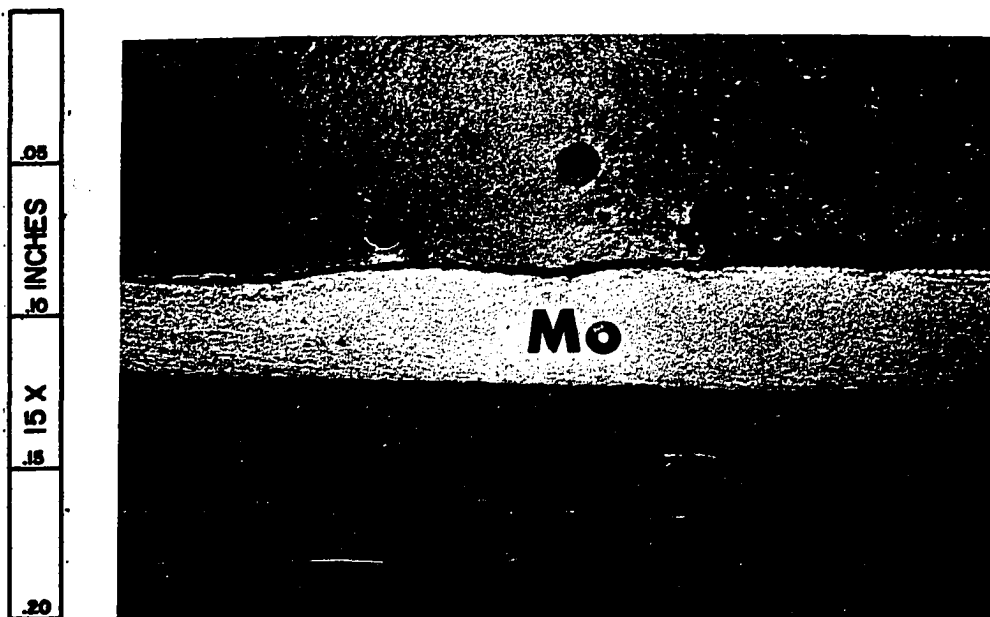


Figure 9. Molybdenum wall from vapor region after testing for 300 hours at 700°C with lead initially containing 10,000 parts per million oxygen in the form of lead oxide. Sample Number 173 (15X)

wall near the surface (<1 mil) appears to be penetration of the molybdenum by lead; however, very little molybdenum (6 ± 3 ppm) was detected in the lead.

The high oxygen tests (1,000 and 10,000 ppm oxygen) indicated the formation of a brittle boundary layer which covered both the liquid and vapor molybdenum wall. This layer was identified by x-ray diffraction as lead molybdate (PbMoO_4). Localized solution attack (10 and 25% of the 35 mil wall) was noted at several spots on the vapor wall. Figure 9 shows this attack on the vapor wall of the 10,000 parts per million oxygen sample. The lead was very easily removed from the molybdenum capsule due to the brittle boundary layer.

Results of these tests indicate minimum corrosion of molybdenum by liquid lead when the oxygen content of the lead is nearly that at the solubility limit. Both higher and lower oxygen levels were found to cause increased interaction between lead and molybdenum. The attack by high purity lead is simple solution of the molybdenum, while the attack by lead containing large amounts of oxygen is apparently due mainly to the oxide formation.

Corrosion by Cadmium

The results of the corrosion tests with cadmium, which were run for 300 hours at a temperature of 700°C , are summarized in Table 10. Very little attack of the molybdenum by liquid cadmium was noted in any of the tests; however, a very thin boundary layer formation and a precipitate in the cadmium phase were detected in the high oxygen samples.

Due to an interference pattern from the cadmium, it was impossible

Table 10. Results of 700°C cadmium-molybdenum corrosion tests

Sample No.	Duration of Test hours	Form of Cadmium	Oxygen in Cadmium Pretest ppm	Oxygen in Cadmium Post-test ppm	Molybdenum in Cadmium ppm	Remarks
048	300	slug	17	20 ± 2	2	No attack of molybdenum detected. No impurity precipitate detected in cadmium.
131	300	slug	17	18 ± 2	0.8	No attack of molybdenum detected. No impurity precipitate detected in cadmium.
132	300	slug	17	14 ± 3	0.7	No attack of molybdenum detected. No impurity precipitate detected in cadmium.
177	300	slug	64	31 ± 3	5	No attack of molybdenum detected. Very small particles of impurity distributed throughout cadmium noted metallographically. Small amount of oxide and molybdate noted at interface.
186	300	slug plus oxide	200	35 ± 3	0.9	No attack of molybdenum detected. Very small particles of impurity distributed throughout cadmium noted metallographically. Thin oxide boundary layer ($\frac{1}{2}$ mil) noted at interface.
170	300	slug plus oxide	1000	239 ± 10	4	Dark oxide boundary layer (1 mil) covered most of interface. Precipitate of cadmium molybdate noted in cadmium mostly near bottom of capsule and at interface.
171	300	slug plus oxide	1000	194 ± 10	8.6	Dark oxide boundary layer (1 mil) covered most of interface. Precipitate of cadmium molybdate noted in cadmium mostly near bottom of capsule and at interface.
174	300	slug plus oxide	10,000	2039 ± 61	36	Dark oxide boundary layer thicker than 170 and 171 covered interface. Large amount of cadmium molybdate precipitate detected metallographically in cadmium and at interface.

to detect oxygen contents below about seventeen parts per million by the fast neutron activation technique. The low oxygen samples were believed to contain considerably less oxygen than this; however, exact values cannot be given. Three corrosion tests made with low oxygen cadmium indicated no significant change in the oxygen level of the cadmium and no solution of the molybdenum by the liquid cadmium. No interaction was detectable by any of the methods of analysis used. Figure 10 is a photomicrograph of the cadmium-molybdenum interface after one of the tests. The wavy interface due to the lathe finish on the molybdenum remained unaffected. The vapor wall of the capsule was also unaffected as shown in Figure 11. Small droplets noted on the vapor wall were due to the condensation of the cadmium vapor during the relatively fast cooling process.

One corrosion test was run with a cadmium slug containing 64 parts per million oxygen. The cadmium was oxygenated in a molybdenum capsule at 1000°C and in the process picked up thirteen parts per million molybdenum. After corrosion testing in a molybdenum capsule for 300 hours at 700°C, the bulk cadmium contained only 31 parts per million oxygen and five parts per million molybdenum. Apparently some of the molybdenum and oxygen precipitated out on the bottom and walls of the capsule at the corrosion test temperature. Metallographic examination revealed the presence of small particles (<1 mil) scattered throughout the cadmium. These tiny particles contained sharp corners and etched dark, and are believed to be cadmium molybdate (CdMoO_4). The etched appearance was typical of an oxide. A small amount of this dark phase also appeared to be forming at the molybdenum-cadmium interface.

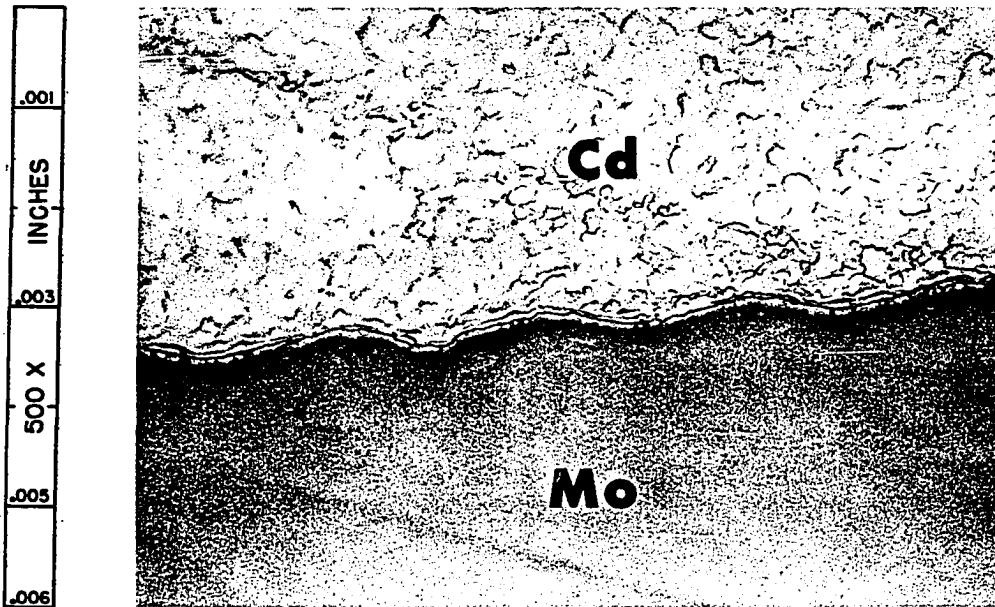


Figure 10. Cadmium-molybdenum interface after testing for 300 hours at 700°C with cadmium containing less than seventeen parts per million oxygen. Sample Number 132 (500X)

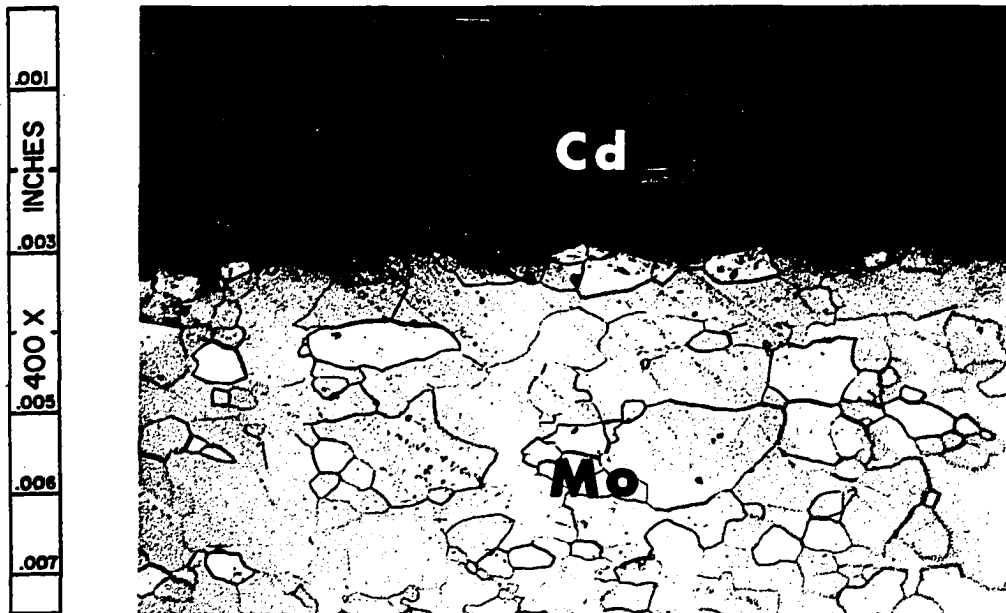


Figure 11. Molybdenum surface from vapor region of capsule after testing for 300 hours at 700°C with cadmium containing less than seventeen parts per million oxygen. Sample Number 131 (400X)

A cadmium sample, containing 200 parts per million oxygen in the form of cadmium oxide powder (CdO), gave results similar to the previous sample. The bulk cadmium contained 35 parts per million oxygen and very little molybdenum. The low impurity content detected may be explained by the fact that a large portion of the tiny particles noted metallographically were near the bottom and sides of the capsule, whereas the sample analyzed for impurity was taken from the central portion of the cadmium. Most of the wall was covered with a thin layer (generally less than one-half mil) of the dark colored phase. X-ray analysis of this boundary layer indicated the presence of cadmium oxide and cadmium molybdate (CdMoO_4). A light grey film and the presence of the cadmium droplets were the only effects noted on the vapor wall of the capsule.

A thicker boundary layer and larger precipitated particles in the cadmium were noted for the 1000 parts per million oxygen samples. Figure 12 shows a typical boundary area for this test. The sharp edged crystals, believed to be cadmium molybdate, appear to form at the boundary. The precipitate particles in the cadmium were much larger than in the previous samples. They appeared to be concentrated near the bottom of the capsule. Figure 13 is a high magnification photomicrograph showing the crystals which were noted near the bottom of the capsule. The peculiar geometries of these crystals make them relatively easy to identify. The molybdenum and oxygen contents, although significantly higher than in the previous samples (200 ppm oxygen and 6 ppm molybdenum), are still probably low since the samples analyzed were taken from the central portion of the cadmium which does not include



Figure 12. Cadmium-molybdenum interface after testing for 300 hours at 700°C with cadmium initially containing 1000 parts per million oxygen in the form of cadmium oxide. Sample Number 170 (500X)



Figure 13. Photomicrograph showing cadmium molybdate (CdMoO_4) precipitate in cadmium after testing in molybdenum for 300 hours at 700°C. Cadmium initially contained 1000 parts per million oxygen in the form of CdO . Sample Number 170 (500X)

the dense portion of the impurity. As in the preceding tests, the regular waves in the molybdenum surface were prominent, thus indicating very little attack.

The 10,000 parts per million oxygen sample was similar in appearance to those just discussed. The relatively higher impurity levels measured (2039 ppm oxygen and 36 ppm molybdenum) agree with the metallographic analysis which indicated more impurity precipitate and thicker boundary layers. Figures 14 and 15 show two magnifications of the impurity precipitate near the bottom of the capsule. A relatively large amount of precipitate was noted throughout this sample which accounts for the higher impurity contents detected. The boundary layer extended almost continuously around the interface and was generally about one mil thick.

The attack of molybdenum by liquid cadmium appeared to be very small for all of the cases tested. Although small amounts of molybdenum were detected in the cadmium for the high oxygen samples, no detectable change in wall thickness was measured for any of the samples and the regular waviness of the molybdenum surface was still detectable in all cases. The amount of corrosion of molybdenum by liquid cadmium appears to increase with the oxygen content of the cadmium; however, very large amounts of oxygen are necessary before significant interaction occurs. The relative ease with which the cadmium was removed from the molybdenum capsule is also indicative of the weak interaction between cadmium and molybdenum.



Figure 14. Photomicrograph showing cadmium molybdate in cadmium after testing for 300 hours at 700°C. Cadmium initially contained 10,000 parts per million oxygen in the form of CdO. Sample Number 174 (500X)

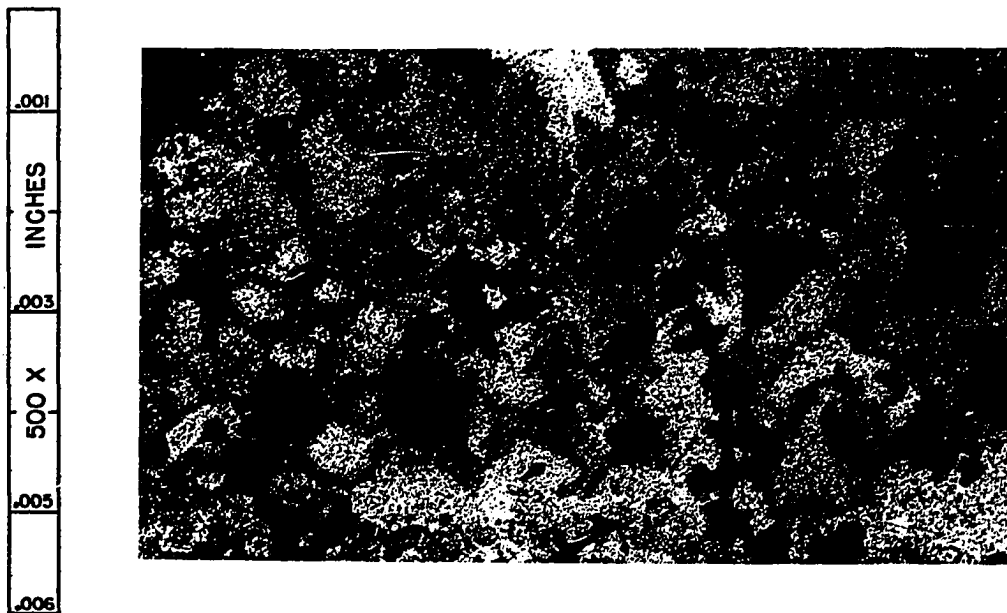


Figure 15. Photomicrograph showing cadmium molybdate precipitate in cadmium after testing for 300 hours at 700°C. Cadmium initially contained 10,000 parts per million oxygen in the form of CdO. Sample Number 174 (100X)

Corrosion by Tin

The corrosion tests with liquid tin in molybdenum capsules were run for periods of 300 to 1000 hours at a temperature of 800°C. The pretest oxygen content of the tin varied from eight to 302 parts per million by weight. The results of the tin-molybdenum corrosion tests are summarized in Table 11.

The low oxygen (8ppm) samples indicated a solution attack of the molybdenum wall after a 300 hour test. Although the wall thickness measurements are not highly accurate, a loss of one mil in the wall thickness of the molybdenum was measured. The solution attack was also confirmed by the presence of molybdenum dendrites detected in the tin. Although the dendrites were more dense near the bottom of the capsule, they did not appear to be attached to the wall, and, therefore, were not considered a boundary phase. The oxygen contents of the tin and molybdenum did not change significantly during the test. Figures 16 and 17 are photomicrographs of the tin-molybdenum interface. Figure 16 was taken near the bottom of the capsule and illustrates the grain growth which occurred near the weld zone. Figure 17 was taken at a point higher up the wall where the grain structure of the molybdenum was unaffected by the weld. The dark interface is due to the strong etchant required to obtain the molybdenum grain structure and does not represent a boundary layer formation. Uniform solution attack was also indicated by the smooth interface and the difficulty encountered in removal of the tin from the capsule confirms the absence of any boundary layer.

Table 11. Results of 800°C tin-molybdenum corrosion tests

Sample No.	Duration of Test hours	Form of Tin	Oxygen in Tin		Remarks
			Pretest ppm	Post-test ppm	
129	300	slug	8	7 ± 3	Uniform solution attack of one-half mil on molybdenum wall. Molybdenum dendrites noted in tin. No boundary layer was formed at interface. Tin adhered strongly to capsule wall.
130	300	slug	8	6 ± 3	
158	300	granulated	126	15 ± 3	Boundary layer ($\frac{1}{2}$ mil) of two phases covered most of molybdenum surface. Gray columnar crystals ($\text{MoSn}_{1.5}$) formed on molybdenum surface and small amount noted throughout tin. Yellowish second phase of boundary layer believed to have high oxygen content. Tin was easily removed from capsule.
159	300	granulated	126	8 ± 3	
035	500	granulated	126	10 ± 3	Boundary layer ($\frac{1}{2}$ mil) of two phases covered most of molybdenum surface. Gray columnar crystals ($\text{MoSn}_{1.5}$) formed on molybdenum surface and small amount noted throughout tin. Yellowish phase of boundary layer believed to have high oxygen content.
043	1000	granulated	126	11 ± 3	Boundary layer ($\frac{1}{2}$ -1 mil) of two phases covered molybdenum surface. Gray columnar crystals were longer than in previous tests and more were noted throughout tin than in 500 hour test. High oxygen content yellowish phase was also present.
044	1000	granulated	126	7 ± 3	
162	300	slug	302	7 ± 3	Boundary layer (1 mil) of two phases covered molybdenum surface. Larger amount of yellowish phase detected in these samples. Considerably more of gray crystals noted throughout tin than in previous tests. Tin was easily removed from capsule.
163	300	slug	302	8 ± 3	
178	300	granulated	90 ^a	6 ± 3	Boundary layer (1-2 mil) of two phases covered molybdenum surface. More of the yellowish phase was noted than in previous samples. Relatively high amount of gray $\text{MoSn}_{1.5}$ impurity scattered throughout tin. Tin was easily removed from capsule.
184	300	granulated	90 ^a	9 ± 3	

^aOxygen impurity believed by author to be considerably higher than value reported.

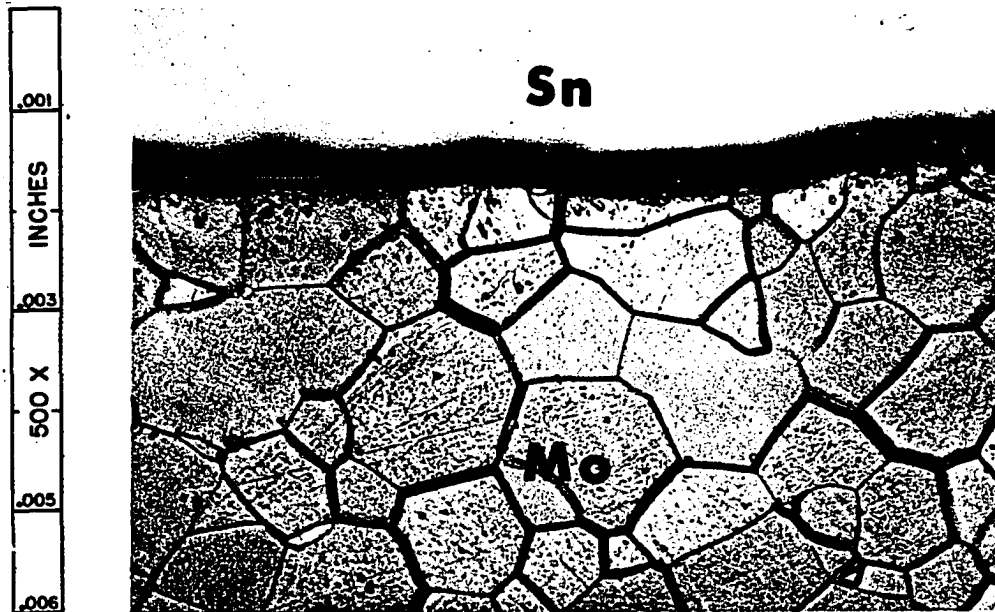


Figure 16. Tin-molybdenum interface near weld zone after testing for 300 hours at 800°C with tin initially containing eight parts per million oxygen. Sample Number 130 (500X)

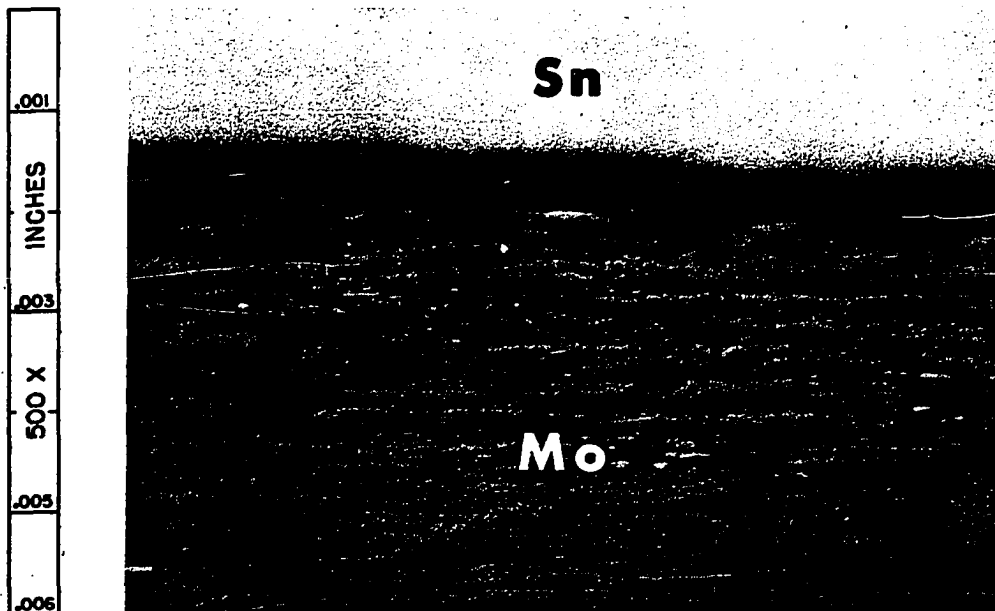


Figure 17. Tin-molybdenum interface in central portion of capsule after testing for 300 hours at 800°C with tin initially containing eight parts per million oxygen. Sample Number 130 (500X)

Two samples were tested for 300 hours with tin initially in slug form and an oxygen content of 302 parts per million by weight. A boundary layer about one mil thick covered the entire molybdenum surface which was exposed to the liquid tin. Two phases were detected in this boundary layer. Gray columnar type crystals appeared to form on the molybdenum surface and grow into the liquid tin. Figure 18 illustrates this phase of the boundary layer and the columnar type growth. Figure 19 is a photomicrograph of the same boundary layer formation obtained using a different etchant. The area surrounding the gray crystals was yellowish in color and distinctly different from the tin phase. The gray columnar phase was also scattered throughout the tin phase; however, no molybdenum dendrites were noted in the tin. Figures 20 and 21 are photomicrographs showing the presence of the gray phase in the tin. This phase is probably the compound $\text{MoSn}_{1.5}$ since it has the appearance of an intermetallic compound and the fact that it does not contain oxygen. The oxygen content of the post-test sample was found to be only eight parts per million which is the same level as the high purity samples and much less than the pretest value. Since a considerable amount of this gray phase was noted throughout the tin and little oxygen was detected, it apparently consists only of molybdenum and tin. Since the oxygen level of the tin was reduced considerably, the oxygen apparently is present in the yellowish phase noted along the boundary.

The remaining samples were prepared using granulated tin. Samples were tested for 300, 500, and 1000 hours using "as received" granulated

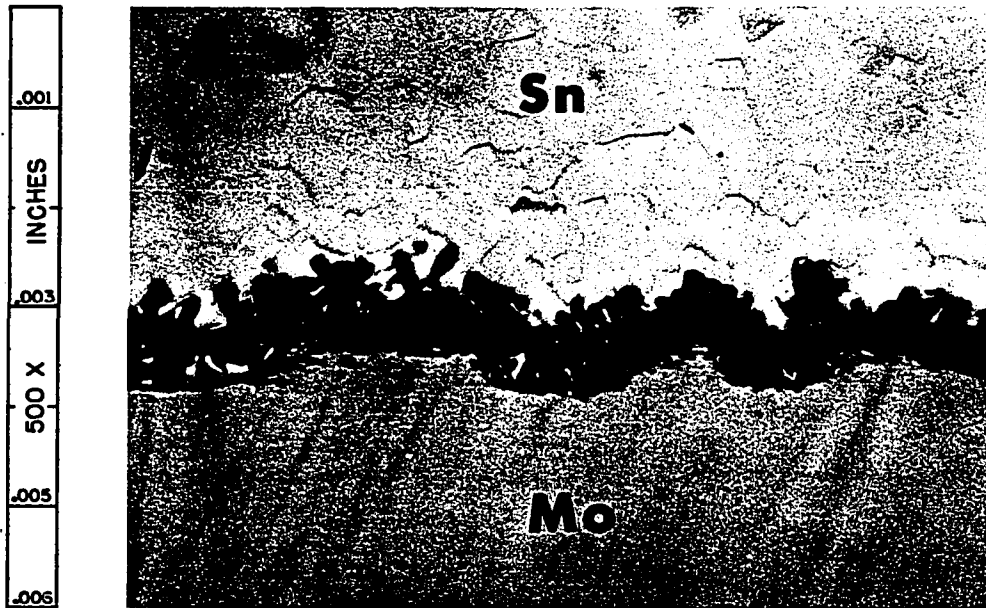


Figure 18. Boundary layer at tin-molybdenum interface after testing for 300 hours at 800°C with tin initially containing 302 parts per million oxygen. Sample Number 162 (500X)

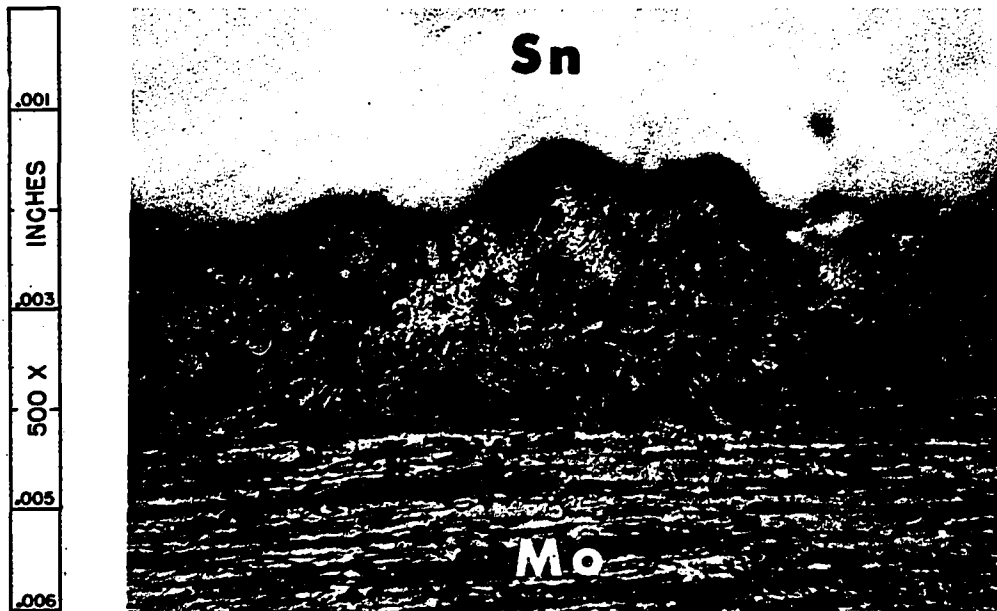


Figure 19. Boundary layer of Figure 18 with chemical etch. Sample Number 162 (500X)



Figure 20. Gray columnar impurity ($\text{MoSn}_{1.5}$) in tin matrix after testing for 300 hours at 800°C with tin initially containing 302 parts per million oxygen. Sample Number 162 (500X)



Figure 21. Gray columnar impurity ($\text{MoSn}_{1.5}$) in tin matrix after testing for 1000 hours at 800°C with tin initially containing 126 parts per million oxygen. Sample Number 044 (500X)

tin which initially contained 126 parts per million oxygen. The results of the 300 hour tests were similar to those of the higher oxygen (302 ppm) tests just discussed except that the boundary layer formed was generally less than one-half mil thick. Very little of the gray ($\text{MoSn}_{1.5}$) phase and no dendritic molybdenum was detected in the tin. The boundary phase was of more uniform thickness and contained considerably less of the yellowish phase than the previous samples. The results of the 500 and 1000 hour tests were much the same with the 1000 hour test showing a slightly thicker boundary layer. These samples also indicated a slightly higher amount of the ($\text{MoSn}_{1.5}$) distributed throughout the tin; however, the amount was considerably less than that for the higher oxygen (302 ppm) samples. Figure 22 is a photomicrograph of the 500 hour sample which illustrates very well the columnar growth of the boundary phase. These gray columnar crystals ($\text{MoSn}_{1.5}$) in the 500 and 1000 hour tests were in general longer than in the shorter tests which supports the conclusion of the growth process.

Two samples were also tested with granulated tin which had been oxygenated at 200°C for two hours. The granules were considerably discolored during the oxidizing process and were believed to contain a relatively high oxygen content; however, oxygen analysis of a slug melted in a graphite crucible indicated only 90 parts per million oxygen. It is believed that some of the oxygen in the form of tin oxide probably separated out during the melting process. Since the oxidized granules were used in the corrosion test sample, it is believed that the tin in these samples contained a higher amount of oxygen than

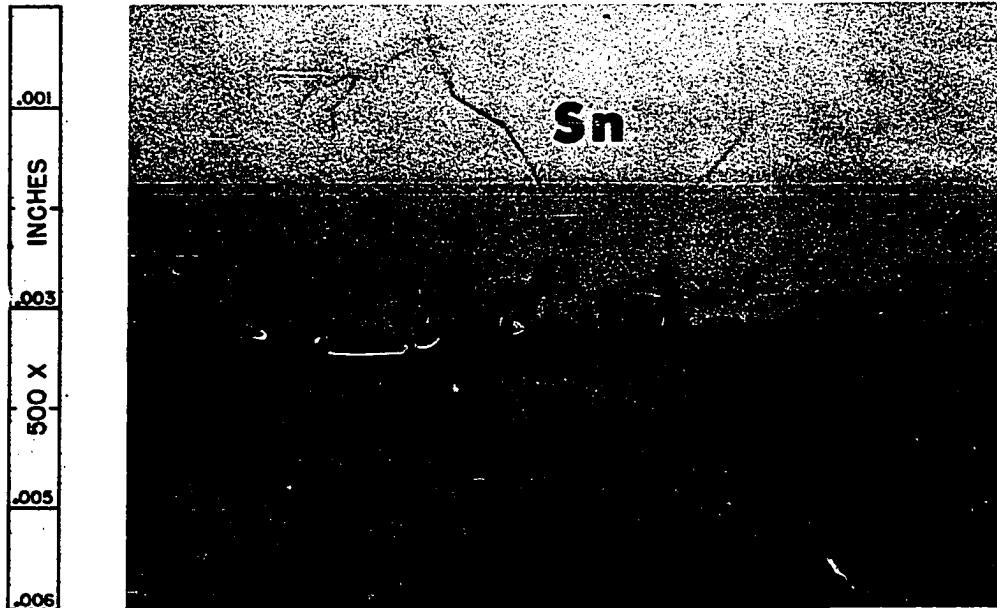


Figure 22. Gray columnar boundary phase after testing for 500 hours at 800°C with tin initially containing 126 parts per million oxygen. Sample Number 035 (500X)

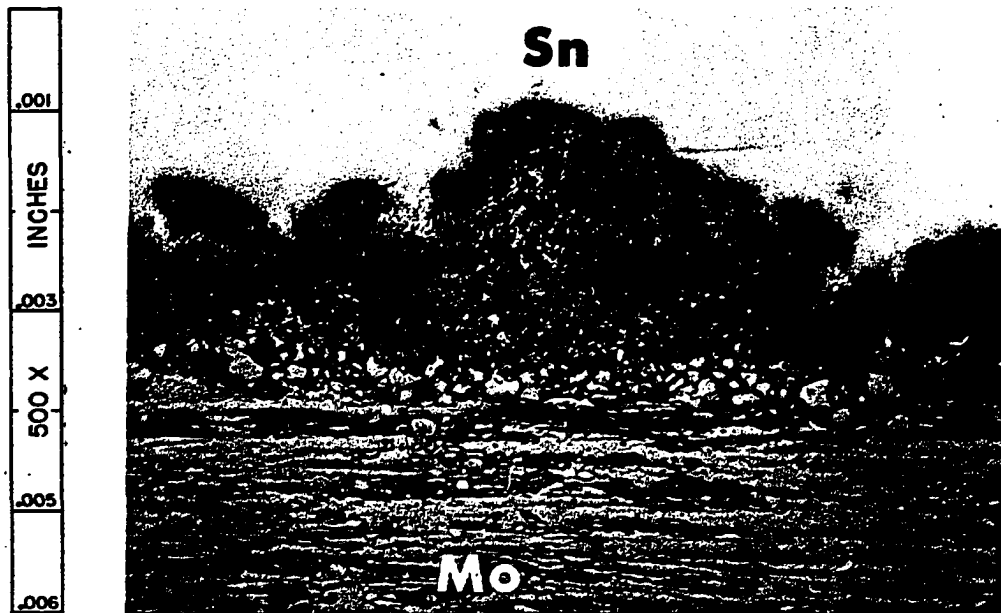


Figure 23. Boundary layer at tin-molybdenum interface after testing for 300 hours at 800°C. Sample Number 178 (500X)

detected in the oxygen samples. The results of the corrosion tests also confirm the higher oxygen level since a thicker boundary layer (up to 2 mil) was noted for these samples than for any of the other samples. Figure 23 is a photomicrograph of the boundary phase of one of these samples. A larger amount of the yellowish phase is also noted in the boundary layer along with a small amount of a new black phase. A small amount of this black phase is noted in Figure 23 near the molybdenum. This dark phase is believed to be tin oxide. This sample, as in all of the previous samples, indicated a very low oxygen content (6 ± 3 ppm) in the bulk tin after the corrosion test.

The high purity tin samples were the only ones in which dendrites of molybdenum were noted in the tin and no boundary layer was formed. The tin also adhered strongly to the molybdenum in this case. The oxygen content of the tin is apparently responsible for the boundary layer which formed on all of the other samples. Two phases were detected in the boundary layer and the thickness appeared to be a function of the oxygen content even though the gray phase did not contain any oxygen. Apparently the presence of oxygen was required to form the intermetallic compound ($\text{MoSn}_{1.5}$) since none was detected in the low oxygen tests. The amount of both phases appeared to increase with higher oxygen levels of the pretest tin and the columnar crystals appeared to grow longer for the 1000 hour test. The low oxygen content in the post-test tin for all the samples indicates that the oxygen must be present in the yellowish phase of the boundary layer. Easy removal of the tin from the capsule was noted when the boundary layer was

present. The molybdenum apparently remained unchanged since no significant change in the oxygen level and no tin was detected in the wall after the surface layers were removed.

Corrosion by Zinc

The results of the zinc tests were considerably different from those of the other liquid metals tested. The zinc diffused completely through the molybdenum wall and interacted with the nickel in the Inconel shield. The molybdenum capsule remained intact except for a few cases where the wall was slightly deformed by the nickel-zinc compound which formed on the inside of the Inconel shield. A period of less than ten hours was required for some of the zinc to completely penetrate the molybdenum wall and after 100 hours the capsules were completely empty of zinc. The compound which formed on the inside of the Inconel to a thickness of up to 75 mils, was very hard and brittle and could not be identified by x-ray techniques. In the 100 hour tests some nickel from the Inconel also diffused into the molybdenum wall, and in a few cases was even detected as a residue of NiZn inside the molybdenum capsules.

Since the diffusion of both the zinc and the nickel was along grain boundaries, the grain size of the molybdenum would have a considerable effect on the diffusion rate. This effect was noted since significant grain growth in the molybdenum was caused by the electron beam welding process. Large grain size was noted in the end caps and both ends of the tubing for a distance of about one-fourth the length of the capsule. Figures 24 and 25 illustrate the large difference in

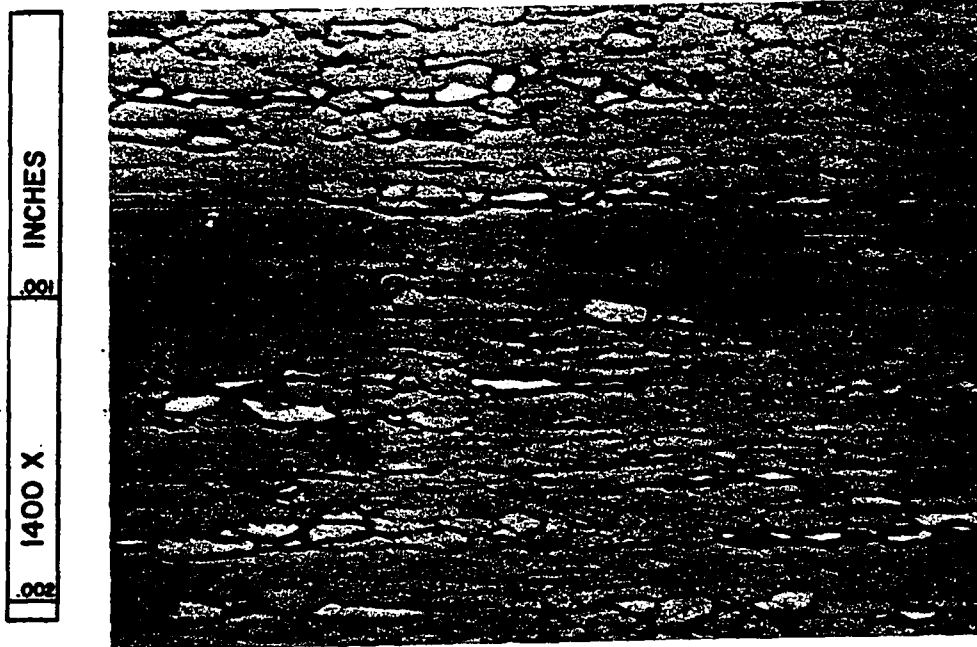


Figure 24. Molybdenum grain structure typical of central portion of capsule wall (1400X)



Figure 25. Typical molybdenum grain structure near ends of capsule (1400X)

grain size noted between the end and the center of the capsules. Due to the greater amount of grain boundaries available in the central portion of the capsule, the majority of the diffusion would be expected to occur in this region. Figures 26 and 27, which are photomicrographs of different regions of the same capsule, illustrate the presence of high impurity content in the grain boundaries of the small grains.

As was discussed in the experimental procedure, no interaction between molybdenum and Inconel was expected since none was detected after special compatibility tests were run. Also, no interaction between molybdenum and Inconel was noted in the tests with the other liquid metals. The presence of nickel in the molybdenum was somewhat surprising and was apparently due to the zinc interactions. The NiZn residue, which was found in a few of the capsules, leads one to suspect that this compound was involved in the transport of the nickel; however, high oxygen was also noted in the molybdenum after the 100-hour tests even when the original oxygen content of the zinc was very low.

Several problems were encountered in analyzing the corrosion specimens since the zinc had completely diffused out of the capsules in the 100-hour tests. It was impossible to determine the oxygen and molybdenum content of the zinc for these cases. Accurate determination of the amount of zinc which diffused out of the capsule was impossible since it was difficult to remove the zinc from the capsule and part of the specimen was needed for other types of analyses. The weight loss was determined by measuring the average depth of zinc remaining in the bottom of the capsule and calculating the volume and weight from this.

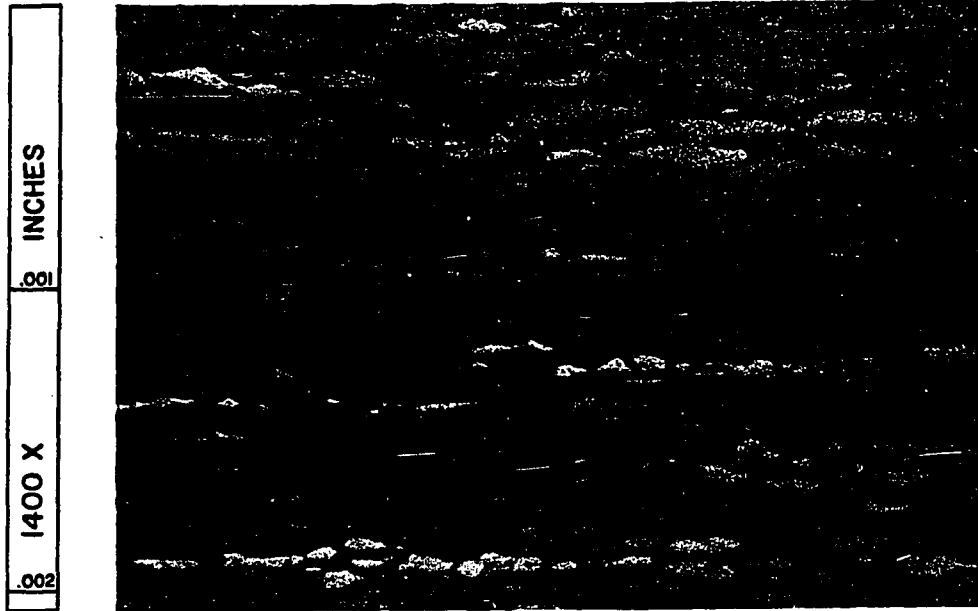


Figure 26. Typical molybdenum grain structure showing high impurity level in area of small grain size. Sample Number 148 (1400X)



Figure 27. Typical molybdenum grain structure showing relatively low impurity level in area of large grain size. Sample Number 148 (1400X)

The zinc content of the molybdenum wall was determined by spectrographic analysis and is given relative to the intensity of the lines. The relative intensities range from zero to a value of ten for a zinc content of the order of 1000 parts per million. Although a linear relationship between the intensity of the lines and the zinc content is not a valid assumption, it is probably a fair approximation and will give values satisfactory for this investigation. The oxygen content of the molybdenum was determined by vacuum fusion techniques and was found to be about 50 parts per million for the pretest molybdenum. The change in oxygen content of the molybdenum capsule is listed when a significant change was detected. An increase of less than 50 parts per million oxygen in the molybdenum was generally considered negligible.

The results of the short term corrosion tests (10 hours) are summarized in Table 12 and those of the long term tests (100 hours) in Table 13. High zinc content, negligible change in oxygen level, and no detectable nickel were noted for the molybdenum in the short term tests. Uniform solution of the molybdenum to the extent of its solubility in zinc occurred in less than two hours with no significant further increase in ten hours. One system tested with granulated zinc containing 119 parts per million oxygen indicated a much higher molybdenum content (1220 ppm) than the other samples. This sample also indicated the highest zinc loss from the capsule which resulted in an insufficient amount of zinc remaining in the capsule to obtain a sample for oxygen analysis. The zinc content of the molybdenum wall

Table 12. Results of 700°C zinc-molybdenum corrosion tests after ten hours exposure^a

Sample No.	Form of Zinc	Oxygen in Zinc Pretest ppm	Oxygen in Zinc Post-test ppm	Molybdenum in Zinc ppm	Zinc in ^b Molybdenum	Oxygen Change ^c in Molybdenum ppm	Remarks
161 ^a	slug	10	15 ± 3	259	6	n ^c	Two grams of zinc diffused into molybdenum. No interaction of zinc with Inconel was noted. Uniform solution of molybdenum to extent of solubility in zinc. Tiny particles (0.1 mil) of molybdenum noted throughout zinc.
160	slug	10	26 ± 3	354	5	n	Nine grams of zinc diffused into molybdenum and some zinc interacted with Inconel shield. Uniform solution of molybdenum to extent of solubility in zinc. Tiny particles (0.1 mil) of molybdenum noted throughout zinc.
168	slug	188	18 ± 2	302	7	n	Three grams of zinc diffused into molybdenum and some zinc interacted with Inconel shield. Uniform solution of molybdenum to extent of solubility in zinc. Tiny particles (0.1 mil) of molybdenum noted throughout zinc.
157	granulated	119	n.a. ^d	1220	10	n	Eleven grams of zinc diffused into molybdenum and some zinc interacted with Inconel shield. Uniform solution of molybdenum greater than solubility in zinc. Particles of molybdenum (larger than previous samples) noted throughout zinc were more dense near bottom of capsule.
180	granulated plus oxide	1000	131 ± 5	291	6	n	Three grams of zinc diffused into molybdenum and some interacted with Inconel shield. Uniform solution of molybdenum to extent of solubility in zinc. Small particles of molybdenum (<1 mil) were noted throughout zinc. Most of zinc oxide was separated at top of zinc left in the capsule.
181	granulated plus oxide	10,000	813 ± 25	505	5	n	Eight grams of zinc diffused into molybdenum and some interacted with Inconel shield. Uniform solution of molybdenum exceeding the solubility limit for pure zinc. Small particles (up to 1 mil) more dense than in previous samples were noted throughout zinc. Most of zinc oxide was separated at the top of the zinc in the capsule.

^aResults of Sample 161 are given after only two hours exposure time.

^bZinc content is listed relative to intensity of spectrographic lines based on a maximum intensity of ten.

^c"n" - negligible change in oxygen level.

^d"n.a." - sample not analyzed due to insufficient quantity of zinc remaining in capsule.

Table 13. Results of one hundred hour zinc-molybdenum corrosion tests

Sample No.	Test Temperature °C	Form of Zinc	Oxygen in Zinc Pretest ppm	Zinc in ^a Molybdenum	Oxygen Change in Molybdenum ppm	Remarks
148	700	slug	10	2	491	All of zinc diffused through molybdenum wall leaving capsule completely empty with clean walls. Zinc-nickel compound formed (60 mil) on inside of Inconel shield deforming molybdenum slightly. Very weak nickel detected in molybdenum.
167	700	slug	188	1	n ^b	All of zinc diffused through molybdenum wall leaving capsule completely empty with clean walls. Zinc-nickel compound formed (60 mil) on inside of Inconel shield deforming capsule slightly. Trace of nickel detected in molybdenum.
182	700	granulated plus oxide	1000	1	305	All of zinc diffused through molybdenum wall leaving a thin film on capsule wall. Zinc-nickel compound (60 mil) formed on inside of Inconel shield. Faint trace of nickel detected in molybdenum.
183	700	granulated plus oxide	10,000	5	103	All of zinc diffused through molybdenum wall leaving thin film on capsule wall and a powdery residue of ZnO on lower wall. Zinc-nickel compound formed (60 mil) on inside of Inconel shield deforming capsule considerably. Trace of nickel detected in molybdenum.
147	800	slug	10	7	278	All of zinc diffused through molybdenum wall leaving a thin film on capsule wall. Zinc-nickel compound formed (60 mil) on inside of Inconel shield deforming capsule slightly. Moderate nickel detected in molybdenum.
156	800	granulated	119	8	1007	All of zinc diffused through molybdenum wall leaving a thin film on capsule wall and a ball of residue (0.25 gram) of NiZn and ZnO in bottom of capsule. Zinc-nickel compound formed (60 mil) on inside of Inconel shield deforming molybdenum wall considerably. Strong nickel detected in molybdenum.

^aZinc content is listed relative to intensity of spectrographic lines based on a maximum intensity of ten.

^b"n" - negligible change in oxygen level detected.

was also the highest of any sample analyzed. Figure 28 through 33 are photomicrographs of the grain structure of the molybdenum wall after exposure to zinc (ten hours at 700°C) initially containing 10, 119, and 1000 parts per million oxygen.

The ten hour tests indicate little change in oxygen content of the zinc for the low oxygen (10 ppm) samples; however, the samples containing 188 parts per million oxygen show a significant decrease in oxygen content to eighteen parts per million. The higher oxygen content of the zinc apparently decreased the diffusion rate of the zinc considerably, since about three times as much zinc was lost from the low oxygen sample (9 grams) as from the 188 parts per million oxygen sample (3 grams). No correlation could be drawn between the sample containing 188 parts per million oxygen and a sample which was prepared from granulated zinc containing 119 parts per million oxygen. The relatively small difference in oxygen level was not expected to have much effect; however, the results were considerably different. The main difference in these two samples was the form of the zinc metal placed in the capsule. Comparison of the granulated zinc (119 ppm oxygen) with the high oxygen samples of granulated zinc plus zinc oxide revealed a higher diffusion rate for zinc with lower oxygen level. This result agrees with that obtained by comparing the two oxygen levels of zinc in slug form.

Results of the 100-hour tests indicate the presence of nickel in the molybdenum and essentially no zinc left inside the capsules. The tests run at 700°C generally indicate a relatively low zinc content in

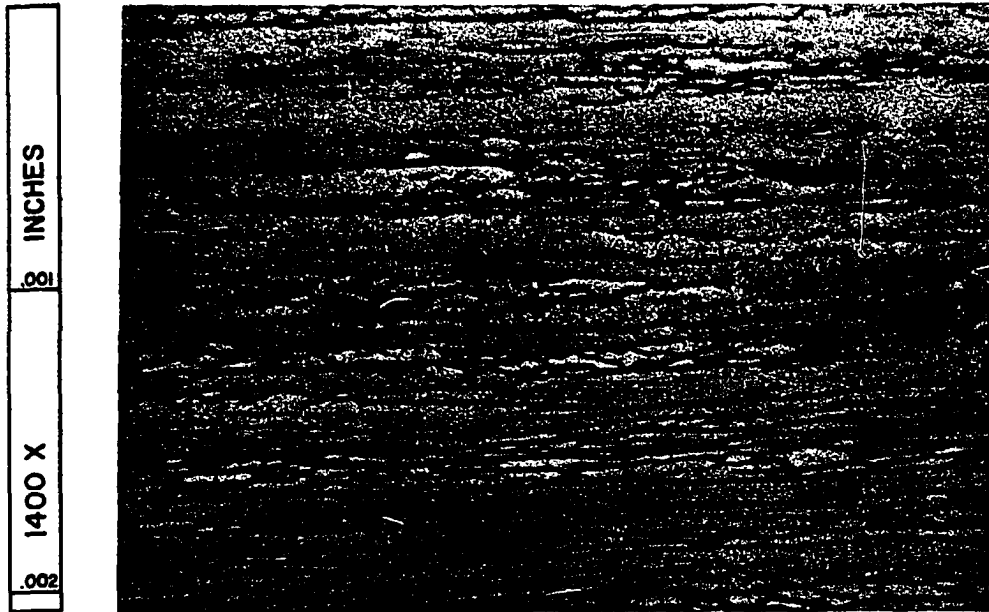


Figure 28. Molybdenum grain structure in central portion of capsule after exposure to zinc (10 ppm oxygen) for ten hours at 700°C. Sample Number (1400X)

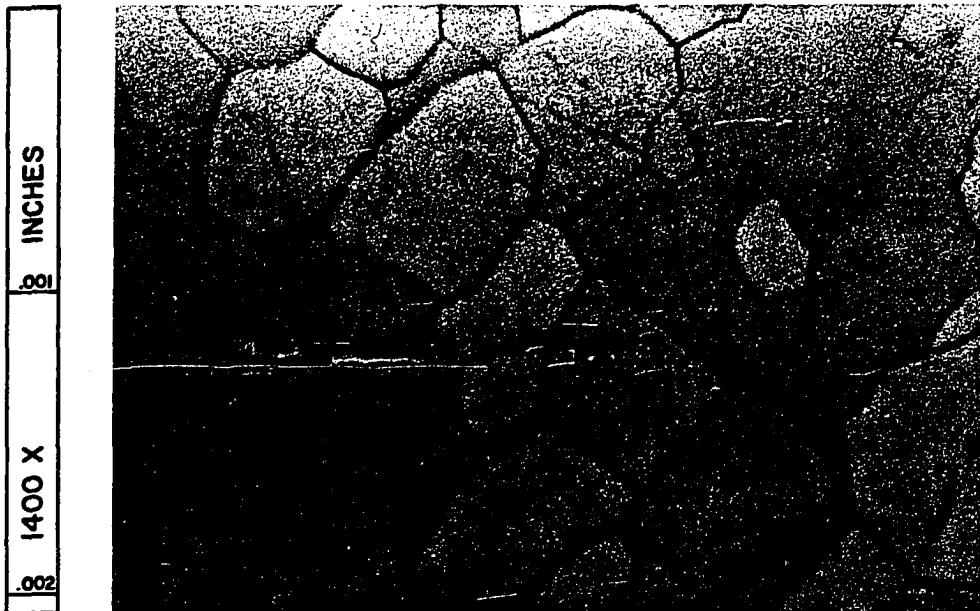


Figure 29. Molybdenum grain structure near end of capsule after exposure to zinc (10 ppm oxygen) for ten hours at 700°C. Sample Number 160 (1400X)

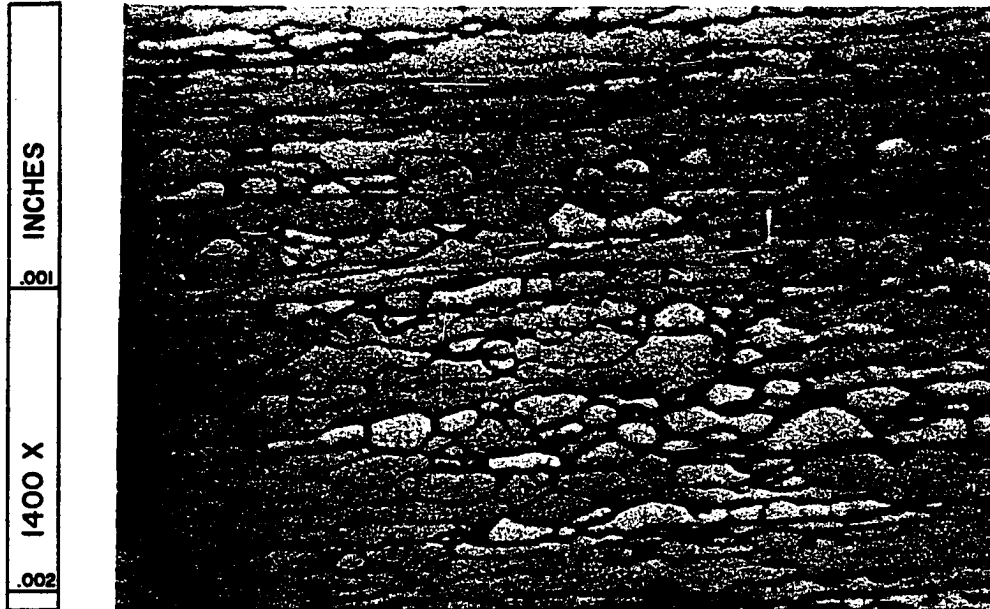


Figure 30. Molybdenum grain structure in central portion of capsule after exposure to zinc (119 ppm oxygen) for ten hours at 700°C. Sample Number 157 (1400X)

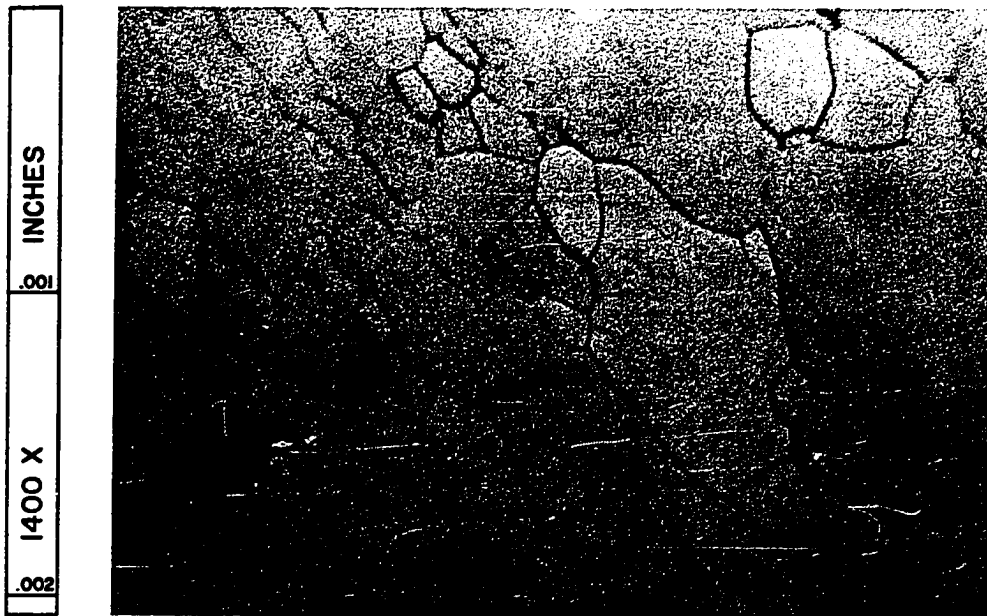


Figure 31. Molybdenum grain structure near end of capsule after exposure to zinc (119 ppm oxygen) for ten hours at 700°C. Sample Number 157 (1400X)

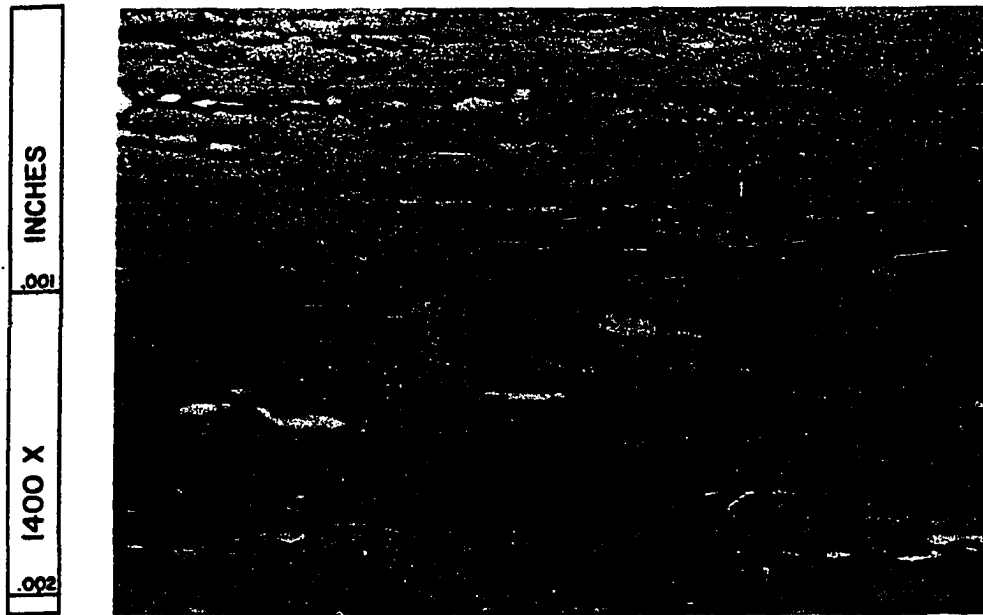


Figure 32. Molybdenum grain structure in central portion of capsule after exposure to zinc (1000 ppm oxygen) for ten hours at 700°C. Sample Number 180 (1400X)



Figure 33. Molybdenum grain structure near end of capsule after exposure to zinc (1000 ppm oxygen) for ten hours at 700°C. Sample Number 180 (1400X)

the molybdenum. An increase in oxygen content of several hundred parts per million was also noted for the molybdenum after the 100 hour tests at both 700 and 800°C, while the nickel content of the molybdenum was much higher for the 800°C tests. The nickel content also appeared to increase with an increase in exposure time, at least up to 300 hours. Figures 34 through 36 illustrate the increased impurity content of the molybdenum wall for the 100 hour tests. The dark areas in the photomicrographs are believed to be an oxide in the molybdenum grain boundaries. Figure 37 shows the increased impurity content in the large grain boundaries after testing for 300 hours at 800°C. The inside of the molybdenum capsules which contained low oxygen zinc were relatively clean, whereas a residue of oxide remained in the capsules which originally contained zinc oxide. The residue of one of the 800°C tests contained a considerable amount (0.25 grams of residue) of the intermetallic compound NiZn which indicates that both zinc and nickel diffused completely through the 35 mil molybdenum wall.

Although complete agreement between all the samples was not attained, it appears that when the same form of zinc is used, the diffusion rate of zinc through molybdenum is decreased with an increase in oxygen content of the zinc. The results of these tests indicate, however, that molybdenum cannot be used to contain zinc even at low pressures and for short periods of time.

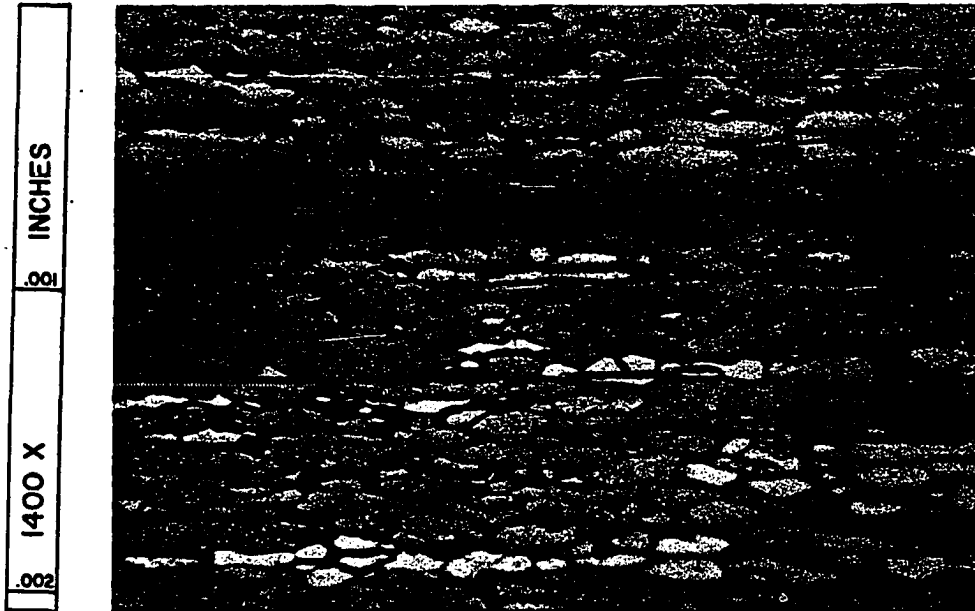


Figure 34. Molybdenum grain structure showing high impurity in central portion of capsule after exposure to zinc for 100 hours at 700°C. Sample Number 148 (1400X)

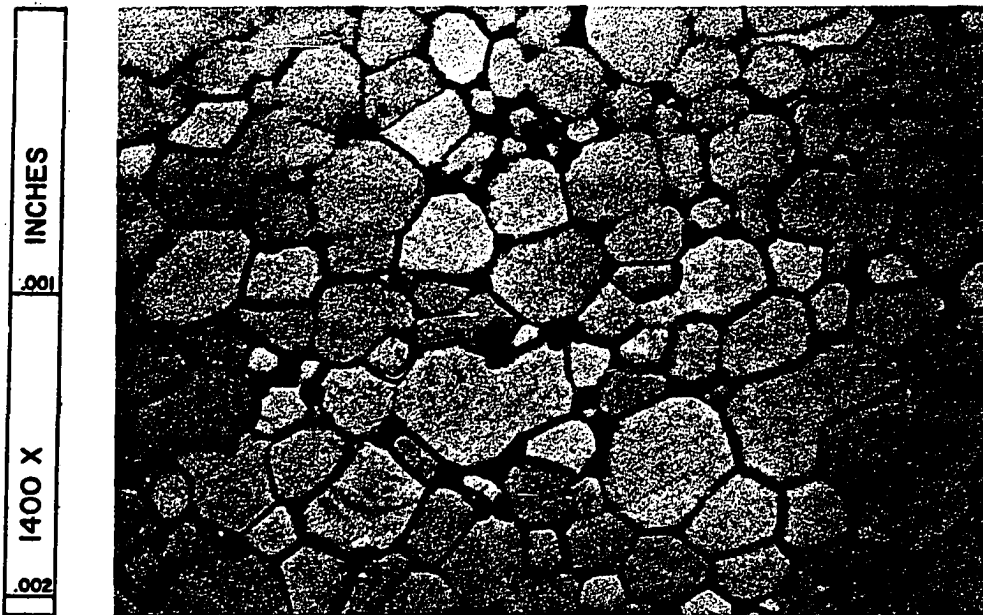


Figure 35. Molybdenum grain structure showing grain boundary impurity after exposure to zinc for 100 hours at 700°C. Sample Number 148 (1400X)

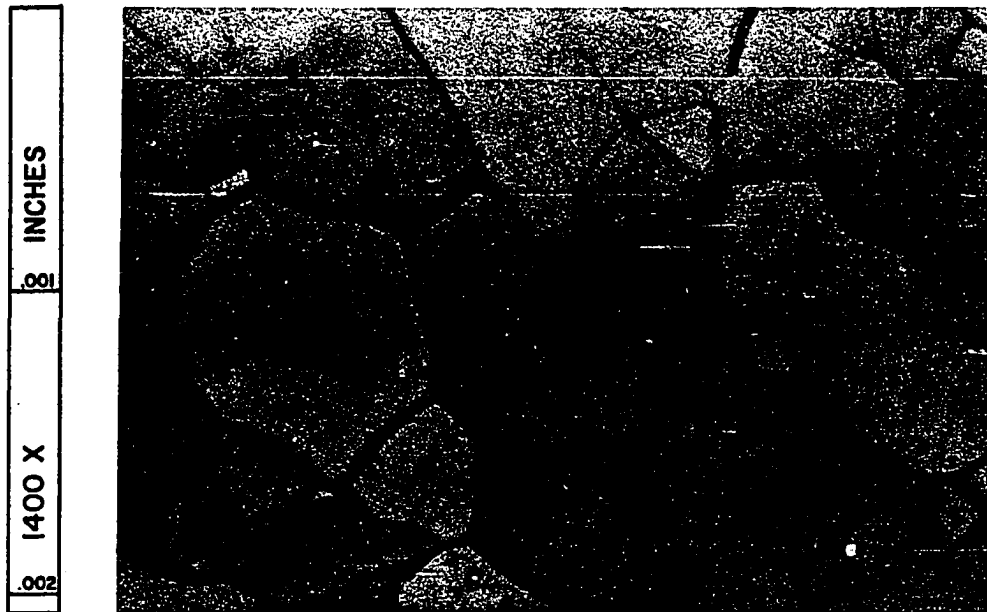


Figure 36. Molybdenum grain structure near end of capsule showing impurity in grain boundaries after exposure to zinc for 100 hours at 700°C. Sample Number 148 (1400X)

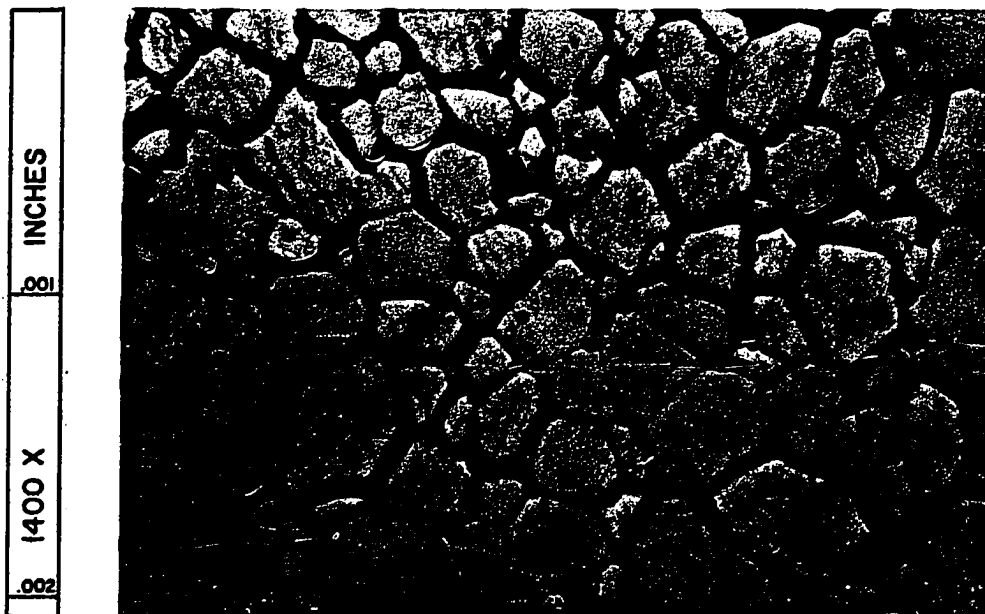


Figure 37. Molybdenum grain structure near end of capsule showing very high impurity content in grain boundaries after exposure to zinc for 300 hours at 800°C. Sample Number 038 (1400X)

CONCLUSIONS

Four possible effects of oxygen on liquid metal corrosion have been discussed. These include any corrosion effect caused by the equilibrium redistribution of oxygen between the solid and liquid metal, a change in solubility limits because of the oxygen, the formation of complex oxides such as molybdates, and the formation of low melting or loosely adhering molybdenum oxides.

The results of the lead tests were somewhat unexpected; however, an explanation can be given. As expected, the oxygen content of the lead after test was reduced to very low values for all cases except for the tests with high purity lead, in which case the oxygen level did not change significantly. Little attack of the molybdenum wall by the liquid lead was noted and low molybdenum content was found for all cases except the high purity lead tests. The molybdenum content found in the low oxygen samples was considerably greater than the solubility limit listed in Table 1. The oxygen in the lead apparently forms an oxide film on the molybdenum which protects the molybdenum from attack. This film must be lead molybdate (PbMoO_4) since no oxides of molybdenum or lead were detected. For the tests in which high oxygen levels were attained by the addition of lead oxide, layers of lead molybdate also covered the vapor walls of the capsules. Apparently only a small amount of oxygen is required for the film since the solution attack was not noted with tests containing 26 parts per million oxygen. The boundary layer film must adhere strongly to the wall since the molybdenum and oxygen contents of the lead were very low for the samples in which the film was assumed to form.

The cadmium tests indicated increased attack of the molybdenum with an increase in oxygen content; however, a large amount of oxygen was required for a significant effect. The cadmium tests showed no detectable attack for the low oxygen samples. A boundary layer of cadmium oxide and cadmium molybdate was noted in the samples in which oxygen was added. The cadmium oxide was attracted to the molybdenum walls leaving the cadmium with a relatively low oxygen level. The formation of cadmium molybdate crystals apparently took place at the interface and in this case the molybdate did not adhere strongly to the wall since a considerable amount was noted in the cadmium. The oxygen and molybdenum analyses of the cadmium also support this explanation.

Tin was the only liquid metal which was reported to alloy with molybdenum ($\text{MoSn}_{1.5}$), and there is some disagreement as to the existence of this intermetallic compound. In some of the tests a phase was formed which etched gray and was believed to be this intermetallic compound. The two-phase boundary layer which was noted in most of the samples apparently required the presence of oxygen for this formation since no boundary layer was detected for the low oxygen samples. The boundary layer thickness also appeared to be a function of the oxygen content. The oxygen from the tin must be in the yellowish phase of the boundary layer since the gray crystals were noted throughout the tin and the oxygen level of the tin was very low for all cases. The oxygen apparently affects the valence state of the molybdenum or tin which then allows the formation of the compound.

The results of the zinc tests did not show a definite effect of the oxygen on the liquid metal corrosion. The calculations for the distribution coefficient of oxygen between zinc and molybdenum indicated that zinc would have a high affinity for any oxygen in the molybdenum. The tests made with zinc in slug form indicated that the diffusion rate of zinc through the molybdenum was less for higher oxygen content which is what one might expect if the diffusion is caused by an affinity for the oxygen in the molybdenum. Tests with variable oxygen content of the molybdenum would be helpful in confirming this. The tests with granulated zinc tended to agree with the lower diffusion rate with higher oxygen content; however, no correlation could be drawn between the tests with zinc in slug form and in granulated form. The 800°C tests showed a high nickel content in the molybdenum after a 100 hour test. The significant difference between the 700 and 800°C tests are probably caused by an oxide eutectic of molybdenum and nickel oxides with a melting point below 800°C.

RECOMMENDATIONS FOR FURTHER STUDY

The object of this investigation was to further the understanding of the effects of interstitial impurities on the liquid metal corrosion of the refractory metals. This study has included only one of the interstitial impurities and only one of the refractory metals. Since the metals studied in this investigation all have relatively low limits of solubility for oxygen, a similar study with components having higher oxygen solubilities would be enlightening. Further study of the other interstitial impurities should also be made.

Several problems directly related to this investigation also deserve further study. The corrosion test duration and the test temperature were not primary variables in this investigation. Further tests with the same systems should be made with systematic time variations. The effect of higher temperature, particularly for lead and tin, should also be determined in view of the low melting temperatures which have been reported for oxides of molybdenum.

A further sidelight of this investigation was the rapid diffusion of the zinc through the molybdenum wall. Only a few cases of diffusion of a liquid metal through a solid metal capsule have been reported and the factors affecting this phenomena have not been investigated thoroughly. Further study of the zinc-molybdenum system should prove interesting and enlightening.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Glenn Murphy and Mr. Ray Fisher for the advice and encouragement given during this investigation.

The author would like to thank Mr. Norman Linder for his assistance in the sample preparation and Mr. Robert Cash for his suggestions and advice during the preparation of the report.

Recognition is also extended to Mr. Richard Clark and Mr. Wayne Stensland for their assistance in the oxygen analysis of the liquid metals, Mr. Charles Peters for the analytical analyses, and Mr. Harlan Baker for the metallographic work.

The deepest appreciation is expressed to the authors wife, Glenda Kay, for her encouragement, patience, and moral support during the course of this investigation.