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# CORROSION OF FERROUS ALLOYS IN EUTECTIC LEAD-LITHIUM ENVIRONMENT

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Corrosion data have been obtained on austenitic prime candidate alloy (PCA) and Type 316 stainless steel and ferritic HT-9 and Fe-9Cr-1Mo steels in a flowing Pb-17 at. % Li environment at 727 and 700 K (454 and 427°C). The results indicate that the dissolution rates for both austenitic and ferritic steels in Pb-17Li are an order of magnitude greater than in flowing lithium. The influence of time, temperature, and alloy composition on the corrosion behavior in Pb-17Li is similar to that in lithium. The weight losses for the austenitic steels are an order of magnitude greater than for the ferritic steels. The rate of weight loss for the ferritic steels is constant, whereas the dissolution rates for the austenitic steels decrease with time. After exposure to Pb-17Li, the austenitic steels develop a very weak and porous ferrite layer which easily spalls from the specimen surface.

## 1. INTRODUCTION

The eutectic Pb-17 at. % Li alloy has been proposed as the tritium breeder and/or as a coolant for fusion reactors that operate on the D-T fuel cycle. The Pb-17Li alloy is attractive for this application because of the neutron multiplication in the lead, which enhances the tritium breeding performance. It is also less reactive with air or water than liquid lithium. The use of liquid Pb-17Li for such applications requires an assessment of the compatibility with containment materials. The corrosion and mass transfer of structural material can be deleterious in any application of circulating liquid metals. Corrosion in the form of uniform or selective dissolution, intergranular penetration, and interstitial-element transfer to and from the liquid metal can result in significant wall thinning and deposition of corrosion products that may cause severe flow restrictions and excessive accumulation of radioactive material in unshielded regions.

Very little information is available on the corrosion of structural materials in liquid Pb-17Li alloy. The corrosion and compatibility of austenitic Type 316 stainless steel and ferritic HT-9 alloy have been investigated in static Pb-17Li capsules.[1-3] However, no data exist on the corrosion of materials in a circulating Pb-17Li environment. This paper presents information on the corrosion behavior of several austenitic and ferritic steels in flowing eutectic Pb-17Li alloy.

## 2. SPECIMENS AND EXPERIMENTAL PROCEDURES

Corrosion tests were conducted in a forced-circulation loop consisting of a high-temperature test vessel with a heat exchanger section and a cold leg. The eutectic alloy was prepared in a separate vessel and transferred into the loop The total volume of the loop is ~2 liters. A schematic of the loop and the mixing vessel is shown in Fig. 1. Approximately 6 liters of the alloy was prepared by melting a known quantity of lead in the mixing vessel under a purified argon environment and adding small amounts of lithium (~10 mℓ per addition). The liquid Pb-Li alloy was maintained at ~733 K (460°C)

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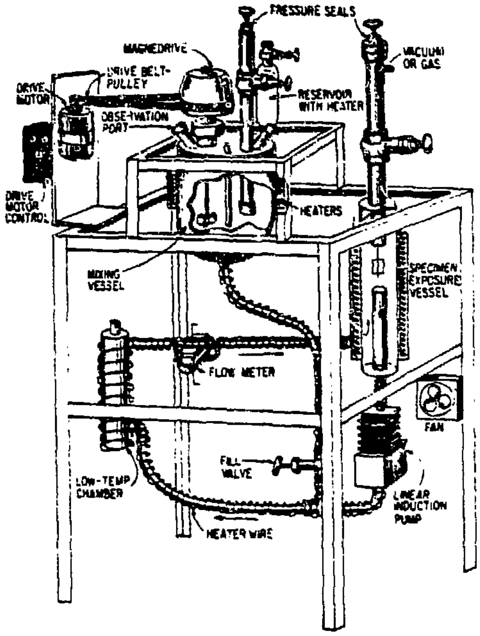


FIGURE 1
Schematic of the Pb-17Li test loop

with constant stirring during the lithium additions.

The reactions between liquid lithium and lead were observed through the two ports in the cover of the mixing vessel. Initially, the surface of the liquid lead was covered with a grayish-black layer of lead oxide, which prevented proper wetting between liquid lithium and lead. As the concentration of lithium increased in the alloy, the gray oxide layer was replaced by a white oxide film, probably lithium oxide. The reaction between lithium and lead for each lithium addition proceeded as follows: Upon contact with the lead, the lithium drops displaced the oxide film and formed a pool on the surface. For the next 20 to 40 s, the layer of lithium in contact with lead solidified, possibly owing to the formation of a lithium-rich lead compound. Then this solid dissolved rapidly in the lead, releasing intense heat in the process. The reaction produced an orange-red flame-like color at the solid-liquid interface. A grayish solid remained floating on the surface; on stirring, this gradually dissolved in the lead.

The eutectic alloy was bottom poured into the loop after it was analyzed to check the composition and determine the concentration of interstitial elements such as O, N, and H. Several analyses show that the composition is Pb-16.3 at. % Li and the concentrations of O, H, and N are 260, 22, and <10 ppm, respectively.

Flat corrosion specimens, ~70 x 10 x 0.3 mm in size, of Type 316 stainless steel, prime candidate alloy (PCA), Fe-9Cr-1Mo steel, and HT-9 alloy were exposed to flowing Pb-17Li at 727 and 700 K (454 and 427°C) for up to 3300 h. The compositions of the various alloys are given in Table I. During exposure, the cold-leg temperature was maintained at 573 K (300°C). The ferritic steels, HT-9 and Fe-9Cr-1Mo, were exposed in the normalized and tempered condition. Two different heat treatments were employed for each of the other materials, viz., 25% cold-worked (CW) and 25% CW plus 2 h at 1023 K for PCA, and solution-annealed and 20% CW for Type 316 stainless steel. The specimens were periodically removed from the loop for weight change measurements. After each exposure, the corrosion specimens were cleaned in static lithium at ~563 K (290°C). Subsequently, they were washed in alcohol and water. This procedure was repeated several times till no further weight change was observed for the specimens. Control specimens were also exposed with the corrosion specimens in lithium to monitor any weight change during the cleaning operation. No measurable weight change was observed for the control specimens.

TABLE I. Chemical Compositions of Austentic and Ferritic Steels

| Alloy | Content, wt % | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Ni | Mo | Mn | Si | P | S | C | N | Other |
| PCA | 14.0 | 16.2 | 2.3 | 1.8 | 0.40 | 0.010 | 0.003 | 0.05 | 0.010 | 0.24Ti |
| 316 SS | 17.0 | 13.4 | 2.49 | 1.9 | 0.64 | 0.024 | 0.020 | 0.07 | 0.034 | |
| HT-9 | 12.0 | 0.6 | 1.03 | 0.5 | 0.22 | 0.006 | 0.002 | 0.21 | 0.003 | 0.32V, 0.5W |
| 9Cr-1Mo | 8.8 | - | 0.92 | 0.4 | 0.36 | - | - | 0.098 | 0.011 | 0.21V, 0.06Nb |

## 3. RESULTS

The corrosion behavior was evaluated by measuring the change in weight of the specimens exposed to flowing Pb-17Li for different times. The exposed specimens were examined metallographically to study the nature and extent of the corrosive interactions. The weight loss in flowing Pb-17Li at 727 and 700 K is shown in Fig. 2 for annealed and 20% CW Type 316 stainless steel and in Fig. 3 for the ferritic steels. Data from tests in static Pb-17Li capsules[2] are also included in the figures. The results show that for both austenitic and ferritic steels, the weight loss in flowing Pb-17Li is significantly greater than in static capsules. Specimens exposed to static Pb-17Li show little or no weight loss after 1000 to 3000 h, whereas the specimens continue to lose weight in flowing Pb-17Li.

The dissolution rates of both austenitic and ferritic steels in flowing Pb-17Li are an order of magnitude greater than in flowing lithium.[4-7] However, the overall corrosion behavior of the various alloys is similar to that in lithium. For example, the rate of weight loss for the austenitic Type 316 stainless steel reaches a steady-state value (shown by the dashed lines in Fig. 2) after an initial period of high dissolution rate. The weight losses with time for austenitic steels may also be expressed by a parabolic law; these predictions are shown by the solid curves in Fig. 2. In a flowing lithium environment, the weight loss for Types 304 and 316 stainless steel with time follows a power law relationship given by

$$W = Kt^n, \qquad (1)$$

where W is weight loss in g/m$^2$ and t is time in hours. K and n are constants. The corrosion data in lithium yield an average value of 0.7 for the time exponent n.[7]

In both lithium and Pb-17Li environments, the dissolution rates for the ferritic steels are constant. Figure 3 shows that at 700 K

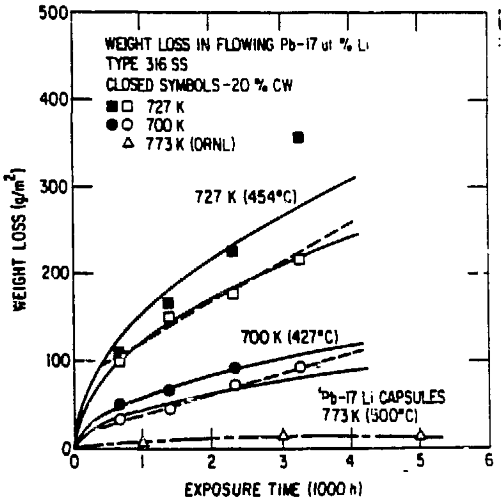


FIGURE 2
Weight loss versus exposure time for annealed and 20% cold-worked Type 316 stainless steel exposed to flowing Pb-17Li at 727 and 700 K. Each symbol type represents weight loss for a single specimen after various exposure times.

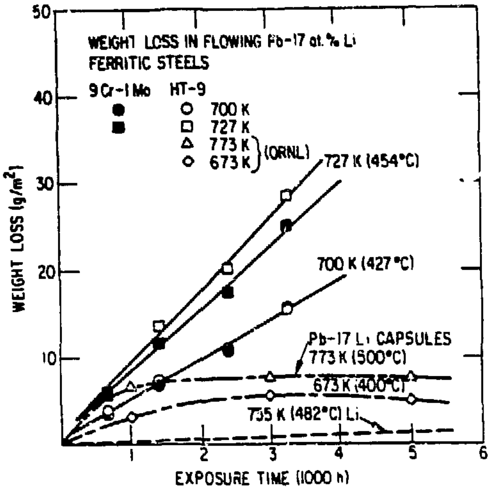


FIGURE 3
Weight loss versus exposure time for HT-9 alloy and Fe-9Cr-1Mo steel exposed to flowing Pb-17Li at 727 and 700 K. Each symbol type represents weight loss for a single specimen after various exposure times.

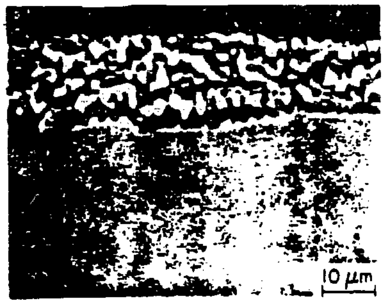
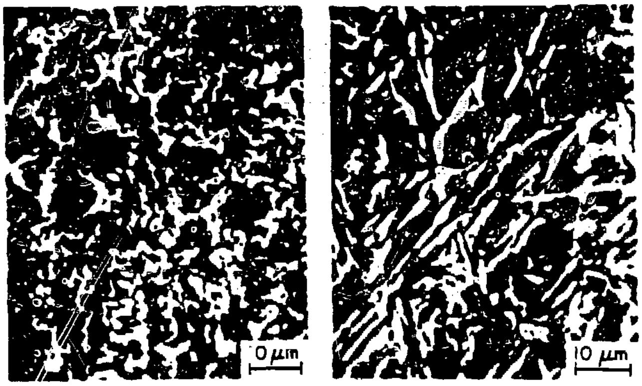


FIGURE 4
Micrograph of the ferrite layer formed on annealed Type 316 stainless steel exposed for 1400 h in flowing Pb-17Li at 727 K

the dissolution rates for HT-9 and Fe-9Cr-1Mo steel are comparable, and at 727 K the dissolution rate for the HT-9 alloy is slightly higher than that for Fe-9Cr-1Mo steel. The weight losses for the austenitic stainless steel are an order of magnitude greater than for the ferritic steels, and the weight loss for the CW Type 316 stainless steel is ~25% higher than for the annealed steel. For all alloys, the loss in weight at 727 K is a factor of ~2 greater than at 700 K.

Metallographic examination of the exposed specimens revealed that the austenitic Type 316 stainless steels develop a very porous and weak ferrite layer. The ferrite layer formed on the annealed Type 316 stainless steel exposed for 1400 h in Pb-17Li at 727 K is shown in Fig. 4. A typical energy-dispersive x-ray analysis of the ferrite layer reveals a composition of ~95% iron and small amounts of chromium and molybdenum. Austenitic stainless steels are known to develop a ferrite layer after exposure to lithium owing to preferential leaching of nickel, and to a lesser extent chromium, from the steel. However, the ferrite layer formed in a flowing Pb-17Li environment is very weak and full of cavities and holes. The ferrite layer was not observed over the entire surface area of the specimens exposed to Pb-17Li. The weak ferrite layer probably spalls either during exposure to Pb-17Li or during cleaning of the specimens in lithium. This behavior would influence the weight loss of the austenitic stainless steels exposed to a flowing Pb-17Li environment. The corrosion data in Pb-17Li represent the loss in weight due to the loss of the entire degraded ferrite layer on the specimens. In contrast, the weight loss in a flowing lithium environment is primarily due to the selective dissolution of substitutional elements from the steel.

Micrographs of the surface of the annealed Type 316 stainless steel and HT-9 alloy specimens exposed at 727 K for 3300 h in a flowing Pb-17Li environment are shown in Fig. 5. The surface of Type 316 stainless steel shows significant corrosion and is full of cavities and holes. The HT-9 alloy has an etched appearance with some corrosive attack along the grain boundaries and martensitic



(a) (b)

FIGURE 5
Micrographs of the surface of (a) annealed Type 316 stainless steel and (b) HT-9 alloy exposed for 3300 h in flowing Pb-17Li at 727 K

lathe boundaries. However, examination of cross sections of the specimens reveals little or no internal corrosion.

Specimens of PCA were also exposed for 905 h in flowing Pb-17Li at 727 and 700 K. Weight loss in the specimens after the first cleaning in lithium was comparable to that in the CW Type 316 stainless steel. However, the PCA specimens continued to show weight loss upon subsequent cleaning. Consequently, an accurate value of weight loss could not be obtained for these specimens. After each cleaning, grayish flakes or powdery deposits were observed on the specimen surfaces. Metallographic examination of the specimens revealed that the gray flakes were sections of the ferrite layer that broke off from the specimen surface. Micrographs of the loose ferrite layer are shown in Fig. 6. The surface has a very porous and etched appearance. Corrosion along the grain and twin boundaries can be seen clearly. X-ray analyses showed that the composition of the ferrite layer was similar to that observed for Type 316 stainless steel.

## 4. CONCLUSIONS

Corrosion data in a flowing Pb-17Li environment indicate that the dissolution rates for both austenitic and ferritic steels are an order of magnitude greater than in flowing lithium. The influence of time, temperature, and alloy composition on the corrosion behavior in Pb-17Li is similar to that in flowing lithium. The weight losses for the austenitic steels are an order of magnitude greater than for the ferritic steels, and the weight loss for CW Type 316 stainless steel is higher than for the annealed steel. The rate of weight loss for the ferritic steels is constant, whereas the dissolution rates for austenitic steels decrease with time. For annealed and cold-worked Type 316 stainless steel, the weight loss with time in flowing Pb-17Li follows a parabolic law. For Type 316 stainless steel and HT-9 alloy, the weight loss in flowing Pb-17Li is significantly greater than in static Pb-17Li capsules.

After exposure to flowing Pb-17Li, the austenitic steels develop a very weak and porous ferrite layer. This layer easily

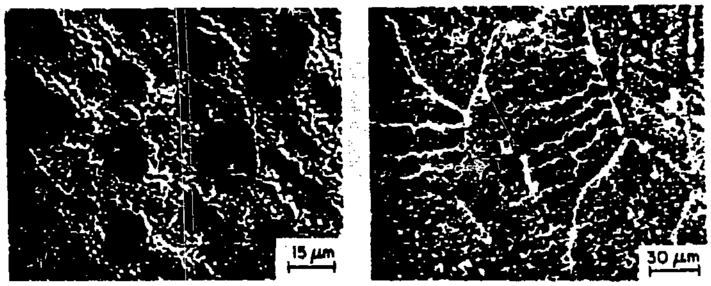


FIGURE 6
Micrographs of the loose surface layer of ferrite on PCA exposed at 727 K for 905 h in a flowing Pb-17Li environment

breaks off from the specimen surface either during the exposure to Pb-17Li or during cleaning of the specimens in lithium. Consequently, the corrosion data in a Pb-17Li environment represent loss in weight due to the loss of the entire degraded ferrite layer and not from the selective dissolution of substitutional elements from the steel. Additional data from specimens exposed to flowing Pb-17Li for long times are required to establish the long-term corrosion behavior of materials in a Pb-17Li environment.

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