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COMPATIBILITY OF STRUCTURAL MATERIALS WITH  
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Abstract

Both liquid mercury and liquid lead-bismuth eutectic have been proposed as possible target materials for spallation neutron sources. During the 1950s and 1960s a substantial program existed at Brookhaven National Laboratory as part of the Liquid Metal Fuel Reactor program on the compatibility of bismuth, lead, and their alloys with structural materials. Subsequently, compatibility investigations of mercury with structural materials were performed in support of development of Rankine-cycle mercury turbines for nuclear applications. This paper reviews our understanding of the corrosion/mass-transfer reactions of structural materials with these liquid-metal coolants. Topics to be discussed include the basic solubility relationships of iron, chromium, nickel, and refractory metals in these liquid metals, the results of inhibition studies, the role of oxygen on the corrosion processes, and specialized topics such as cavitation corrosion and liquid-metal embrittlement. Emphasis will be placed on utilizing the understanding gained in this earlier work on the development of heavy-liquid-metal targets in spallation neutron sources.

Introduction

Both liquid mercury and liquid lead-bismuth eutectic have been proposed as possible target materials for spallation neutron sources (1). The purpose of this paper is to review the work on compatibility of structural materials with these liquid metals that was performed at Brookhaven National Laboratory (BNL) with emphasis on the understanding gained on these corrosion processes and how these results and models can assist in predicting the behavior of materials in a liquid mercury or lead-bismuth spallation target.

The work on compatibility of materials with liquid bismuth and lead-bismuth eutectic was performed in support of a liquid metal fueled reactor (LMFR) program, which was underway in the Nuclear Engineering Department at BNL from approximately 1950 to 1962 (2). While the temperatures in the proposed LMFR were higher (400-550°C) than those in current spallation source designs (150-250°C), the general principles of materials selection and solid metal-liquid metal compatibility, developed during the LMFR studies, should be applicable to spallation source design as well in many areas.

Solubility-Driven Corrosion and Mass Transport

Corrosion by liquid bismuth of metallic materials in a flowing liquid heavy metal system is driven by the differences in solubility of the constituents of the structural material, as illustrated in Figure 1, sketched for the mass-transport of iron from steels through a Bi, Pb, or Hg circuit (3). From this model, the corrosion rate of a solid metal at any point,  $i$ , in the system is

$$C R_i = \alpha(S_{o_i} - S_i), \quad (1)$$

where  $S_{o_i}$  is the solubility of the metal at the temperature point  $i$ , and  $S_i$  is the concentration of the metal dissolved in the liquid at point  $i$ , and  $\alpha$  is a rate constant, which is usually related to the rate of diffusion through the boundary layer. In a flowing, recirculating system, the precipitation process in the "cold leg" or heat removal part of the circuit often controls the steady-state concentration of solute, so that the corrosion rate is a function of both the maximum and minimum temperatures in the circuit. This means that corrosion at the highest temperature can be reduced by increasing the minimum temperature in the circuit as well as by reducing the maximum temperature.

Solubilities of Structural Metals in Bi, Pb, Bi-Pb Eutectic and Mercury

The useful structural materials for containing these liquid metals are those that form no solid alloys with Bi, Pb, or Hg; these are all metals that form monotectic type phase diagrams with the liquid. Nearly all these monotectic systems are with body-centered cubic (bcc) metals. (An exception is copper, which, while face-centered cubic (fcc), also forms monotectic systems with Bi and Pb.)

Most of the early work was concentrated on the use of steels for containing these liquid metals. The solubilities of the principal constituents of structural and stainless steels - iron, chromium, nickel and manganese, are shown in Figure 2 (4). Nickel and manganese both form intermetallic compounds with bismuth, and are much more soluble than the bcc metals iron and chromium. For this reason, nickel-bearing (austenitic) stainless steels were not seriously considered for the LMFR.

Adding lead to bismuth reduces the solubility of Fe, Cr, and Cu in a continuous fashion (5), isotherms for iron are shown in Figure 3; similar but less-detailed curves were obtained for the other metals (5).

Therefore, considering the corrosion equation (1), the corrosion rate of iron would be expected to decrease as the lead content increases, as shown in Figure 4.

Solubilities of Other BCC Metals in Bismuth

From the solubility curve in a monotectic system, one can estimate a heat of solution ( $\Delta H$ ) and an entropy of solution ( $\Delta S$ ). For the bcc metals in liquid bismuth, (and, by analogue, in liquid Pb or Hg) the value of  $\Delta H$  was found in our measurements (6) to be related to the melting point of the solute and decrease to zero at a melting point slightly above 2500°C. Thus, all metals with melting points greater than 2600°C were totally insoluble in Bi, as shown in Figure 5. These metals were also found to be fully corrosion-resistant (in the absence of oxygen) to bismuth.

Solubilities of Structural Metals in Mercury

In the 1960's, work was performed at BNL on the compatibility of a number of materials with liquid mercury in support of the development of a mercury

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turbine for a compact nuclear power source for space applications. The solubility measurements are given in Figure 6 (7). Again, the species that form intermetallic compounds with Hg (Ni, Zr, Ti) are more soluble than the bcc metals Fe, Cr, V, Nb, and Ta (which was totally insoluble). The relative corrosion rates estimated from the solubility curves are given in Figure 7. By "normalizing" these calculated rates to that of Fe, one can see that Cr, Ni, Ti, and Zr would be selectively leached from a steel, and Nb and Ta would be enriched in it by the mass transfer process. Tantalum itself was found to be totally resistant to corrosion by liquid mercury.

#### Special Topics

Special consideration to the following topics needs to be made in selecting a material for containing these liquid metals: the role of oxygen, liquid metal embrittlement, cavitation-erosion in high velocity systems. Each of these is reviewed briefly below.

#### The Role of Oxygen

Since the oxides of Bi, Pb, and Hg are generally less stable than the oxides that form on steels, little effect of oxygen on catalyzing mass-transfer has been observed with these metals, in contrast to extensive experience in liquid sodium circuits. Also, because the minimum circuit temperature affects the corrosion rate, as noted above, cold-trapping to reduce the liquid metal oxygen content, as practiced in sodium circuits, is not advisable with the heavy liquid metals.

In the LMFR project, the need to maintain both the uranium fuel and the corrosion inhibitor (Zr) in the circuit required the addition of an oxygen-getter (Mg) to the liquid. This addition not only protected the U and Zr from oxidation, but cleaned up any residual oxides on the steel surface and promoted "wetting" of the steel by the liquid metal and heat-transfer between the solid and liquid metals. In the Hg work, an inhibitor (Ti) and a getter (Mg) were generally added to the corrosion loops, as developed by Nerad and associates at GE for a Hg turbine (8). The possible role of these oxide films in a low-temperature spallation target is discussed below.

#### Liquid Metal Embrittlement

Some metals are known to be embrittled by liquid metals. The embrittlement of Al by Hg and most metals by liquid gallium is well recognized (9). In unpublished work in our laboratory (10), it was noted that, for monotectic systems, the calculated value of  $\Delta H$  was related to the interfacial energy, suggesting that solid metals with a low value of  $\Delta H$  in a given liquid metal might be susceptible to liquid metal embrittlement. The bcc metal with the lowest value of  $\Delta H$  in mercury is niobium (Figure 6); laboratory U-bend tests show Nb - and especially Nb - 1% Zr materials were indeed embrittled by Hg at 760°C (7).

#### Cavitation-Erosion

Because of the high specific gravity of the heavy liquid metals, care must be taken in circuit design to prevent cavitation at high velocities, where the velocity head readily exceeds the pressure head in some cases. Figure 8 shows some examples of this phenomenon on steel in a pumped liquid bismuth system. Areas where changes occur in pipe diameter and flow direction are particularly susceptible.

#### Discussion

The relevance of these higher temperature data to spallation source design at temperatures below 300°C is not immediately apparent; extrapolation of solubilities to this temperature range is not particularly useful, since, in liquid alloys containing much less than 1 atom solute per million atoms of solvent, equilibration times become extremely long, as the effects of the solute atom on both the physical and electron structure of the liquid metal become vanishingly small.

The role of the oxide films is also difficult to assess: in many cases, the relatively stable oxides on a stainless steel should prevent wetting and improve corrosion resistance. However, the intense ion and fast neutron bombardment of these targets would be expected to make the oxide films less protective.

Also, the role of these films on heat transport needs to be considered; wetting - i.e., a film-free interface - may improve heat transfer, but promote liquid metal corrosion.

Generally, the bcc steels would be expected to have the best resistance to the liquid metals; however, they are also prone to radiation embrittlement. Consequently, suggestions have been made that austenitic stainless steels might perform satisfactorily at these low temperatures: even the solubility of Ni extrapolates to low levels in Hg at these temperatures (17 atoms/million at 200°C) (11), and these austenitic steels have much better radiation resistance than the bcc steels at low temperatures.

In addition to the role of surface oxides, noted above, the possible role of radiation-assisted segregation at the grain-boundaries of austenitic stainless steels needs to be evaluated. Chromium depletion and nickel enrichment have been observed in the grain boundaries of stainless steels irradiated at temperatures below 300°C. At a dpa of approximately 10, a 50 to 100% enrichment has been seen in grain-boundary nickel content (12), as indicated schematically in Figure 9. While the nickel solubility in Hg is at 200°C is low, the tendency of these Ni-rich areas to form the Ni-Hg intermetallic compound NiHg<sub>6</sub>, which decomposes peritectally at 280°C, (11), could potentially cause grain boundary attack at high dpa (estimated dose rates as high as 0.45 dpa/day have been made for spallation target containers) (1).

#### Conclusions

- The solid metals that are most resistant to corrosion by heavy liquid metals are the high-melting bcc metals; these include ferritic steels and the refractory metals.
- Liquid metal embrittlement is a potential concern with some high-melting point materials, most notably Nb and Nb 1% Zr, in liquid mercury and bismuth.
- Flowing circuits need to be carefully designed to minimize cavitation in these high mass liquids.
- Radiation-induced segregation at the grain boundaries needs to be carefully investigated for the target design conditions, especially if nickel-bearing austenitic stainless steels are chosen for target containers.
- The possibility of coating the surface of the stainless steel with a thin layer of Tantalum in the high irradiation field areas should be considered, should a stainless steel be selected for a liquid metal target.

#### References

1. CONF-96031D1, Proceedings of the International Workshop on the Technology and Thermal Hydraulics of Heavy Liquid Metals, Schruns, Austria, March 25-28, 1996.
2. C. Williams and F.T. Miles, "Liquid Metal Fuel Reactor Systems for Power," Chem. Eng. Prog. Symposium Ser. 50#11 (1954), 245-252.
3. J.R. Weeks and D.H. Gurinsky, "Liquid Metals and Solidification," ed. B. Chalmers (ASM, Cleveland, 1958), 106.
4. J.R. Weeks, "Lead, Bismuth, Tin and Their Alloys as Nuclear Coolants," Nuclear Engineering and Design, 15 (1971), 363-372.
5. J.R. Weeks and A.J. Romano, "Liquidus Curves and Corrosion of Fe, Ti, Zr, and Cu in Pb-Bi Eutectic Alloy," Corrosion 25 (1969), 130.
6. J.R. Weeks, "Liquidus Curves of Nineteen Dilute Binary Alloys of Bismuth," ASM Trans. Quart. 58 (1965), 302.
7. J.R. Weeks, "Liquidus Curves and Corrosion of Fe, Cr, Ni, Co, V, Nb, Ta, Ti, and Zr in 500-750°C Mercury," Corrosion 23 #4, (April 1967), 96.

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