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LIQUID Li-Pb-Bi, A NEW TRITIUM BREEDER*

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Summary

In light of their potential utility as tritium breeder-blanket materials, a study was conducted to identify and characterize low-melting phases in the lithium-lead-bismuth system. It is found that a low-melting ternary phase field did in fact exist, e.g., compositions with ≤20 atom percent lithium and Pb/Bi = 0.773 melted at or below 140°C. In addition, the qualitative reactivity of Li-Bi-Pb alloys with water was tested, and although minimal evidence of exothermic chemical reaction was observed, a physical vapor explosion did occur in one of the tests.

Introduction

Liquid lithium-lead alloys such as $Li_{0.17}Pb_{0.83}$ eutectic offer a number of attractive features as tritium breeding media for fusion reactors. These include excellent tritium breeding and neutron attenuating properties, relatively low chemical reactivity, low tritium solubility, and advantages inherent to liquid metals.[1-3] The properties of lithium-lead alloys were recently reviewed.[2,3] Probably the most serious potential problem for these materials is corrosion, particularly at high temperatures, i.e., 500°C or greater. The lowest melting composition, the $Li_{0.17}Pb_{0.83}$ eutectic, melts at 235°C. Allowing a reasonable margin above the melting point, the operating temperature "window" spans a range of only about 200°C, i.e., from about 300° to 500°C, and it is possible that this "window" could be even narrower, because corrosion data are not well established for this material.

In 1980, the relative merits of including a low-temperature tritium breeding blanket in INTOR were evaluated.[4] Although at that time the existence of Li-Bi-Pb alloys was not established, it was proposed that a liquid alloy of approximate composition $Li_{0.1}Pb_{0.4}Bi_{0.5}$ might have a melting point of around 125°C, and would, therefore, be a good tritium breeding medium.[4]

Because the chemical properties of lead and bismuth are quite similar, the ternary Li-Bi-Pb alloy is expected to have chemical behavior similar to $Li_{0.17}Pb_{0.83}$. The phase diagrams for all three binary systems Li-Bi, Li-Pb, Pb-Bi are well established.[6] The general shape of the Li-Bi and Li-Pb systems are stikingly similar, both having high melting stoichiometric compounds at about 75 atom percent lithium, and both having the lowest melting eutectic compositions with about 15 atom percent lithium. The eutectic $Li_{0.17}Pb_{0.83}$ melts at 235°C and the eutectic $Li_{0.14}Bi_{0.86}$ melts at 243°C. The lowest melting point in the Pb-Bi phase diagram is that of the eutectic $Pb_{0.437}Bi_{0.563}$, which is 125°C. Considering the chemical similarities of lead and bismuth and their similar behavior with binary lithium alloys, it was then supposed that additions of ten to twenty atom percent lithium to the binary lead-bismuth eutectic should produce a low-melting ternary alloy,[4] i.e., $Li_{0.1}Bi_{0.5}Pb_{0.4}$. It is expected that this ternary alloy should have low lithium activity and, therefore, have low chemical reactivity with oxidizing media. For example, it should not vigorously react with water. In addition, the ternary alloy should have very low solubility for hydrogen (and tritium). Described below is the preparation of the ternary alloys and measurement of the melting points. Also presented are the key results of qualitative tests of the reactivity of these alloys with water.

Experimental

The experimental procedures used for preparation of and studies of the ternary alloys are described in detail in a separate report.[6] Lead and bismuth of 99.999% stated purity were melted and filtered in a helium glovebox having a measured moisture level of 0.4 ppm. The lithium was purified by melting, skimming, and bottom-pouring in the helium glovebox. Samples of approximately 200 mg were prepared by weighing stoichiometric amounts of the three purified metals into 304 stainless steel cups. The steel cups weighed about

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1.4 g. The samples were weighed in the glovebox on an analytical balance calibrated to ≤0.0002 g. They were then heated for approximately three hours at 500°C, cooled and taken to the differential thermal analysis (DTA) unit in a sealed jar.

The samples were then placed in a Rigaku TG-2000 DTA, whereby they were briefly exposed to air. The DTA was operated with a helium purge. The samples were heated to approximately 200°C and cooling curves were determined. The samples were then heated to temperatures from 300°C to as high as 600°C in order to ensure that no high-melting phases were present. Repeated cycling was found to gradually lower the melting points in some instances, possibly owing to oxidation of lithium. The DTA temperatures were calibrated against potassium nitrate (m.p. 128°C) and indium (m.p. 156°C) standards. Indium was used as the reference sample.

The qualitative reactivity of the ternary alloys was tested by heating samples and dropping them into preheated water. This method has been previously described.[7] The samples, weighing about 90 g, were heated to 500°C and dropped into a 1.4 ℓ volume of water preheated to approximately 90°C. The tests were recorded on high-speed (240 frames per second) color film.

Results and Discussion

The measured freezing points for various additions of lithium to the binary lead-bismuth eutectic are shown in Fig. 1. Upon cooling, two distinct peaks were observed for all samples which contained lithium. The higher curve is the upper limit of the liquid and solid region, i.e., the liquidus curve. The lower curve represents freezing of the eutectic.

The melting curves consistently showed only one peak, occurring at about 126°C. This suggests that the measured liquidus point may have some sub-cooling i.e., the true liquidus may be higher than the measured values in Fig. 1. Two types of experimental variables were used to assess this possibility. First, the temperature scan rate, routinely at 5°C per minute, was varied from 2.5°C per minute to 10°C per minute. Over this range, the measured liquidus peak did not change. Secondly, by repeated cycles of cooling, melting, and cooling again it was possible to reproduce the liquidus freezing point within 1°C. It is, therefore, believed that the degree of sub-cooling is small, probably less than 5°C.

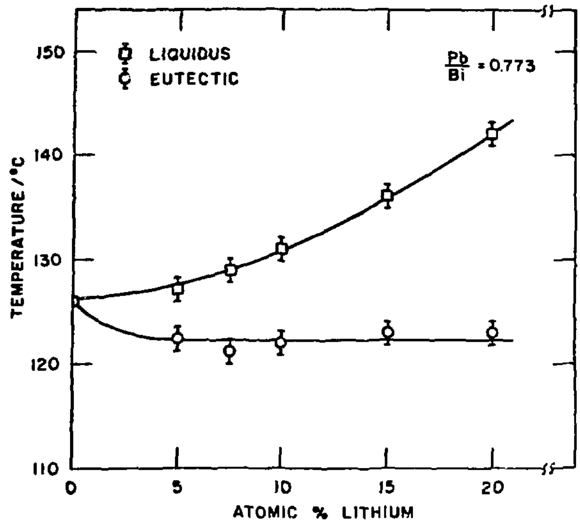

Fig. 1. Summary of observed phase changes.

The chemical reactivity of the ternary alloys with water was tested by heating samples to about 500°C and dropping them into ~90°C water. The results are shown in Table 1. Although there was little evidence of chemical reaction, in one of the tests a vapor explosion occurred. However, the vapor explosion could not be reproduced in two additional attempts. It is noted that such physical processes as vapor explosions can occur between systems such as lead and water.

Table 1. Results of the Drop Tests*

Drop #	Atom % Li	Weight	Alloy Temp.	Water Temp.	Observations
SB-15	10	89.84 g	495°C	88°C	Vapor Explosion
SB-16	0	91.55 g	503°C	92°C	Minimal Effects
SB-17	10	89.46 g	504°C	93°C	Minimal Effects
SB-18	10	93.38 g	500°C	93°C	Minimal Effects

*Pb/Bi = 0.773.

Neutronically, bismuth should be quite similar to lead with respect to neutron attenuation and neutron multiplication properties. Bismuth-lead alloys having as little as five to ten atom percent lithium should be excellent tritium breeding media but some enrichment of the lithium-6 may be required.

Bismuth has two significant problems with respect to its use as a fusion reactor tritium breeder. First, resources are very limited, to the extent that there is sufficient bismuth for only a few fusion reactors and, therefore, Li-Pb-Bi could not be used for commercial reactors. Still, the ternary alloys could be used in experimental reactors (e.g., INTOR[1]) or for irradiation and out-of-pile engineering tests. The second problem is that neutron irradiation of bismuth will produce significant quantities of polonium isotopes (e.g., ^{210}Po, a high-energy α-emitter). (The amounts of polonium isotopes have not been quantitatively determined.) While this is not a question of feasibility, it is an unattractive feature, particularly for large-scale application. Overall, it appears that the ternary Li-Pb-Bi alloys are interesting candidates for limited application for near-term fusion reactors or for small-scale nuclear and non-nuclear test simulations.

Conclusions

Liquid Li-Pb-Bi alloys are interesting candidates for use in a near-term reactor or for blanket simulations. In terms of chemical reactivity and hydrogen solubility, they should be quite similar to Li-Pb alloys, e.g., $Li_{0.17}Pb_{0.83}$. The added feature of low melting point is quite attractive. For example $Li_{0.1}Pb_{0.4}Bi_{0.5}$ melts at about 130°C. If corrosion at higher temperature is a concern for this material, one could operate at temperatures about 100°C lower than for $Li_{0.17}Pb_{0.83}$ and about 50°C lower than lithium. Neutronically, bismuth is similar to lead. Thus $Li_{0.1}Pb_{0.4}Bi_{.5}$ is expected to have excellent tritium breeding and neutron attenuation properties. There are, however, areas of significant concern. Bismuth reserves are very limited, so that the ternary alloys could only be used in a few experimental reactors such as INTOR. Bismuth produces significant quantities of polonium isotopes (e.g., ^{210}Po) with neutron irradiation. This potentially severe effect has not been quantified.

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