Thermal Properties and Corrosiveness of Eutectic LiF-PbF₂ Melt

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Abstract

Thermal data of eutectic LiF-PbF₂ melt, i.e., specific heat, heat of fusion and entropy of fusion, have been measured with DSC and given in tabular form. The results of corrosion tests for various metals and alloys in eutectic LiF-PbF₂ melt under a helium atmosphere at 700 °C show that the ionization tendencies of materials are in the following order:

Another type of a corrosion test, such as a long-run corrosion test for copper loop, has also been performed.

1. INTRODUCTION

In the fusion reactors, which use a deuterium-tritium fuel, a blanket is required to breed tritium. Liquid Li compounds, e.g., molten alloys (Li-Pb and Li-Bi-Pb), binary molten salt (LiF-BeF₂) and also liquid Li alone have been proposed as tritium breeding materials, as well as solid ones. Materials in the liquid state are not suffered from irradiation damage nor from phase transition and have high

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thermal conductivities. In addition to that, molten salt offers much less pumping load than liquid metals do under a high magnetic field. Among salts containing Li, LiF is a prominent candidate as a molten blanket material. However, since LiF has a high melting point (1115 K), another component should be added to obtain a moderate operating temperature. As such additives, a compound containing a neutron multiplier, e.g., Be and Pb, is favourable.

In the foregoing works on the properties of molten LiF-PbF₂ salts, the revised phase diagram of this system and the recovery behaviour of tritium from neutron-irradiated LiF-PbF₂ pellets as a function of temperature have been extensively elucidated^{1,2}. At present, however, information on thermal properties of eutectic LiF-PbF₂ melt and the materials for a container of eutectic LiF-PbF₂ melt, is required for further progress of the fusion reactor technology. There are no published data on specific heat of eutectic LiF-PbF₂ melt to be used in blanket and on corrosion rates of corrosion-resistant materials in eutectic LiF-PbF₂ melt. This is the reason why the present work is carried out.

2. EXPERIMENTAL

Materials

Super pure quality LiF and PbF₂ were purchased from Merck and dried in vacuo at 180°C for 20 hr before use for measurement of thermal property, e.g., specific heat. Reagent-grade LiF and PbF₂ from Wako Junyaku and from Morita Chemical were found to be adequate to use without further purification in finding corrosion-resistant materials.

Apparatus

Specific heat measurements were carried out with a Perkin Elmer Model DSC-2 differential scanning calorimeter. A mixture of LiF and PbF₂ with a eutectic composition (40 mol % LiF-60 mol % PbF₂), 9.6 mg in weight, was placed in a gold pan. A sample with known specific heat, e.g., alumina (28.7 mg), was used as an external standard. The use of the external standard simplifies the experimental operation and increases its accuracy. The temperature was calibrated by the use of metal indium (In : m.p.=156.6 °C) and potassium chromate (K₂CrO₄ : m.p.=670.5 °C). All the experiments were carried out under a nitrogen atmosphere. A noise which appeared in the chart of DSC was removed satisfactorily by drying LiF-PbF₂ before run. The heat of fusion of

eutectic LiF-PbF_2 melt was also determined by means of DSC. In this case, the metal indium, the heat of fusion of which has been known accurately, was chosen as an external standard.

The test on finding materials for the container was achieved by the use of a crucible for the corrosion test, as shown in Fig. 1. At the bottom of a SiO_2 tube a silicone rubber plug was mounted, through the plug two fine silica tubes for gas inlet and outlet, and a copper tube for a chromel-alumel thermocouple were inserted. The crucible for the corrosion test was placed on an alumina pedestal supported with a copper bipod. The corrosion test was performed under a helium atmosphere. After each run the salt mixtures were dissolved into aqua regia and the resultant solution was analyzed with a Varian Techtron Model 100 atomic adsorption spectrophotometer. The reduction of crucible

Fig. 1 Apparatus used in the corrosion test of crucibles.

Table 1. Heat capacity (C_p), heat of fusion (ΔH_{fus}) and entropy of fusion (ΔS_{fus}) of eutectic LiF-PbF_2 melt.

	C_p (J/mol K) 660~720 °C	ΔH_{fus} (kJ/mol) 580 °C	ΔS_{fus} (J/mol K) 580 °C
LiF-PbF_2 (PbF_2 :59~62mol%)	91.3 ± 9.6	17.37 ± 0.88	20.22 ± 1.00

wall thickness was estimated from the analytical results. The long-run test was carried out

by the use of a loop made of the material chosen in the corrosion test. Such a loop filled with LiF-PbF_2 eutectic melt was heated for about 80 hr at 740°C under the helium atmosphere in the furnace providing temperature gradients about 60°C in the vertical and about 20°C in the horizontal. The loop used and the whole experimental assembly arranged in the furnace cavity are respectively shown in Figs. 2a and 2b.

Fig. 2 Apparatus used in the corrosion test of a loop (a) and a copper loop (b).

3. RESULTS AND DISCUSSION

Thermal properties of eutectic LiF-PbF_2 melt

The experimental specific heat of eutectic LiF-PbF_2 melt over the temperature range of $660\sim 720^\circ\text{C}$ is summarized in Table 1. The

present value of specific heat for eutectic LiF-PbF_2 melt is slightly higher than that calculated from the published value for LiF (64.4 J/mol K) and that for PbF_2 (100.4 J/mol K). In view of the high volatility of PbF_2 at high temperature, it is not surprising that the obtained value of specific heat shows less accuracy, an error being as much as 10 percent. The entropy of fusion was calculated from the observed heat of fusion and is listed in Table 1.

Corrosion rates for various metals and alloys

Materials, such as brass, SUS 304, monel, nickel, copper, and phosphorous bronze, were selected for the corrosion test. In the case of alloy, the dissolution of less noble elements in alloy owing to the corrosion is much easier than that of noble metal. The reduction of wall thickness of crucible, therefore, was calculated from the obtained analytical value of less noble component of the alloy in the eutectic LiF-PbF_2 melt at 700°C . The experimental results are

summarized in Fig. 3; it shows that the pure copper is the most favourable corrosion-resistant material for a container of eutectic LiF-PbF_2 melt although the pure nickel is also favourable. Since the monel metal provided commercially contains a small amount of Mn and Fe besides the alloying element Cu, the calculated value of the reduction of wall thickness is based on the analytical values of

both Mn and Fe. The calculated value based on the Mn content in eutectic LiF-PbF_2 melt agreed with that based on the Fe content. Therefore, it would follow that an ionization tendency of Mn in eutectic LiF-PbF_2 melt at 700°C is almost identical to that of Fe. The result of SUS 304, in which chromium is considered to be the least noble component, is also shown in Fig. 3. When we assume that the activities of less noble components in alloy are unity, it is reasonable to estimate that the ionization tendencies of various components of tested alloy in eutectic LiF-PbF_2 melt at 700°C are in

Fig. 3 Corrosion of various metals and alloys (crucible test).

the following order:

It should be noted that although Mn may be in much less noble position according to the standard free energy of formation listed in Table 2^{3,4)}, such an

Table 2. Standard free energies of formations per gram atom of fluorine ($\Delta G_{f, \text{F}_2}$) for various metal fluorides at 1000 K^{3,4)}.

Metal Fluoride	$\Delta G_{f, \text{F}_2}$ $\times 10^2$ (kJ/g atom of F)
CuF ₂	-2.0
NiF ₂	-2.5
PbF ₂	-2.7
FeF ₂	-2.7
FeF ₃	-2.9
MnF ₂	-3.3
CrF ₂	-3.1
ZnF ₂	-3.0

order is shown to be of nearly the same order derived from standard free energies of various metal fluorides, except for tin fluoride, at 1000 K.

Before leaving this corrosion test we mention briefly the

long-run test of the copper loop. The obtained result for the loop test is shown in Fig. 4, together with the result for the crucible test. The corrosion of the loop shows a slightly higher value than that for the crucible. This is merely because the average temperature at which the loop test has been carried out, highest and lowest temperature being 780 °C and 700 °C respectively, is higher than that at which the

Fig. 4 Comparison of the crucible test with the loop test.

crucible test has been achieved. Thus, no substantial difference between the loop test and the crucible test is observed.

We should finally stress a nuclear reaction of copper induced by a neutron. Various nuclear reactions of copper induced by both fission (thermal) and fusion (14 MeV) neutrons are given in Table 3^{5,6)}. Newly constructed fusion machines, e.g., JT-60 (JAERI Tokamak-60), JET (Joint European Torus), and TFTR (Tokamak Fusion Test Reactor), are operated intermittently; these are known as puls-operated fusion machines. Radioactive isotopes with long half-lives, i.e., ^{63}Ni and ^{60}Co , are not likely to be produced significantly. From a cross

Table 3. Nuclear reactions induced by fission (thermal) and fusion (14 MeV) neutrons^{5,6)}.

Energy of Neutron	Type of Reaction	Cross Section (barn)	Half-life
Thermal	$^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}$	3.9 ± 0.8	12.8 hr
	$^{65}\text{Cu}(n, \gamma)^{66}\text{Cu}$	1.8 ± 0.4	5.14 min
14 MeV	$^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}$	0.0025 ~0.004	12.8 hr
	$^{65}\text{Cu}(n, 2n)^{64}\text{Cu}$	0.9~0.97	12.8 hr
	$^{65}\text{Cu}(n, p)^{65}\text{Ni}$	0.0021 ~0.029	2.56 hr
	$^{63}\text{Cu}(n, 2n)^{62}\text{Cu}$	0.5~0.56	9.8 min
	$^{63}\text{Cu}(n, p)^{63}\text{Ni}$	0.0016 ~0.12	92 y
	$^{63}\text{Cu}(n, \alpha)^{60}\text{Co}$	0.0013 ~0.038	5.26 y

section listed in Table 3, it is found that the produced radioactive isotopes are ^{62}Cu and ^{64}Cu . Both radioactive isotopes, however, have the short half-lives. It means that induced radioactivity decreases rapidly after a shutdown of pulsed operation. We can

, thus, say that the copper is the most promising material for the container of eutectic LiF-PbF_2 melt.

4. CONCLUSION

Thermal data of eutectic LiF-PbF_2 melt, i.e., specific heat, heat of fusion, and entropy of fusion, have been measured with DSC and are given in tabular form. The pure copper has been found from the results of corrosion test to be the most favourable corrosion-resistant material in eutectic LiF-PbF_2 melt at 700 °C. On the basis of the results of the corrosion test for various materials, it was also found that the ionization tendencies of various materials in

eutectic LiF-PbF_2 melt at 700°C are in the following order:

Another type of corrosion tests, such as the long-run corrosion test for copper loop, has also been performed, indicating no difference between the results of the crucible test and the loop test for the corrosion of copper.

In addition to the corrosion resistance of copper, good nuclear property of copper, i.e., short half-lives of copper isotopes produced under irradiation, has been stressed.

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