—Communication—

Eutectic Composition and Temperature of the $\text{LiF}-\text{BaF}_2-\text{MgF}_2$ System and Liquidus Temperature of the $(\text{LiF}-\text{BaF}_2-\text{MgF}_2)_{\text{eutectic}}-\text{ZrF}_4$ System

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1. Introduction

In the IFR (Integral Fast Reactor) concept, metal or metal alloy fuels such as U-Pu-Zr are proposed and the spent fuel is expected to be reprocessed by electrolysis in the molten chloride system. Although melting points of metal fluorides are generally higher than those of corresponding chlorides, Li, Mg or Ba fluorides are much less hygroscopic than their chlorides. Moreover, according to Hamer et al.¹⁾ molten fluoride system may offer larger difference of decomposition potential between objective metal ion and supporting metal ones than chloride melts. We initiate the work in the hope that the ternary system of $\text{LiF}-\text{BaF}_2-\text{MgF}_2$ with eutectic composition shall be used as a supporting electrolyte on electrowinning of Zr in the molten fluoride system. In our system, Zr is extracted into the molten salt from molten Zn metal in a graphite crucible and effectively recovered without disproportionation with Zr^{2+} ($\text{Zr}^{4+} + \text{Zr}^{2+} \rightarrow 2\text{Zr}^{3+}$).²⁾ For this purpose we determined the eutectic composition and temperature of this system by

differential scanning calorimetry (DSC). Then we measured the liquidus temperature of the quasi binary system $(\text{LiF}-\text{BaF}_2-\text{MgF}_2)_{\text{eutectic}}-\text{ZrF}_4$.

2. Experimental

Used chemicals were analytical reagent grade (LiF : Merck >99.9%; BaF_2 : Central Glass >99.9%; MgF_2 : Morita Chemicals >99% and ZrF_4 : Central Glass >99.9%). The thermal analysis was carried out by Parkin-Elmer DSC-2, which was calibrated by In and K_2CrO_4 . Samples pulverized under Ar atmosphere in a glove box were charged in Au pans and sealed. During these experiments N_2 gas flowed.

Solidified samples in the Au pan could not be easily dissolved by water. To use the Au pan repeatedly, solvent to dissolve the solidified sample was searched.

3. Results and Discussion

In the light of Bukhalova and Belezhnaya's phase diagram³⁾ the lowest eutectic temperature was searched, then we obtained $\text{LiF} : \text{BaF}_2 : \text{MgF}_2 = 59.1 : 15.9 : 25.0$ with eutectic temperature of 911K, which is slightly different from Bukhalova and Belezhnaya's results, i.e., $\text{LiF} : \text{BaF}_2 : \text{MgF}_2 = 52.8 : 21.7 : 25.5$ with the eutectic temperature of 927K. Solidified sample of the $\text{LiF}-\text{BaF}_2-\text{MgF}_2$ system is not easily dissolved by water. Some molten salts such as KHSO_4 and aqueous solutions were tested to dissolve the sample, so that we found that the sample is completely dissolved by highly concentrated aqueous solution of

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AlCl_3 with small amount of HCl at about 380K. Dissolution rates of other samples are listed in Table 1 and 2.

Liquidus temperatures of the quasi binary system $(\text{LiF}-\text{BaF}_2-\text{MgF}_2)_{\text{eutectic}}-\text{ZrF}_4$ were also determined. The liquidus temperature of this system is depicted in Fig. 1. We estimated the eutectic composition and temperature of this system $\text{LiF} : \text{BaF}_2 : \text{MgF}_2 : \text{ZrF}_4 = 35.5 : 9.5 : 15.0 : 40.0$ and 777K. Fig. 1 shows us that the liquids temperature of this system probably increases with increase of ZrF_4 near $\text{ZrF}_4 = 0$. Then effective extraction of Zr from the Zn melt might require previous addition of ZrF_4 , depending on an operating temperature.

References

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Table 1 Dissolution rate of $\text{LiF}-\text{BaF}_2-\text{MgF}_2$ by molten salts

Salt	T/K	t/min	k/wt%
KHSO_4	573	5	16
$\text{KNO}_3-\text{NaNO}_2$	773	10	31
NaNO_3	793	15	72
	793	28	98
$\text{LiNO}_3-\text{KNO}_3$	823	10	72
KNO_3	573	5	13

Table 2 Dissolution rate of $\text{LiF}-\text{BaF}_2-\text{MgF}_2$ by aqueous solutions

Salt	T/K	t/min	k/wt%
$\text{Al}_2(\text{SO}_4)_3$	378	10	9
$\text{AlCl}_3 + \text{HCl}$	379	10	100

Fig. 1 Liquidus temperature of the $(\text{LiF}-\text{BaF}_2-\text{MgF}_2)_{\text{eutectic}}-\text{ZrF}_4$ system.