

Thermoanalytical investigation of fluoride composites for latent thermal storage ^α

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Abstract

Latent thermal storage is promising for space applications because of its high storage density. In the present study, we investigated promising fluoride storage materials and their composites with porous media by heat flux differential scanning calorimetry (DSC). Specially designed sample pans were used for the measurements of heat of fusion. A discussion is included on the supercooling and heat of fusion for LiF, LiF–CaF₂, LiF–MgF₂, and their composite materials with porous silicon carbide or carbon.

INTRODUCTION

Latent thermal storage has the possibility of quite high storage density. Among several thermal storage techniques, it is therefore the most promising for space use at high temperatures, such as solar dynamic power generation and material production. In the research and development of latent thermal storage systems, appropriate storage materials with a high heat of fusion must first be developed. The melting temperatures of the storage materials should match the operation temperatures of the systems considered. For example, Brayton cycle and Stirling cycle solar dynamic power generation systems require storage materials with melting temperatures around 1000 K.

In order to improve heat transfer in latent thermal storage units, composite storage materials of molten salt with ceramics have been proposed [1,2]. Composites of molten carbonate with oxide ceramics are candidates for waste heat recovery. Petri et al. [1] demonstrated the good heat transfer characteristics of direct heat exchange between heat transfer gas and carbonate/ceramics composites.

For space use at high temperatures, such as solar dynamic power generation, lithium fluoride and its eutectics are promising [3]. We proposed

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composite materials of molten fluorides and porous silicon carbide [4] or porous carbon [5] in order to reduce the specific mass of the storage unit and the mechanical stress of the container arising from volume change on fusion, and also to enhance thermal conduction within the storage materials.

In the present study, a thermoanalytical investigation was carried out on candidate fluoride salts and their composites with silicon carbide or carbon.

EXPERIMENTAL

Samples

The salts (LiF, CaF₂ and MgF₂) used for the present study are listed in Table 1 together with the mixtures and the composites prepared. For LiF, materials from three different sources and with different purities were used to investigate the effect of purity on the latent heat. The salts were used without further purification.

Eutectic salts were prepared as follows. The component salts obtained from Aldrich Chemical Co., Inc. were first weighed to obtain the eutectic composition, and about 1 g of the mixture was melted and then cooled

TABLE 1

Purity and composition of samples

(a) Single salts

Material	Purity (%)
LiF (Aldrich Chemical Co., Inc.)	99.99
LiF (Rare Metallic Co., Ltd.)	99.9
LiF (Soekawa Chem. Co., Ltd.)	99.9
CaF ₂ (Aldrich Chem. Co., Inc.)	99.95
MgF ₂ (Aldrich Chem. Co., Inc.)	99.95

(b) Composites and mixtures ^a

Material	Molten salt (wt.%)
LiF/SiC ^b	34.6
LiF/C-1 ^c	-
LiF/C-2 ^c	-
LiF-CaF ₂ (80.5-19.5 mol.%)	100
LiF-CaF ₂ (80.5-19.5 mol.%) / SiC ^b	24.4
LiF-MgF ₂ (67-33 mol.%)	100
LiF-MgF ₂ (70-30 mol.%)	100

^a LiF from Aldrich Chemical Co., Inc. (99.99% purity) is used.

^b Composite materials.

^c LiF/C-1 and LiF/C-2 are composites with the carbon surface-treated by CVD of SiC at high and low deposition rates, respectively.

slowly in a nitrogen atmosphere. About 10 mg of the eutectic mixture was used for each DSC measurement.

Porous silicon carbide (β -SiC) with pores several micrometers in diameter was supplied by Ividen Co., Ltd., and porous carbon was supplied by Mitsubishi Pencil Co., Ltd.

Preparation of composites

The composite with silicon carbide was easily formed by dipping the carbide into the molten fluorides in a nitrogen atmosphere. However, it was difficult to form the composite with porous carbon owing to its low wettability. We tried to improve the wettability by such treatments as

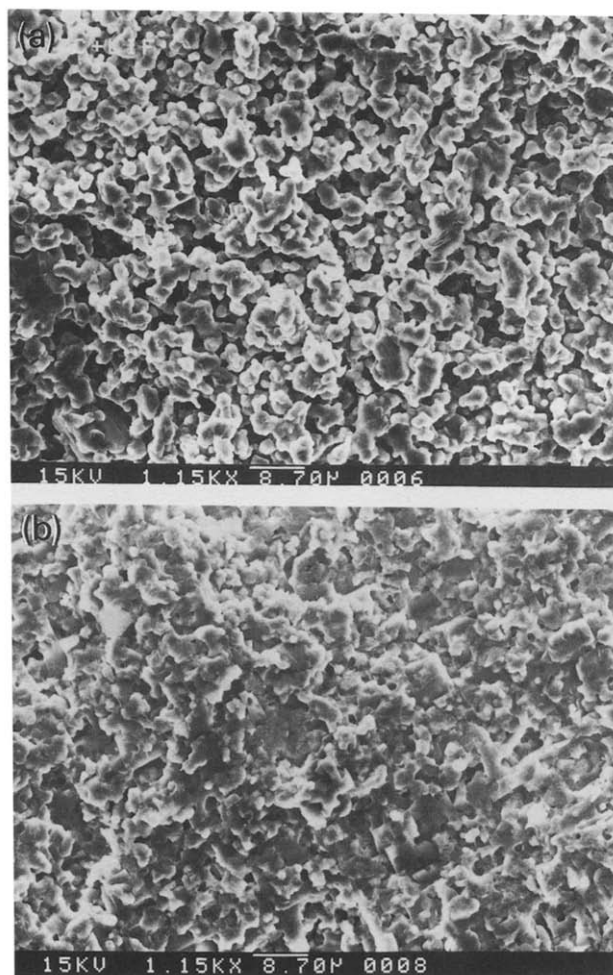


Fig. 1. SEM micrographs of (a) porous SiC and (b) the LiF/SiC composite.

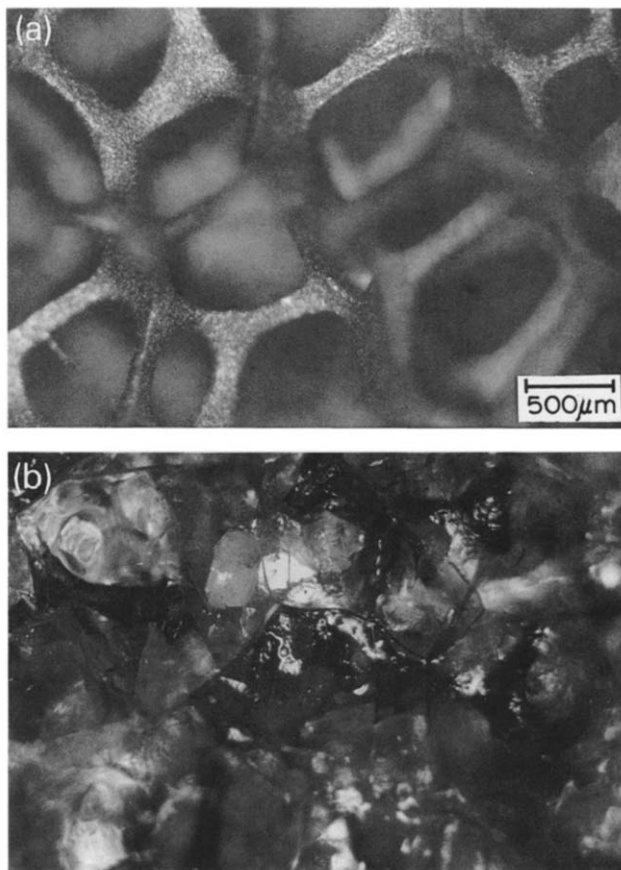


Fig. 2. Micrographs of (a) porous carbon and (b) the LiF/C-2 composite.

oxygen sputtering, boiling in nitric acid, etc. Only formation of silicon carbide by chemical vapor deposition (CVD) was successful. Two types of CVD treatment were applied: high and low deposition rates. A larger amount of silicon carbide was deposited on the porous carbon at the high deposition rate.

LiF/C-1 and LiF/C-2 are the composites produced with the carbon treated at high and low deposition rates, respectively. Figure 1 shows the images of scanning electron microscopy (SEM) for the LiF/SiC composite of 34.6 wt.% LiF together with the porous SiC. As can be seen from the figure, the composite is formed uniformly. We confirmed the uniformity also by energy dispersive X-ray analysis (EDX). The micrographs of the composite with porous carbon are also shown in Fig. 2.

Apparatus

A TG-DTA apparatus (Rigaku Denki Co., Ltd.) and a heat flux DSC instrument (Perkin-Elmer DTA 1700) were used. Since the fluoride salts

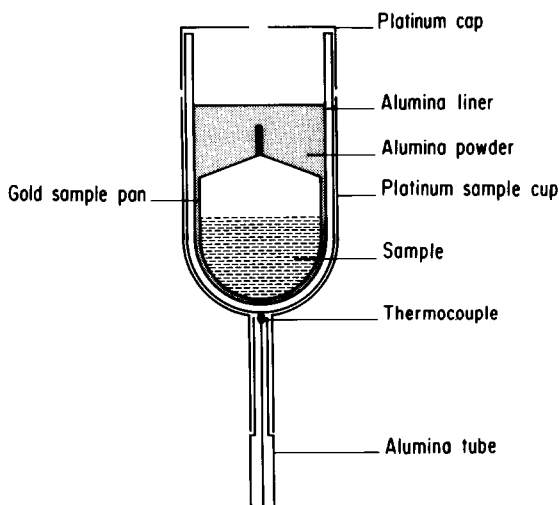


Fig. 3. Sealed gold sample pan and arrangement around the sample pan in DSC.

usually have a high vapor pressure and they readily creep up in a sample pan at high temperatures, we evaluated various kinds of sample pan for use in the DSC measurements. Some of the samples were sealed in a gold sample pan specially made to fit inside the alumina liner supplied by Perkin-Elmer. Some were measured in an open sample pan made of graphite, which is compatible with molten fluoride salts and prevents creep.

Figure 3 shows an example of the arrangement around the sample pan. In this case, LiF was sealed in the gold sample pan and put into an alumina liner. The gold sample pan was covered with fine alumina powder to make the radiation heat flux from the sample uniform. We also made a platinum cap to cover the platinum sample cup. The use of the platinum cap was confirmed to be quite effective in making the radiation heat flux uniform and in obtaining reproducible measurements.

Temperature calibration was made using standard materials: indium, tin, lead, zinc, aluminum, silver and gold. The proportionality constant of the apparatus was determined for each kind of sample pan. The measurements

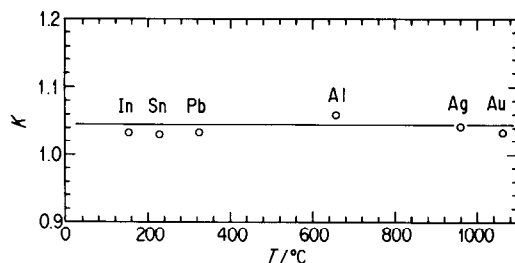


Fig. 4. Proportionality constant of DSC.

of heat of fusion with an alumina sample pan on the above standard materials showed that the proportionality constant is almost temperature independent at least between 400 and 1200 °C, as shown in Fig. 4. An NBS SRM-760 (K_2CrO_4) was used to determine the proportionality constant for other sample pans. The measurements were made at heating and cooling rates of 10 K min^{-1} under nitrogen gas flow.

We also made microscopic observation of the LiF–SiC composite under controlled heating and cooling conditions with the MS–VHE of Shinku Riko, Inc.

RESULTS

DSC curves are shown in Figs. 5, 6, 8 and 10; melting and solidification temperatures and heats of fusion are plotted against the cycle number in Figs. 7 and 9.

Lithium fluoride

The melting and solidification temperatures and heats of fusion of samples with different purities are listed in Table 2. Although the melting temperatures are almost the same, the heats of fusion show a slight difference. The difference exceeds the experimental error, so that it seems to be due to the difference in the purity of the samples. As can be seen from Fig. 5, the DSC peak is broad for the samples of 99.9% purity. Their heat of fusion is, however, still high from a practical viewpoint.

Figure 6(a) shows DSC curves of LiF with 99.99% purity at the second and 25th runs. The LiF was sealed in a gold sample pan in this case. As can be seen, supercooling did not take place and the shapes of the melting and

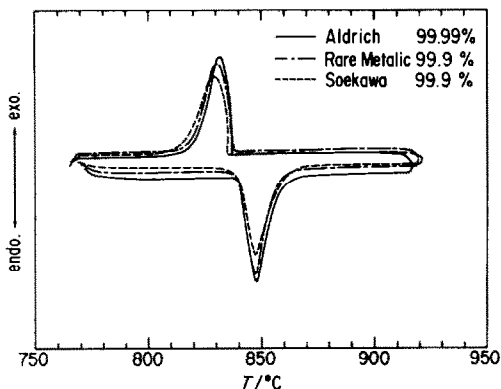


Fig. 5. DSC curves for LiF of different purities measured with a sealed gold pan.

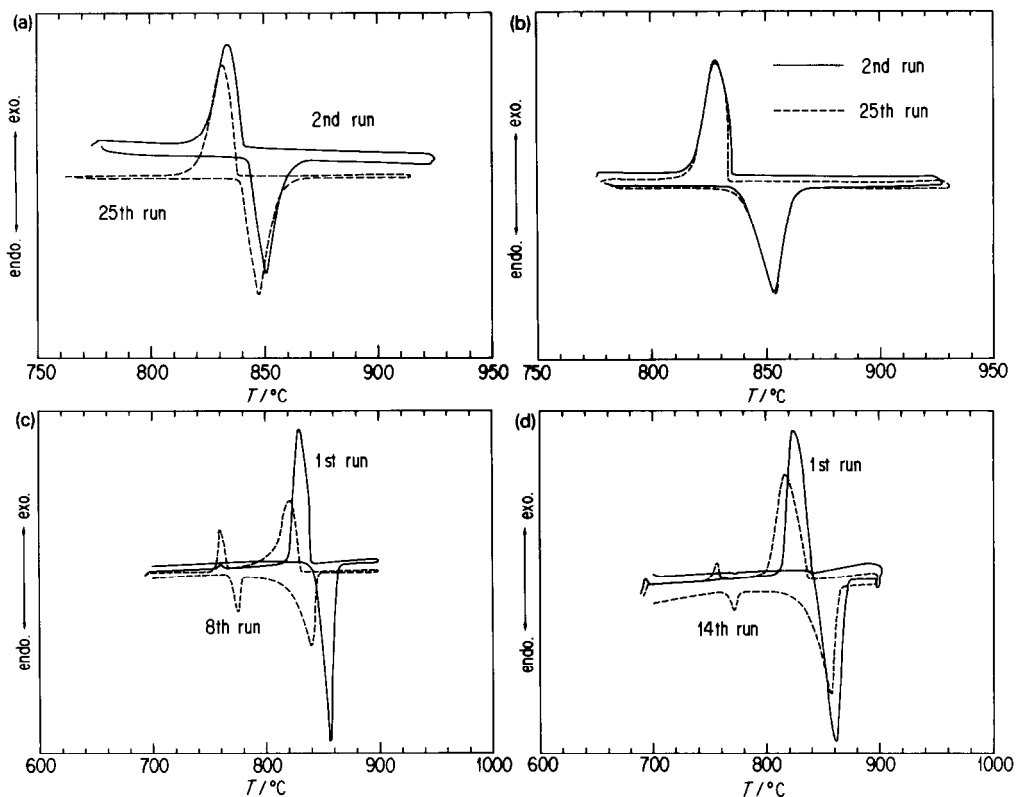


Fig. 6. DSC curves for (a) LiF of 99.99% purity, (b) LiF/SiC composite, (c) LiF/C-1 composite, and (d) LiF/C-2 composite. The curves in (a) were measured with a sealed gold pan, and those in (c) and (d) were measured with an open graphite pan.

solidification peaks were unchanged during 25 heating and cooling cycles. The melting and crystallization temperatures and heat of fusion were almost unchanged (Fig. 7(a)).

When the measurements on LiF were made with an open graphite pan, the heat of fusion slightly decreased. The decrease was easily explained from the weight loss due to the high vapor pressure of LiF at high temperatures.

TABLE 2

Melting temperature and heat of fusion of different LiF specimens

Material	T_m ($^\circ\text{C}$)	Δh_m (kJ kg^{-1})
LiF (99.99%), Aldrich	844.8	1015
LiF (99.9%), Rare Metallic	844.4	991
LiF (99.9%), Soekawa	843.5	956

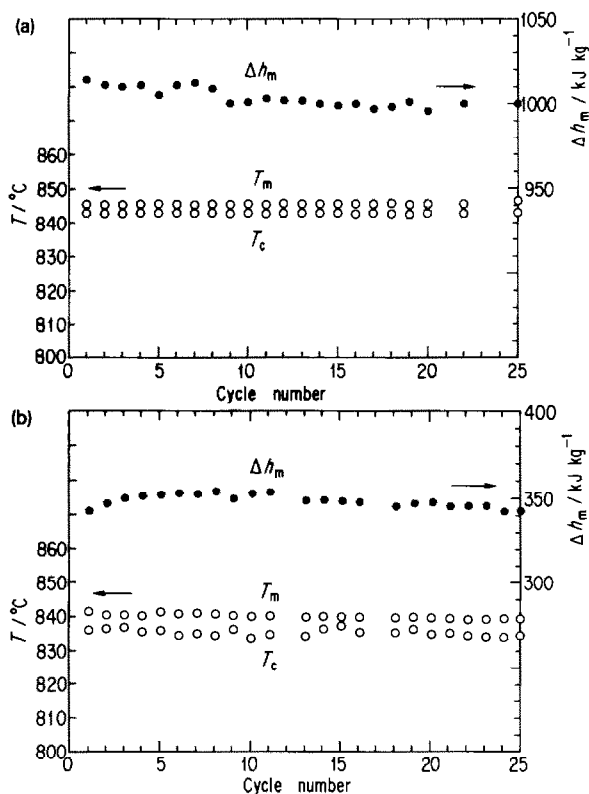


Fig. 7. Change in heats of fusion and melting and solidification temperatures vs. cycle number of heating and cooling for (a) LiF and (b) LiF/SiC composite.

LiF/SiC composite

DSC measurements were made on the composite of LiF and SiC using an open graphite sample pan. The results at the second and 25th runs are shown in Fig. 6(b). The shapes of the melting and solidification peaks were a little broader than those for LiF only (Fig. 6(a)), but they were almost unchanged during 25 cycles of heating and cooling. The melting and crystallization temperatures and heat of fusion were almost unchanged also in this case (Fig. 7(b)). These facts suggest that the composite is chemically and thermally stable.

Preliminary TG-DTA experiments showed that the peak shape was deformed when air was not completely removed from the apparatus before starting the flow of nitrogen gas. The deformation is due to the reaction of LiF with SiC and oxygen.

We also made microscopic observations of the composite during heating and cooling. During melting, a small amount of molten LiF came out of the

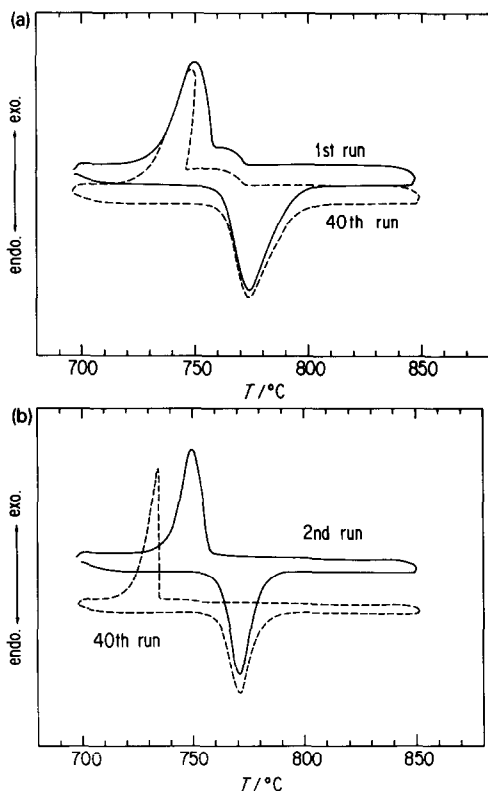


Fig. 8. DSC curves for (a) LiF-CaF_2 and (b) $(\text{LiF-CaF}_2)/\text{SiC}$ composite measured with an open graphite pan and a sealed gold pan, respectively.

porous SiC. However, LiF was absorbed during solidification, i.e. the porous media can keep molten fluoride in the small open pores.

LiF / C composite

Melting and solidification peaks were sharp at the first run; however, another peak appeared in a lower temperature region and its area gradually increased during repeated melting and solidification cycles. At the same time the area of the main peak decreased, as shown in Fig. 6(c) (LiF/C-1) and Fig. 6(d) (LiF/C-2). The melting temperature also decreased. Degradation of LiF/C-1 (high deposition rate of SiC) was more serious, as shown in the figures. After several cycles, separation of LiF from the carbon matrix was observed for both the composites. In order to clarify the reason for these phenomena, characterization of the carbon and the thin layer of SiC is necessary.

Eutectic LiF-CaF₂ mixture (80.5-19.5 mol.%)

DSC measurements were made on the eutectic mixture of LiF and CaF_2 using an open graphite sample pan. The melting temperature was de-

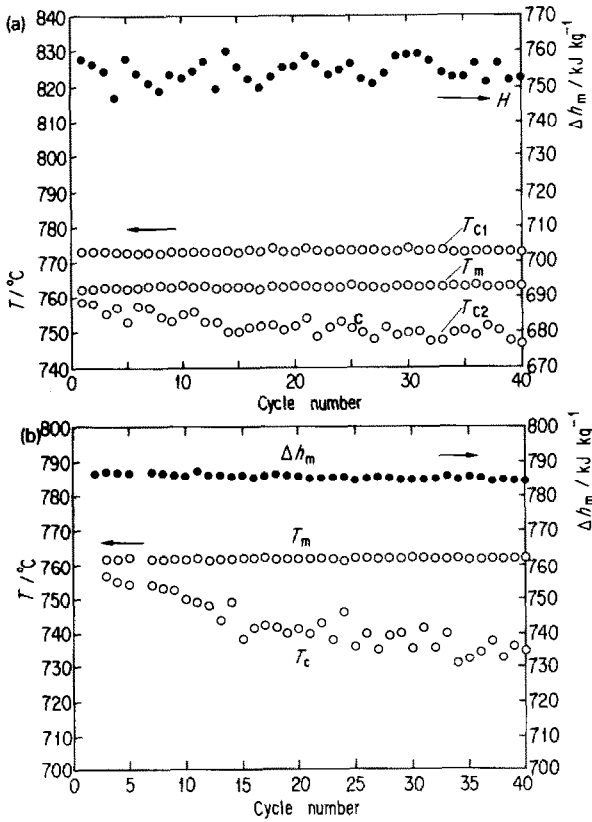


Fig. 9. Change in heats of fusion and melting and solidification temperatures vs. cycle number of heating and cooling for (a) LiF-CaF₂ and (b) (LiF-CaF₂)/SiC composite. T_{c1} and T_{c2} are the onset temperatures of the shoulder and the main part of the peak.

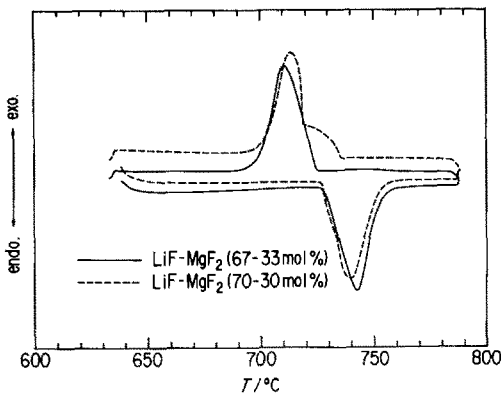


Fig. 10. DSC curves for LiF-MgF₂ (67-33 mol.%) and LiF-MgF₂ (70-30 mol.%) measured with an open graphite pan.

terminated to be 763°C from the DSC curve (Fig. 8(a)); however, the crystallization peak suggests a possibility that the composition prepared differed from the true eutectic composition. The onset temperature of the main peak decreased during repeated heating and cooling cycles (Fig. 9(a)).

(LiF–CaF₂)/SiC composite

The composite of LiF–CaF₂ and SiC was sealed in a gold sample pan and DSC curves were obtained for 40 cycles of melting and solidification (Fig. 8(b)). Supercooling was observed, although the heat of fusion was still unchanged. The degree of supercooling gradually increased (Fig. 9(b)).

LiF–MgF₂ mixtures (67–33 mol.% and 70–30 mol.%)

DSC measurements were made on two compositions: LiF–MgF₂ (67–33 mol.%) and LiF–MgF₂ (70–30 mol.%) (Fig. 10). According to the present study, the latter seems to be an off-eutectic composition since its curve showed a shoulder.

DISCUSSIONS

Supercooling

As can be seen in Figs. 6 and 7, LiF shows slight supercooling; however, this does not increase as the cycle number increases. The crystallization temperature of LiF–CaF₂ and of its composite with SiC, however, decreases greatly with increasing numbers of heating and cooling cycles. The melting temperature and the heat of fusion are almost constant. The reason for the large supercooling is not yet clear; further investigation is needed.

Heat of fusion

Heats of fusion of all the molten salts measured are listed in Table 3, together with the literature values and the estimated values on the assumption of the additivity of the entropy of fusion. The melting temperatures are also listed in the table. The present value of the heat of fusion of LiF of high purity is slightly smaller than the value given by Janz et al. [6].

The heat of fusion of LiF–CaF₂ (757 kJ kg⁻¹) was close to the value estimated on a simple assumption of the additivity of entropy of fusion (667

TABLE 3

Melting temperature, solidification temperature and heat of fusion of LiF, LiF-CaF₂, LiF-MgF₂, and their composites with porous SiC

Material	T_m^a (°C)		T_c^a (°C) Measured	Δh_m^a (kJ kg ⁻¹)		
	Meas- ured	Litera- ture		Meas- ured	Litera- ture	Calcu- lated ^c
LiF (99.99%)	845	848 [7]	841	1015	1037 [7]	
LiF/SiC	844		837	335		
LiF-CaF ₂ (80.5-19.5 mol.%)	763	765 [8]	774 ^b	757	820 [6]	656
LiF-CaF ₂ (80.5-19.5 mol.%) / SiC	762		758	174		
LiF-MgF ₂ (67-33 mol.%)	730	742 [10]	726	490	917 [9]	761
LiF-MgF ₂ (70-30 mol.%)	728	728 [6]	735 ^b	516	520 [6]	770

^a T_m , melting temperature; T_c , solidification temperature; Δh_m , heat of fusion.

^b Determined from the onset temperature of the solidification peak having a shoulder.

^c Calculated on an assumption of additivity of entropy of fusion.

kJ kg⁻¹), and it was reasonably high. This eutectic mixture should thus be a candidate for a latent thermal storage material for space use as well as LiF.

The data for LiF-MgF₂ (70-30 mol.%) were in good agreement with the value obtained by Misra [7], and less than the estimated value. LiF-MgF₂ (70-30 mol.%) showed a higher heat of fusion than LiF-MgF₂ (67-33 mol.%). The DSC peak of the former, however, has a shoulder, showing that the composition is off-eutectic. Anyway, it should be excluded from the candidate materials from a practical viewpoint.

Possible application of the composites as latent thermal storage materials

From the DSC measurements and microscopic observation, the composites of the fluoride salts with porous SiC proved to be candidates as latent thermal storage materials for space use: they are chemically and thermally stable in the temperature range between 750 and 900°C.

The composite with porous carbon treated by CVD of SiC, however, is not stable enough chemically. The reason for the appearance of the second peak in the DSC curve is not yet clear. Some reaction is to be expected if the SiC deposited on the surface of the carbon includes free silicon or SiO₂. In such a case, the optimum condition for CVD should be found. At the moment, the composite with porous carbon treated by CVD cannot be used as a latent thermal storage material.

CONCLUSIONS

We carried out DSC measurements on candidate fluoride latent thermal storage materials: LiF and eutectics of LiF-CaF₂ and LiF-MgF₂, and their composites with porous SiC or carbon.

Most of the materials showed only a few degrees of supercooling, but LiF–CaF₂ and its composite with SiC showed large supercooling, which increased with increasing numbers of heating and cooling cycles. This phenomenon should be investigated further.

Heats of fusion were determined from the DSC measurements. LiF and LiF–CaF₂ and their composites showed reasonably high heats of fusion. The heat of fusion of LiF–MgF₂ was, however, so low that it should be excluded from the candidate latent thermal storage materials for space use.

A novel concept of composite latent thermal storage materials between fluoride salts and porous SiC is promising. For the composite with porous carbon, further research effort is needed.

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