Anti-blocked Composite Material of MgSO₄×7H₂O - KAl(SO₄)₂×12H₂O for Thermal Energy Storage

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Abstract. The preparation and characterization of anti - blocked composite material consisting of $MgSO_4·7H_2O$ and $KAl(SO_4)_2·12H_2O$ for thermal energy storage are reported in the present article. The preparation is performed by co-melting method by adding $CaCO_3$ as the anti-blocking agent. The thermal properties of the composite are studied. The results show that: the phenomenon of phase separation disappears in the composite system during all the tested procedure for sample with the mass ratio of 9: 1; the enthalpy is about 800kJ / kg after 60 heating-cooling cycles; the solidifying temperature of this anti-blocked composite keeps almost unchanged. Thus, this composite material has the potential to be used as low temperature phase change thermal storage material.

Introduction

The advantage of phase change thermal storage material is its higher latent heat [1-2]. Therefore, it plays a significant role in some actual industries, such as aerospace, energy-efficient buildings, solar energy utilization, etc.

As to inorganic hydrated salts, they could be effective phase change thermal storage materials due to their higher latent heat of fusion and melting point arranging from a few degrees to more than a hundred degree, which includes metallic halide salts of alkali and alkaline earth metals, sulfates, phosphates, vinegar salt and other salt hydrate. However, there exists phase separation and super-cooling in sole component inorganic hydrated salt once melting. Because of these disadvantages, some improvements have been done to modify its property [3-5]. Kuznik prepared composite materials by combing zeolite and dehydrated $MgSO_4$, it found that the thermal storage density of this composite reaches to 45% of the theoretical value, and its property remains unchanged after some heating - cooling cycles [6]. Song studied the supercooling phenomena of $KAl(SO_4)_2·12H_2O$ by means of cold fingering and adding nucleating agent. The results showed that the supercooling of $KAl(SO_4)_2·12H_2O$ can be reduced to zero as 2% nucleating agent $MgCl_2·6H_2O$ added, meanwhile there is no change of the phase transition temperature of $KAl(SO_4)_2·12H_2O$ [7].

Wang et al used two types of hydrated salts to prepare a phase change material, which is stable and no phase separation [8]. Liang et al studied the melting behaviour of the binary hydrated salts system for cold storage by DSC test, it showed a higher phase change latent heat [9].

However, there is still blocking phenomenon in composite material of $MgSO_4·7H_2O$ and $KAl(SO_4)_2·12H_2O$ with some mass ratio [10], such as 9:1, etc.

In the present article, anti - blocked thermal storage composite material is prepared from $MgSO_4·7H_2O$ and $KAl(SO_4)_2·12H_2O$ by adding $CaCO_3$ powder as anti-blocking agent, and it is characterized by DTA, step cooling and heating – cooling cyclic tests, as well as heat release test. The co-melting is employed to perform the preparation. It aims to provide a technical support to the study of phase change thermal storage material at low temperature.

Preparation and Basic Test

Chemicals. The main chemicals include: $MgSO_4·7H_2O$, Tianli Chemical Reagent Co. Ltd., Tianjin, purity of 99%; $KAl (SO_4)_2·12H_2O$, Zhengzhou Paiey Chemical Reagent, Zhengzhou, purity of 99.5%; $CaCO_3$, Xi'an Chemical Reagent, Xi'an, purity of 99.5%.

Instruments. JJ124BC electronic balance (Max = 120g, Min = 20d, d = 0.1mg), DF-101S constant temperature heater with magnetic stirrer, a thermometer (apuhua TM-902C, −50°C ~ 1300°C, accuracy 0.1°C), HCT-1 differential scanning calorimetry balance, DZF-6030 vacuum oven, etc. are employed as experimental instruments.

Basic Properties of $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$. The experimental procedure is as follows,

(1) 10g of $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ is poured into the mill ground milling to fine powder, respectively, and then each fine powder is poured into individual test tube;

(2) Each filled test tube is placed in the thermostat heating magnetic stirrer with a constant temperature heater, and kept half an hour after the material fully melting;

(3) Each filled test tube is removed from the thermostat heating magnetic stirrer and stood at room temperature, its temperature data is recorded once every 10s, step cooling curve is drawn after the temperature tests;

(4) 10mg samples of $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ is taken, respectively, to conduct their DTA test, the temperature ranges from room temperature to 150°C with heating rate of 1°C/ min.

The experimental step cooling curve and DTA curve are shown in Figs. 1 and 2, respectively.

Fig.1 indicates that the molten $MgSO_4 \cdot 7H_2O$ starts to crystallize at 51.8°C, then there is a temperature rising to 60.4°C because of the releasing of latent heat, which implies a super-cooling of 8.6 °C.

Fig. 2 shows the DTA curve of $MgSO_4 \cdot 7H_2O$, there is three endothermic peaks during heating process, the peaks are located at 46.1°C, 81.4 °C and 106.4°C, respectively. The total phase change latent heat is 811.97kJ/kg, which exhibits a high latent heat of phase change material.
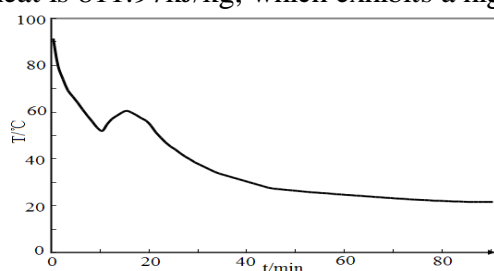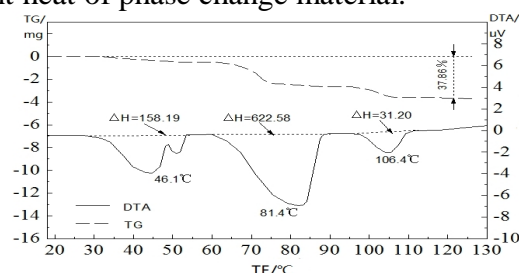

Fig.1 step cooling curve of $MgSO_4 \cdot 7H_2O$ Fig. 2 DTA curve of $MgSO_4 \cdot 7H_2O$

Fig. 3 is the step cooling curve of $KAl(SO_4)_2 \cdot 12H_2O$, it indicates that the molten of $KAl(SO_4)_2 \cdot 12H_2O$ starts to crystallize at 63.0°C, then there is a temperature rising to 73.4 °C because of the releasing of latent heat, which implies a supercooling of 10.4°C.

Fig. 4 presents the DTA curve of $KAl(SO_4)_2 \cdot 12H_2O$, a large latent heat of 882.58kJ/kg is shown, the phase transition temperature is at 75.7 °C.
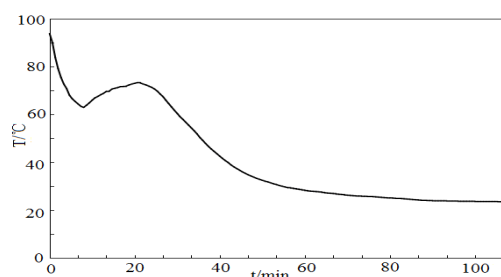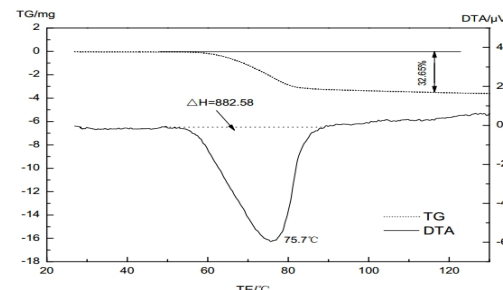

Fig. 3 step cooling curve of $KAl(SO_4)_2 \cdot 12H_2O$ Fig. 4 DTA curve of $KAl(SO_4)_2 \cdot 12H_2O$

Preparation of Phase Change Heat Storage Composite Material and its Property Test

Preparation of Phase Change Heat Storage Composite Material. The preparation process of phase change heat storage composite material is as follows,

(1) The milled $MgSO_4 \cdot 7H_2O$ and $KAl(SO_4)_2 \cdot 12H_2O$ powders are mixed and poured into a test tube, the total amount is 10g with the mass ratio of 9:1; Then 0.5 g milled anti-blocking agent $CaCO_3$ is poured into the test tube.

(2) The filled test tube is placed in the thermostat heating magnetic stirrer with a constant temperature heater, and kept half an hour after the material fully melting;

(3) The test filled tube is stood at room temperature, its temperature data is recorded once every 10s, step cooling curve is drawn after the temperature tests.

Step Cooling Curve Analysis of Composite Materials. Fig. 5 shows the step - cooling curves after 10, 20, 30, 40, 50 and 60 times heating – cooling cyclings. The tested solidifying temperature T_c from the step - cooling curve is listed in Table 1.
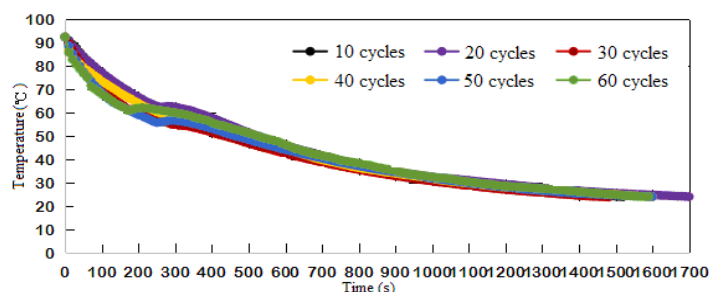

Fig. 5 step cooling curve vs cyclic number

Table 1 the solidifying temperature T_c

No. of cycling	10	20	30	40	50	60
T_c(°C)	60.9	62.5	54.6	59.8	55.8	61.0

As can be seen from Table 1, the solidifying temperature T_c of this anti-blocked composite keeps almost unchanged.

DTA Analysis of $MgSO_4·7H_2O$ - $KAl(SO_4)_2·12H_2O$ Composite. Take about 10mg composite powder of $MgSO_4·7H_2O$ - $KAl(SO_4)_2·12H_2O$ to conduct its DTA test, the temperature ranges from room temperature to 150°C with heating rate of 1 °C /min.

Fig. 6 shows the DTA curve of the anti-blocked composite after 10 heating – cooling cycles, its phase change latent heat is 800.37kJ/kg. While Fig. 7 shows the DTA curve of the anti-blocked composite after 60 heating – cooling cycles, its phase change latent heat is 797.16 kJ/kg. Table 2 shows the latent heat of the composite material by DTA test after each 10 cycles.
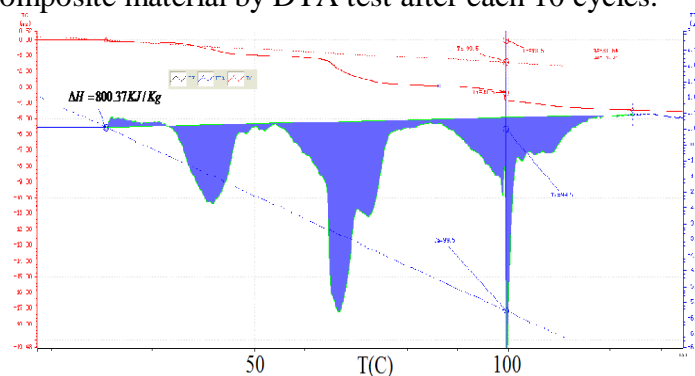

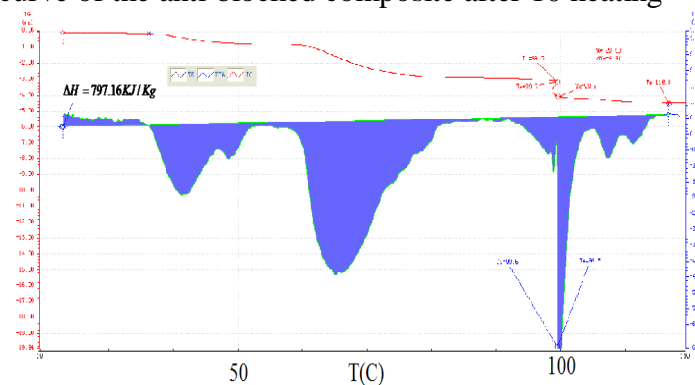Fig. 6 DTA curve of the anti-blocked composite after 10 heating – cooling cycles

Fig. 7 DTA curve of the anti-blocked composite after 60 heating – cooling cycles

Compared Figs. 6 and 7 as well as Table 2, it can be seen that the latent heat of this anti-blocked composite keeps almost the unchanged.

Table 2 Latent heat of the composite material by DTA test after each 10 cycles.

No. of cycling	10	20	30	40	50	60
ΔH (kJ/kg)	800.37	792.22	784.77	756.25	785.60	797.16

Heat Release Test of the Anti-blocked MgSO$_4$·7H$_2$O - KAl (SO$_4$)$_2$·12H$_2$O Composite. Take and pure about 3g composite powder of MgSO$_4$·7H$_2$O - KAl (SO$_4$)$_2$·12H$_2$O into a sealed tube to conduct their release test. The sealed tube is warmed to 80 degree and kept for 30min. Thereafter, the warmed sealed tube is put into an adiabatic vessel with 30 g water to measure the change of temperature, and then compute the heat release amount of the composite. Table 3 shows the heat release amount of the composite material after each 10 cycles.

Table 3 heat release amount of the composite material after each 10 cycles

No. of cycling	10	20	30	40	50	60
ΔW (kJ/kg)				229	316	253

Compared the data in Table 3, it can be seen that the change of heat release amount of the composite material after each 10 circles is not so significant.

Conclusions

(1) The anti-blocking agent CaCO$_3$ is effective for MgSO$_4$·7H$_2$O - KAl(SO$_4$)$_2$·12H$_2$O composite.

(2) The step cooling curve analysis shows that the solidifying temperature of this anti-blocked composite keeps almost unchanged.

(3) The latent heat of this anti-blocked composite keeps almost the unchanged after 60 cycles.

(4) The change of heat release amount of the composite material after each 10 circles is not so significant.

Acknowledgements

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