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Effects of SiO₂ / SiC particles on the thermal stability of carbonate eutectic salt / ceramic composite

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Abstract. Using Na₂CO₃-K₂CO₃ eutectic salt as phase change material, a novel composite was prepared by doping minor amount of SiO₂ or SiC into eutectic salt / ceramic composite. Further, the possible effects of SiO₂ or SiC on the thermal stability of the composite were investigated. The obtained results revealed that SiC can increase phase change enthalpy and meanwhile decrease thermal conductivity. But SiO₂ showed little effects on thermal conductivity although it can reduced phase change enthalpy.

1. Introduction

Energy is the foundation of human survival and development. In the 21st century, with the rapid development of global industry and the increasing demand for energy, the utilization rate of energy is still not very high, and there is a lot of waste, which makes the energy supply more and more tense. Latent heat energy storage based on phase change materials (PCMs) is one of the most effective technique for thermal energy storage [1]. This system is increasingly interesting in recent years because of the high-energy storage density and isothermal characteristics of PCMs [2]. Hence, they are often used as heat storage materials for different purposes such as industrial waste heat recovering, solar energy utilization, active and passive cooling of electronic devices [2], seasonal energy storage and energy-saving building materials [3].

PCMs are usually divided into two kinds from chemical composition: inorganic compounds and organic compounds [4]. Inorganic PCMs include salts or salt hydrates, metals and alloys, whereas organic PCMs are comprised of fatty acids, paraffin, glycols, and alcohols.

In order to eliminate these problems, in recent years, an inorganic salt / ceramic composite phase change energy storage material has been developed. This kind of energy storage material is composed of working substance (phase change material) and carrier matrix (ceramics). Ceramics are porous structures with a size of only a few microns. PCMs are distributed in the ultra porous network of ceramic matrix. Zhang Xingxue [5] prepared Na₂CO₃/MgO energy storage composite material by mixing sintering method. Li Aiju [6] prepared Na₂SO₄/SiO₂ composite material by mixing sintering method also.

In this study, the eutectic salts/ceramic composites were prepared with mixing sintering method. The thermal properties and thermal stability were investigated by differential scanning calorimetry



(DSC), TPS 2200 thermal constant analyzer (Hot disk) and thermogravimetric analysis (TG).

2. Materials and methods

2.1. Materials

Potassium carbonate, K_2CO_3 (purity>99%), sodium carbonate, Na_2CO_3 (purity>99%), and magnesium oxide, MgO (purity>99%), were purchased from Zibo Wu-hong Import and Export Co., Ltd, Tianjin Bo-hua Yong-li Chemical Co., Ltd and Weifang Li-he Powder Technology Co., Ltd, respectively. Silicon dioxide, SiO_2 (purity>99%) and silicon carbide, SiC (purity>99%), were purchased from Changsha Tian Jiu metal material Co., Ltd.

2.2. Preparation of the samples

2.2.1 Preparation of Na_2CO_3 - K_2CO_3 eutectic salts (ES)

The raw materials of Na_2CO_3 and K_2CO_3 were well mixed by ball milling in the weight proportion of Na_2CO_3 : K_2CO_3 =48:52 for 10 h. The mass ratio was at the eutectic point of the Na_2CO_3 - K_2CO_3 binary system determined from the phase diagram generated using FactSage software 7.2. Both the two salts were pre-dried at 393.15K for at least 24h using vacuum oven to exclude moisture. The mixed salt was then melted in a muffle furnace and allowed to equilibrate at 750 °C for 2h to form ES (see Figure1). Afterwards, the mixture was naturally cooled to room temperature and pulverized to powder using a pestle and mortar and stored in sealed containers.

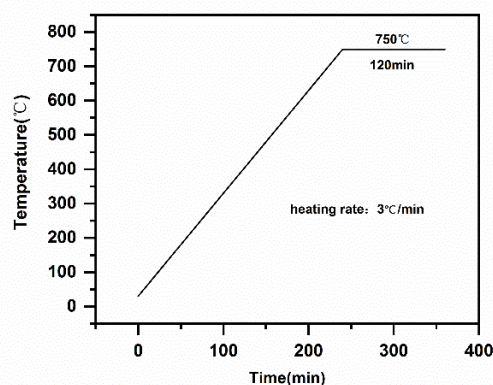


Figure 1. Scheme of preparation of ES.

2.2.2 Preparation of ES /ceramic composites

ES/ceramic composites were prepared with compress mixing-sintering method. The specific components of composites can be seen in Table 1. Then the mixture was pressed via a hydraulic machine in a stainless steel cylindrical mold with a diameter of 12.6 mm to produce a circular sheet. The pressure applied was 8 tons and the holding time was 30 seconds. Finally, the circular sheet was heated in six stages (see Figure 2). Considering moisture absorption of the samples, the samples were kept at 100 °C and 510 °C for half-hour, respectively.

Table 1. The Specific components of composites.

Sample number	K_2CO_3 (wt.%)	Na_2CO_3 (wt.%)	MgO (wt.%)	SiC (wt.%)	SiO_2 (wt.%)
1#	26.4	28.6	45		
2#	26.4	28.6	35	10	
3#	26.4	28.6	35		10

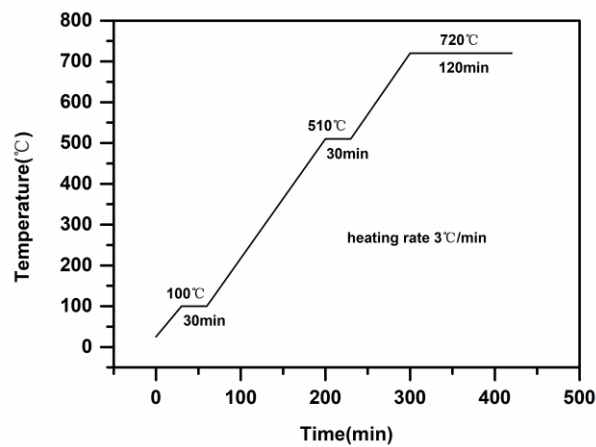


Figure 2. Scheme of sintered process of ES/ceramic composites.

2.3. Characterization

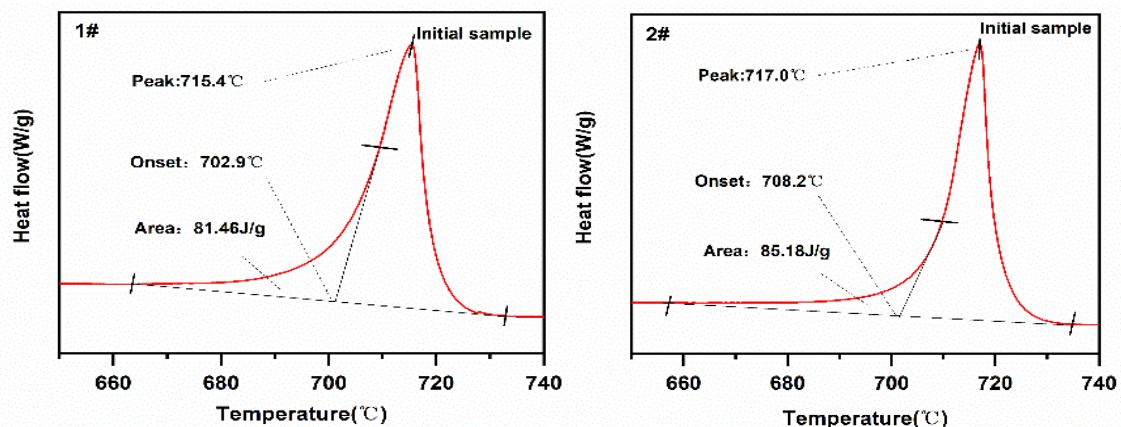
A Simultaneous Thermal Analyzer (STA/TG-MS 449 F5, NETZSCH) was used to measure the thermophysical properties of the PCMs such as onset melting temperature, melting point, latent heat of fusion, and specific heat. The latent heat was carried out from room temperature to 800 °C with a heating rate of 10 °C /min in N₂ atmospheres. The specific heat capacity were experimentally measured by specific heat ratio method using sapphire as standard sample with a temperature range from 25 °C to 700 °C. Thermal conductivity of PCMs were measured by TPS 2200 thermal constant analyzer, Hot disk.

3. Result and discussion

3.1 DSC of the as-prepared samples

Table 2. The experimental values of the samples.

System	Onset temperature	Melting temperature	ΔH_{PCM}
	°C	°C	J/g
Sample 1	702.9	715.4	81.46
Sample 2	708.2	717.0	85.18
Sample 3	703.6	714.8	76.15



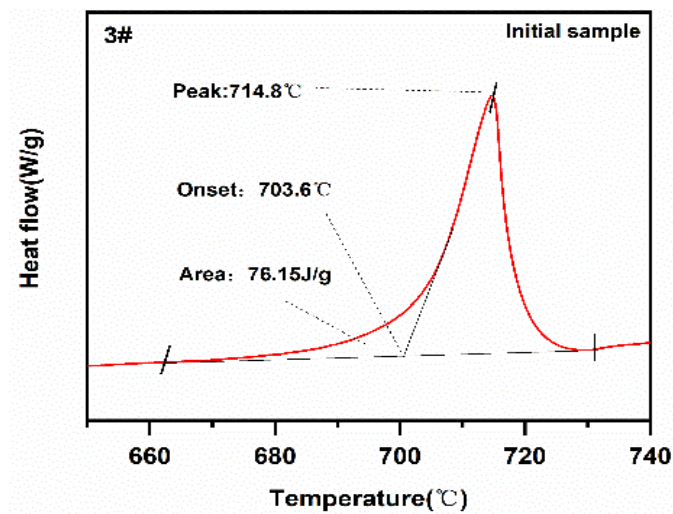


Figure 3. Representative DSC heat flow curve for the melting point and enthalpy of phase change determination of the sample 1, 2, 3 initial sample in N₂ atmosphere

DSC curves of the ES-ceramic composites were given in Figure 3. The corresponding melting temperature, onset temperature and the enthalpy of phase change measured in this work are listed in Table 3. Table 3 indicated both the onset temperatures and melting points of sample 1, 2, 3 are almost the same. The enthalpy of phase change of sample 3 and samples 2 is 6.5% lower and 4.9% higher than sample 1, respectively. It indicated that SiC can increase phase change enthalpy and SiO₂ can reduced phase change enthalpy. DSC shows SiC is benefit for ES-ceramic composites.

3.2 Thermal conductivity of as-prepared samples

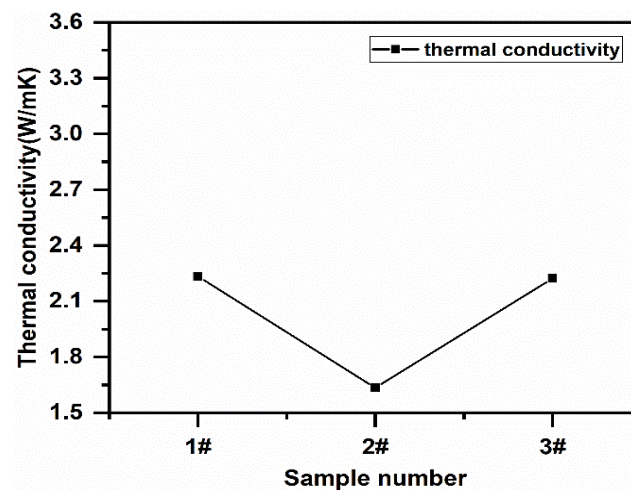


Figure 4. Thermal conductivity curves of sample 1, 2, 3

Thermal conductivity is one of key parameters considered in the selection of a composite-PCM. The thermal conductivity of samples is calculated by $\kappa = D\rho C_p$ and presented in Figure 4. As shown in Figure 4 is that adding SiO₂ can increase thermal conductivity, while SiC can reduce thermal conductivity. It is inconsistent with the description of the literature and needs further study.

4. Conclusions

Using $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic salt as phase change material, a novel composite was prepared by doping minor amount of SiO_2 or SiC into eutectic salt / ceramic composite. Further, the possible effects of SiO_2 or SiC on the thermal stability of the composite were investigated. The obtained results revealed that SiC can increase phase change enthalpy and meanwhile decrease thermal conductivity. But SiO_2 showed little effects on thermal conductivity although it can reduced phase change enthalpy.

Acknowledgement

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