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Novel Na_2SO_4-NaCl-ceramic composites as high temperature phase change materials for solar thermal power plants (Part I)

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ABSTRACT

The eutectic Na_2SO_4-NaCl salt was investigated as a novel high temperature phase change material for solar thermal energy storage due to its low cost and melting point (626.0 °C) interested. The measured melting point and heat of fusion of the eutectic salt are 625.3 °C and 263.3 J/g, which are in agreement with their theoretical values. The eutectic salt shows good thermal stability after 100 melting-freezing thermal cycles in the range of 550–680 °C in air. Three types of the eutectic Na_2SO_4-NaCl-ceramic composites have been designed and evaluated to address the salt' corrosion issues with containment materials. Results show that eutectic Na_2SO_4-NaCl/both α-alumina and mullite composites with a mass ratio of salt to ceramics of 1:1 (wt%) have good thermal stability without cracking as well as with weight losses of 0.50% and 0.74% and the decrease of latent heat by 1% and 2% respectively after 20 thermal cycles, where no phase separation and chemical reaction occur. Their measured melting temperature and latent heat are consistent with their theoretical values. Addition of α-alumina and mullite to the eutectic Na_2SO_4-NaCl salt can reduce the eutectic Na_2SO_4-NaCl salt' supercooling. In contrast, the sample of the Na_2SO_4-NaCl/diatomite composite cracked after the cycles.

1. Introduction

Concentrating Solar Thermal (CST) technology is a commercial renewable energy option for generation of electricity and process heat. The International Energy Agency forecasts CST's contribution of 11% to global electricity by 2050. High temperature (> 600 °C) thermal energy storage (TES) plays a key role in enhancing CST's sustainability and efficiency, but is not yet commercially available.

A latent heat storage system, which uses the enthalpy of phase change (known as phase change materials (PCMs)) to store solar energy, has higher energy storage density compared to the lower temperature (~ 550 °C) commercial sensible heat storage technology based on molten nitrate salts. Furthermore, the high temperature PCMs increase not only the energy storage density but also the high TES temperature allows the TES system to be integrated with higher efficiency power generation cycles, such as the supercritical CO_2 (s-CO_2) technology, rather than the conventional superheated or supercritical steam cycles above 600 °C [1]. Both of these benefits will further reduce the cost and increase potential market penetration of CST technology. Considering the high cost of using high temperature expensive containment materials for the TES system, it is more practical to develop the high temperature PCMs, whose melting temperatures are in the temperature range of 600–700 °C, the lowest temperatures required for running an efficient s-CO_2 Brayton cycle for solar thermal power plants in the medium term.

Metals or alloys, such as Al-Si, Al-Si-Mg and Al-Si-Cu, were investigated as candidates of high temperature PCMs because they can offer the advantages of their high melting temperature, high latent heat and excellent thermal conductivity [2,3]. However, a challenge with the metal alloys as PCMs is their high cost, corrosion issues, and compatibility with shell materials or containment materials. Encapsulated core/shell Al-Si/Al_2O_3 PCM has been reported by some researchers [4,5] to overcome the corrosion issues. He et al. [5] have encapsulated a eutectic Al-Si alloy using Al_2O_3 as shell materials and then evaluated its thermal stability via a thermal cycling test from room temperature to 650 °C. Their results have shown that the weight of the encapsulated Al-Si/Al_2O_3 PCM increases by 3.75% and the latent heat of fusion decreases by 11.5% after 20 thermal cycles due to the consumption of the Al element through Al oxidation in the encapsulated PCM. Zhang et al. [6] have developed Cu-based PCMs encapsulated with a thick Cr-Ni bilayer for high temperature TES (above 1000 °C). They have observed that the thickness of the Cr-Ni shell layer decreases with the increasing

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Table 1
Thermo-physical properties of eutectic Na_2SO_4-NaCl salt.

Composition (wt%)	Melting temperature (°C)	Heat of fusion (J/g)	Specific heat (J/gK)	Cost ($/kg)	Reference
Na_2SO_4(68.05)-31.95NaCl	626	266.3	0.89	0.10	Factsage v6.4

Table 2
Thermo-physical properties of ceramic materials.

Material	Density (kg/m^3)	Specific heat (J/g*K)	Cost ($/kg)
α-alumina	3970	0.88	0.7
Diatomite	2500	0.90	0.5
Mullite	2800	0.70	0.2

number of thermal cycles. After 50 thermal cycles, the formation of ternary Cu-Cr-Ni alloys has been identified, indicating that shell materials of Cr and Ni have penetrated inside and reacted with Cu.

Some inorganic salts were also studied as high temperature PCMs such as fluoride, chloride and carbonate salts due to their low cost, high melting point and large latent heat [7–12]. However, their low thermal conductivity and thermal stability as well as their highly corrosive nature on containment materials at high temperatures have been problematic. In order to solve the problems, development of high temperature salt-ceramic composites is a potential solution for use as high temperature PCMs, where high temperature molten salts as PCMs, are encapsulated by ceramic materials to avoid their corrosion issues with containment materials as well as improve their thermal stability. Moreover, the composites can combine the advantages of latent heat storage of PCMs and the sensible heat storage of ceramics. Qin et al. [13] explored using Na_2SO_4 as a PCM and diatomite as a structure material to formulate the Na_2SO_4-diatomite composite with melting point of 880 °C. Their results show that the Na_2SO_4 salt has an excellent chemical compatibility with diatomite in the composite. The optimum formulation of the composite, in terms of energy density, salt leakage and mechanical strength, contains 45 wt% Na_2SO_4. Liu et al. [14] introduced the porous mullite as a ceramic matrix to prepare the porous mullite/Na_2SO_4 composite. Their results demonstrate that the open pores of the porous mullite matrix can increase the impregnation ratio of the molten Na_2SO_4 inside the mullite matrix, resulting in higher heat storage capability. However, the thermal stability of these composites has not been reported, which is crucial in a real application. Ye et al. [15] examined the Na_2CO_3/MgO composite (melting point of 851 °C) with added multi-walled carbon nanotubes to improve their thermal conductivity. Their SEM results demonstrate that the carbon nanotubes were uniformly dispersed in the composite. The thermal conductivity of the composite increased with the weight fraction of the carbon nanotubes, but they do not report the thermal stability of the composite.

In this paper, we firstly investigated a eutectic Na_2SO_4-NaCl salt as a high temperature PCM candidate with a melting temperature of 626.0 °C and then developed the eutectic Na_2SO_4-NaCl salt/ceramic composites to address its corrosion issues for high temperature TES for solar thermal power plants. In the next paper, an optimum formulation of Na_2SO_4-NaCl salt/ceramic composites will be determined and the long-term thermal stability of the preferred composites will be reported, which is a very important factor for a high temperature TES system. This may provide an insight into developing high temperature salt-ceramic composites with melting temperatures between 600 and 700 °C for solar thermal power plants.

2. Experimental sections

2.1. Design of high temperature PCM composites

The eutectic Na_2SO_4-NaCl salt was selected as a high temperature PCM candidate based on a combination of melting temperature, heat of fusion, thermal-chemical stability and bulk costs of the constituents of the eutectic salt to meet the temperature requirements with melting temperatures in the range of 600–700 °C. The eutectic salt is very cheap as both of its components are made from one raw material (Na_2SO_4) for industrial production of soda ash and rock salt (NaCl). Moreover, Na_2SO_4 is thermally stable. The thermos-physical properties of the eutectic Na_2SO_4-NaCl salt are listed in Table 1.

α-alumina, diatomite and mullite were selected as candidates of structural materials for the Na_2SO_4-NaCl salt/ceramic composites due to their relatively low cost, corrosion-resistance and abundancy. Their physical properties and indicative costs are listed in Table 2.

2.2. Sample preparation

2.2.1. Eutectic Na_2SO_4-NaCl salt

The pre-dried raw materials of Na_2SO_4 (purity ≥ 99%, Sigma-Aldrich) and NaCl (purity ≥ 99%, Sigma-Aldrich), were well mixed by ball milling at the mass ratio of 68.05% (Na_2SO_4) to 31.95% (NaCl) at

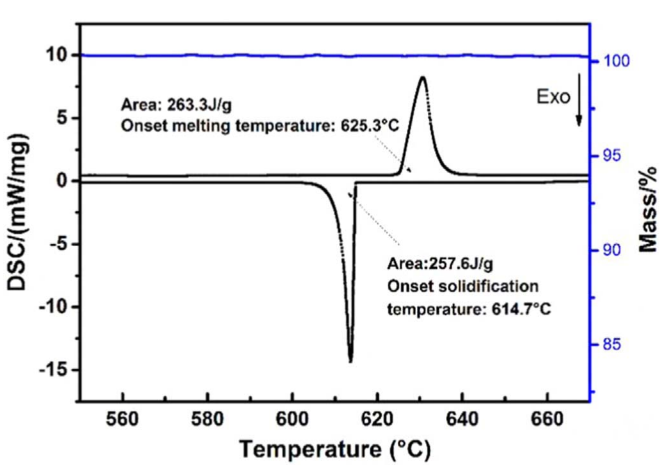

Fig. 1. DSC-TG curves of eutectic Na_2SO_4-NaCl salt.

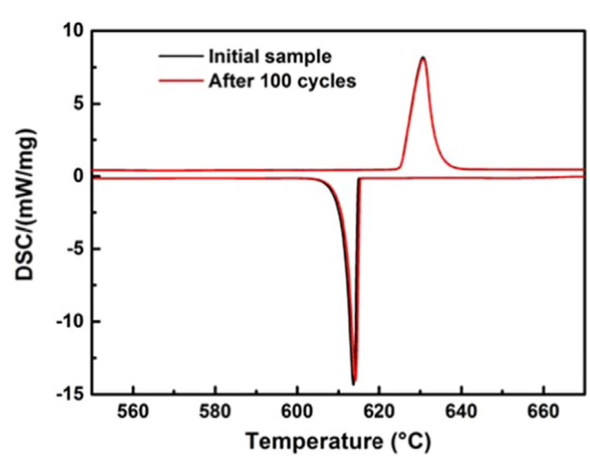

Fig. 2. DSC curves of initial sample and 100-cycling of eutectic Na_2SO_4-NaCl.