Solar Energy Materials & Solar Cells 152 (2016) 155–160

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Eutectic Na_2CO_3–NaCl salt: A new phase change material for high temperature thermal storage

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ARTICLE INFO

Article history:
Received 22 September 2015
Received in revised form
4 March 2016
Accepted 1 April 2016
Available online 14 April 2016

Keywords:
Phase change materials
Melting eutectic salts
High temperature
Thermo-physical properties
Thermal stability

ABSTRACT

In this work, the eutectic Na_2CO_3–NaCl molten salt was investigated as a new high temperature phase change material for solar thermal energy storage. The composition of the eutectic binary salt was determined with the aid of FactSage software and its thermophysical properties were investigated using a Simultaneous Thermal Analyzer (STA) and X-Ray Diffraction (XRD). Inductively coupled plasma analysis has shown that the composition of the as-prepared sample is consistent with the nominal one. The STA results exhibit that the melting point of the eutectic salt is 637.0 °C and its heat of fusion is 283.3 J/g whereas its specific heat is a function of temperature, which all are in agreement with the theoretical values determined by the FactSage software. The thermal stability analysis indicates that the eutectic molten salt has good thermal stability without weight loss in a CO_2 environment at temperatures below 700 °C, compared with 0.51% weight loss in a N_2 atmosphere. The weight loss observed in the latter, is most likely to be due to the salt's decomposition at high temperature. The thermophysical properties of the salt such as melting temperature, latent heat of fusion and solidification, varied marginally after 50 and 100 thermal cycle tests. This demonstrates that the eutectic Na_2CO_3–NaCl salt is a promising high temperature phase change material when used in a CO_2 environment or encapsulation.

1. Introduction

Concentrating solar power (CSP) is one of the most promising solar technologies for substantial generation of renewable electricity and process heat for the chemical, mining and mineral industries. However, high capital and operating costs have prevented widespread implementation of CSP solar technology. Cost-effective high temperature thermal energy storage (TES) is one path to increase CSP value and reduce its cost. A latent heat storage system which uses the enthalpy change associated with a change in phase to store energy, possesses higher energy storage densities as compared with a sensible heat storage system. Moreover, phase change materials (PCMs) can charge and discharge a large amount of heat at a constant temperature during the phase transformation process which is a very important characteristic for the temperature requirement in the heat transfer fluid, solar field equipment and Rankine cycle [1]. The TES systems using high melting point PCMs have been therefore recognized as one of the most advanced energy technologies enhancing the energy efficiency and sustainability. They can reduce not only the size of equipment and containment but also the volume of materials needed for TES, potentially reducing capital cost [2]. However, previous researchers have been mostly focused on low temperature PCMs such as salt hydrates, fatty acids and paraffin waxes etc. [3–7]. There are few research publications on high temperature PCMs due to the corrosion issue and stability problem at high temperatures.

Metals and alloys such as Al–Si, Al–Si–Mg and Al–Si–Cu have been widely investigated for use as high temperature PCMs because of their high melting temperature, high latent heat and excellent thermal conductivity [8–12]. Zhang et al. [10] have developed Cu-based PCMs encapsulated with a thick Cr–Ni bilayer for high temperature TES (above 1000 °C). They have found that the thickness of the Cr–Ni shell layer decreases with the increasing number of cycles. After 50 thermal cycles, the formation of ternary Cu–Cr–Ni alloys has been identified, which means that shell materials of Cr and Ni have penetrated inside and reacted with Cu. Encapsulated core/shell Al–Si/Al_2O_3 PCM has been recently investigated by some researchers [11,12]. He et al. [12] have reported 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 oxidation and consumption of the Al element in the encapsulated PCM. Hence, there is still a challenge with the metal alloys as PCMs in regards to their cost, corrosion issues and compatibility with shell materials or containment materials.

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http://dx.doi.org/10.1016/j.solmat.2016.04.002
0927-0248/

Inorganic salts are another category of high temperature PCMs. Several materials including fluoride, chloride and carbonate salts have been widely investigated because they usually have low cost, high melting point and latent heat [13–17]. However, their low thermal conductivity and thermal stability as well as high corrosive nature on containment materials have been problematic. Previous researches have focused on fluoride salts as they have a very high latent heat and high melting temperature, but fluoride salts are very toxic and expensive which impede their application [13–17]. There is a need to develop new high temperature molten salts, with emphasis on improving their thermal conductivity, thermal stability and minimizing their corrosion for use as high temperature PCMs for high temperature TES.

The eutectic Na_2CO_3–NaCl molten salt has been widely used in a salt bath treatment to process diamond compacts for manufacture of grinding wheels, cutting tooling etc. [18], heavy metal sulphide mineral smelting [19], ceramic materials preparation [20,21] and other engineering processes due to its advantages of low cost and high thermal stability. However, the reports on its thermal properties are very limited and the use of eutectic Na_2CO_3–NaCl molten salt as a PCM is still unexploited.

In this paper, we report the investigation of the eutectic Na_2CO_3–NaCl molten salt for the application of high temperature PCM. In the next stage, a focus will be placed on developing PCM composites or encapsulated PCMs to improve the salt's thermal conductivity and thermal stability as well as reduction of its corrosion. This may provide an insight into developing the eutectic salt for the application of high temperature PCM storage.

2. Experimental sections

2.1. Sample preparation

The pre-dried raw materials of Na_2CO_3 (purity ≥ 99%, Sigma-Aldrich) and NaCl (purity ≥ 99%, Sigma-Aldrich) were well mixed by ball milling in the weight proportion of Na_2CO_3:NaCl = 59.45:40.55 for 10 h. The mass ratio was at the eutectic point of the Na_2CO_3–NaCl binary system determined from the phase diagram generated using FactSage software 6.4. The mixed salt was then dried again and melted in a tube furnace and allowed to equilibrate at 650 °C for 6 h. Afterwards, the mixture was naturally cooled to room temperature and then grounded into powder, dried and preserved for experiments.

2.2. Thermophysical properties measurements

A Simultaneous Thermal Analyzer (STA/TG-MS 449 F1 Jupiter, NETZSCH) was used to measure the thermophysical properties of the eutectic Na_2CO_3–NaCl salt such as onset melting temperature, solidification point, latent heat, decomposition behaviour and specific heat. The evolved gaseous species released from the heating processing were characterized by using the mass spectrometer attached with the STA. For a standard measurement, a sub-sample of 10 mg of the salt was loaded into the 85 μl Pt/Rh crucible for STA analysis. The STA experiments were carried out from room temperature to 700 °C with a heating rate of 10 °C/min in N_2 or CO_2 atmospheres.

The calibration using several heating rates was carried out with standard samples (In, Sn, Bi, Zn and Al) in the above atmospheres prior to any experiments. Each standard sample was measured for three heating and cooling cycles and the average values of onset melting temperature and latent heat were obtained. The calculated conversion factors were then curve-fitted to obtain temperature and sensitivity curves.

The theoretical melting point, latent heat and specific heat of the eutectic salt were calculated using FactSage thermochemical software and databases [22] as references for a comparison with experimental results.

2.3. Thermal cycling

The thermal stability was evaluated through melt-freeze cycling in a high-temperature furnace. Bulk PCM samples (50 g) were used in the stability test. The salt samples were placed in the aluminium oxide crucibles with the volume of 100 ml. Type K omega™ thermocouples with an accuracy of ±0.75%, were covered with aluminium oxide sheaths to protect the thermocouple from the corrosion of the salt. Then the sheathed thermocouples were inserted into the PCM samples. The temperature of the oven was controlled to melt and freeze the eutectic salts with a heating/cooling rate of 10 °C/min in the temperature range of 600–650 °C. In this study, 50 and 100 thermal cycles of the eutectic salt were carried out and the resulting samples were analysed using a STA and XRD.

2.4. Sample characterization

The composition of the as-prepared eutectic Na_2CO_3–NaCl salt was determined with the Inductively Coupled Plasma (ICP) technique. The sodium (Na) was analysed by ICP Optical Emission Spectroscopy (Perkin Elmer OPTIMA 7300 ICPOES) and the chloride (Cl) was analysed by Dionex Ion Chromatography System.

X-ray diffraction (XRD, Philips 1380) was used to identify the changes of the crystalline phases of samples in powder form with 2θ scan from 20° to 90° and a step size of 0.013.

3. Results and discussion

3.1. Thermophysical properties

3.1.1. Melting/solidification point and heat of fusion

The phase diagram of the Na_2CO_3–NaCl binary salt as shown in Fig. 1, indicates that the theoretical eutectic melting point and latent heat of the Na_2CO_3–NaCl binary salt are 632.0 °C and 294.9 J/g respectively.

For comparison, the composition of the as-prepared salt was analysed with ICP and the results are listed in Table 1 along with the nominal weight ratio of the eutectic salt calculated from FactSage 6.4. It can be seen that the actual composition of the prepared salt is similar to the nominal ones within less than a 5% measurement error.

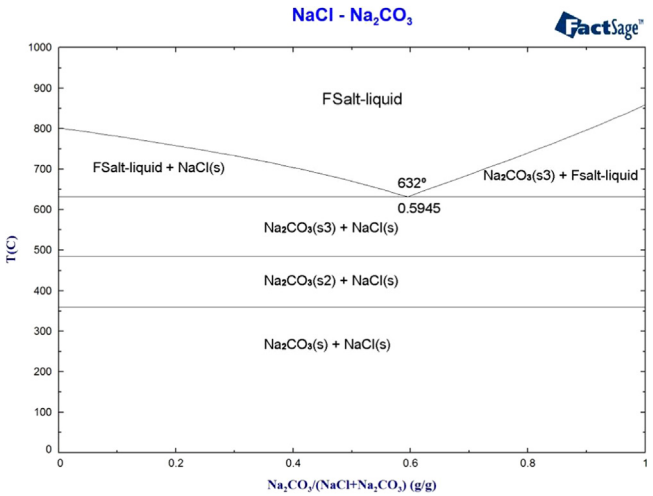

Fig. 1. Phase diagram of NaCl–Na_2CO_3 salt generated using FactSage 6.4.