Powder Technology 282 (2015) 37–42

Contents lists available at ScienceDirect

Powder Technology

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

Sodium sulfate–diatomite composite materials for high temperature thermal energy storage

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ARTICLE INFO

Available online 28 September 2014

Keywords:
Thermal energy storage
Diatomite
Phase change materials
High temperature

ABSTRACT

This work explores the use of sodium sulfate and diatomite to formulate composite materials for high temperature thermal energy storage applications. Sodium sulfate in the composite functions as a phase change material (PCM) and diatomite as a structural skeleton for shape stabilization. It is found that sodium sulfate and diatomite have an excellent chemical compatibility with the PCM melting temperature at around 880 °C. It is shown that the composite containing 45% diatomite gives an optimal formulation in terms of energy density, salt leakage and mechanical strength. The results also suggest that the composite with the optimal formulation has an application window of 890–980 °C. Failures occur to the composite materials at temperatures above 1000 °C.

1. Introduction

Thermal energy storage (TES) has numerous potential applications including solar thermal power generation, industry waste heat recovery, thermal comfort in buildings and packaging of thermal sensitive materials and hence has attracted considerable attention over the past few decades [1–3]. Industrial uptake of the technology, however, has been hindered by a number of challenges including materials, processes and economical aspects. This work concerns TES materials with a particular focus on composite materials consisting of a phase change material (PCM) for latent heat storage and a structural material for shape stabilization. Such composite materials offer a number of advantages including high energy density, good chemical stability and shape stabilization, and high mechanical strength. There are numerous PCMs that can be used for making the composite materials. Examples include paraffin waxes, fatty acids and hydrated salts with low phase change temperatures, and nitrates, carbonates, chlorides, sulfates and their combinations with medium to high phase change temperatures [2,3]. There is also a large range of choices for the shape stabilization materials including silicates, metals, large molecular polymers and expanded graphite [4–6].

This work uses diatomite and sodium sulfate as the structural and phase change materials, respectively. The main reasons for the use of sodium sulfate lie in its high phase change temperature (around 880 °C), environmental friendliness, easy availability and low costs. The use of diatomite is also due to its high specific surface area, great adsorbability, and good thermal and chemical stability at elevated temperatures [7–9]. In the following, a brief review on the use of diatomite as the shape stabilization material is given. Karaman et al. used diatomite to shape stabilized polyethylene glycol and subsequently to achieve a PCM with a phase change temperature at 27.7 °C and a latent heat of 87.09 J/g [10]. They showed that the structural material could hold about 50 wt.% of the PCM. Cyclic heating–cooling experiments showed that the composite material had a good chemical and physical stability. Nomura et al. studied diatomite–erythritol composite materials using a vacuum impregnation method [11]. Erythritol is a polymeric material with a fairly high phase change latent heat of 294.4 J/g. They observed that erythritol fully populated within pores of diatomite and the pore size had an effect on the melting point; the smaller the pore size in the diatomite, the lower the melting point of the PCM. They also showed that the latent heat of the composite material could reach to 83% of pure erythritol. However, thermal cycling tests revealed considerable loss of the phase change materials (25% mass loss after four cycles between the room and 150 °C). Sari et al. studied the use of plaster, cement, diatomite and perlite as shape stabilization materials for organic PCMs with a melting point of 20–35 °C and a latent heat of 38–126 J/g [12,13]. Their results indicated that the diatomite based composite

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http://dx.doi.org/10.1016/j.powtec.2014.08.075
0032-5910/

materials provided a favorable thermal and chemical stability. Little has been found in the literature on the use of diatomite for shape stabilizing high temperature PCMs, which are needed for solar thermal power generation and effective and efficient utilization of industrial waste heat — the main motivation of this work. The work involves formulation and fabrication of the composites, and evaluation of thermal and physical characterization of the materials, and study of chemical and physical stability studies.

2. Experimental

2.1. Raw materials

Both the sodium sulfate and diatomite are in solid form at the ambient temperature. The sodium sulfate was of analytic grade and purchased from China Xilong Chemicals Inc., whereas the diatomite was provided by China Shengzhou Diatomic Manufacturing Inc. Table 1 shows chemical compositions of the diatomite obtained with an X-ray fluorescence analyzer (AXIOS-MAX X, PANalytical B.V.). One can see that silica (82.6%) and alumina (8.2%) are two main components of diatomite and the rest 15 minor components account for less than 10%. Fig. 1 shows a typical image of a diatomite particle obtained using a scanning electron microscope (JSM-7001F, JEOL, Japan). The diatomite has a disc-like shape with many nanoscale open pores. The pores in the edge are seen to be much smaller than that in the middle part, providing sites for taking up molten salt. The morphology shown in Fig. 1 is expected to give a fairly high specific surface area. This was confirmed by BET measurements using an Autosorb-1 device (Quantachrome, USA), which gave a specific surface area of 66.29 m^2/g.

2.2. Fabrication of diatomite–sodium sulfate composites

The fabrication process involved weighing the two particulate materials, followed by grinding them separately at the ambient temperature to a size that could go through a 120-mesh sieve, then thorough mixing and tableting to give disc-like green pellets. To ensure the green pellets to have sufficient mechanical strength for subsequent drying and sintering processes, a small amount of 1 wt.% starch solution was added during the mixing stage. The tableting was done at a pressure of 10 MPa and the resulting green pellets were 13 mm in diameter and 3 mm thick. The green pellets were dried at 120 °C for 2 h before sintering at 900 °C for an hour in an electrical furnace.

2.3. Measurement and analyses

A micro-hardness instrument (MX-6, Shenzhen Shuanhua Instruments, China) was used to measure the harness of the composite thermal energy storage materials and the measurements were at a load of 2 N at the ambient temperature. Chemical composition was determined by using an X-ray fluorescence spectrometer (PANalytical B.V., Netherlands) as mentioned before, whereas chemical compatibility was investigated with a PANalytical X-ray Diffractometer (XRD). The JSM-7001F SEM was used to observe the material surface morphology. Material specific surface areas were measured with the Autosorb-1 specific surface area analyzer. Heat capacity, melting point and latent heat of the raw and composite materials were evaluated by using a SAT449F3 differential scanning calorimeter (DSC, Netzsch, Germany) in an argon environment with the heat capacity measurements using alumina as the standard. Density of the materials was measured using the Archimedes method with ethanol as the liquid.

Table 1
Chemical compositions of the diatomite in mass percentage with total 100%.

Composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	P_2O_5
Content	82.604	8.207	3.573	0.302	1.147	0.638	1.153	0.332	0.340

Composition	SO_3	MnO	ZnO	SrO	ZrO_2	Tb_4O_7	PbO	Cl
Content	1.301	0.034	0.020	0.007	0.003	0.031	0.010	0.299

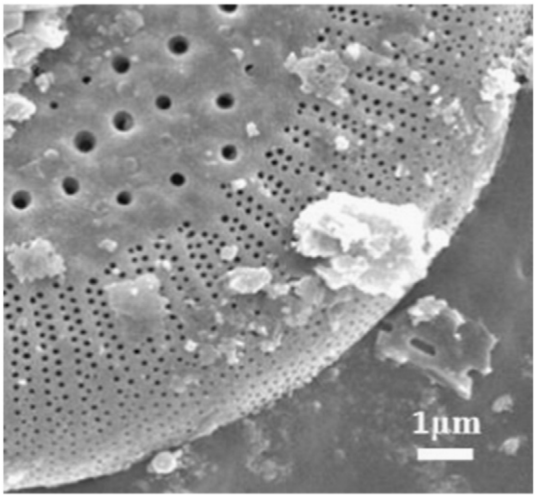

Fig. 1. An SEM image of diatomite microstructure (5000×).

3. Results and discussion

3.1. High temperature chemical compatibility of diatomite and sodium sulfate

Fig. 2 shows the XRD patterns of the composite materials with three different diatomite concentrations, 25%, 35% and 45%. The measurements were done after the composite was sintered. One can see from the figure that the main phases in all the three composite materials are quartz and sodium sulfate. All the peaks in the three XRD patterns show one-to-one position correspondence and no new peaks are observed. However, different dolomite concentrations give different peak intensities. An increase in the sodium sulfate concentration or a decrease in the diatomite concentration leads to an increase in the diffraction intensity particularly at the (113) plane with a peak position of $2\theta = 33.9°$. The intensity of the main diffractive peak of diatomite occurs at $2\theta = 26.5°$, which corresponds to the (101) plane, indicating a significant decrease with decreasing diatomite concentration. These results suggest that the shape stabilization material, diatomite, and the phase change material, sodium sulfate, are highly chemically compatible at high temperatures. Only physical changes could occur for each of the two components [14].

3.2. Physical properties and microstructure

Fig. 3 shows the density and Vickers hardness (HV) of the composite materials as a function of diatomite concentration. Overall, both the density and hardness are seen to increase with increasing diatomite concentration. With increasing diatomite concentration, the rate of density increase is concentration dependent, which is high initially, then tends to level off at a diatomite concentration above 20%, and eventually becomes very high at a diatomite concentration over 45%. The Vickers hardness data shown in the figure is from an average of five measurement points on each specimen surface. It can be seen that, with increasing diatomite concentration, the rate of hardness increase follows a similar trend as that for density except for that the rapid increase occurs at a diatomite concentration of 40%. The above observations on the density change can be reasonably attributed to the difference in the density between the two materials with the diatomite having a much higher density than sodium sulfate. The density difference, however, does not explain the abrupt increase in the rates of density and hardness increase. Visual inspections and SEM