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

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A B S T R A C T
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 skeleton 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. Namura 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 perlrite 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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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 m²/g.

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

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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 tabletting 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 tabletting 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 hardness 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 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.

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 2θ = 33.9°. The intensity of the main diffractive peak of diatomite occurs at 2θ = 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 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
analyses of the sintered samples were therefore carried out. Table 2 shows the results. Samples with a diatomite content of over 40–45% have a perfect appearance without any sign of salt leakage. Samples with less than 20–25% diatomite deform significantly and leakage of salt is serious. Samples with diatomite concentration between 25% and 40% deform slightly and show a small amount of salt leakage, and the extent of the leakage and shape deformation decreases with increasing diatomite concentration. These observations suggest that the abrupt increase in the density and hardness at the high diatomite contents be due to the salt being fully held within the diatomite structure, occupying the intraparticle pores and interparticle voids and hence forming dense pellets. Samples with low diatomite contents could neither hold all the salt in the structure nor support the whole structure, leading to deformation and leakage and hence the low density and hardness. This appears to be in line with the SEM observations shown in Fig. 4, which compares the sintered samples containing 25% diatomite (Fig. 4a) and 45% diatomite (Fig. 4b). The salt is seen to fill the intraparticle pores and also the interparticle voids for the sample with 45% diatomite, whereas the salt appears to have leaked out covering the surface of the diatomite particles.

The results presented above also indicate that the amount of diatomite in the formulation should be higher than approximately 45% by mass to obtain reasonably dense pellets with adequate strength.

3.3. Thermal analyses of the composite materials

Due to inadequate shape stability of pellets with diatomite contents below 40%, thermal analyses were mainly carried out with samples containing 45% diatomite. Fig. 3 shows the effect of diatomite content on volume density, hardness and compressive strength of the composite materials. The figure illustrates that as the diatomite content increases, the volume density, hardness and compressive strength also increase. This is consistent with the observations made in the previous section regarding the sintered samples.
containing 45% diatomite. For comparison, analyses on the pure sodium sulfate were also done. The results are shown in Fig. 5. One can see that the composite materials behave in a similar manner to the pure sodium sulfate salt in terms of phase transition. During the heating process, endothermic peaks at 203–251 °C (peak temperature 240 °C) and 878–906 °C (peak temperature 882 °C) occur to both the composite material and the salt. The 240 °C peak corresponds to a solid–solid crystal phase transition from T-Na2SO4 to γ-Na2SO4, whereas the 882 °C peak is due to melting (solid–liquid phase change). The enthalpy of the melting is found to be 73.9 kJ/kg for the composite material. This is approximately 55% of the latent heat of the pure salt (146.7 kJ/kg), in agreement with the actual concentration of the pure salt.

Measurements were also done on all formulated samples to obtain the melting latent heat and the results are shown in Row 2 of Table 2. In this set of measurements, smaller samples were used and careful measures were taken to ensure the salt and the diatomite had the intended proportion. Calculations were also done to estimate the melting enthalpy using the following equation [15]:

$$\Delta H = \delta \Delta H_{lf}$$

where \(\Delta H\), \(\delta\) and \(\Delta H_{lf}\) are respectively the calculated latent heat of the composite material, the mass percentage of the PCM in the composite and the latent heat of pure sodium sulfate salt. The calculated results are listed in Row 3 of Table 3. One can see that the calculated melting enthalpies are close to but approximately 6–15% lower than the measured data. The exact reasons for the deviations require further investigation but imperfect microstructures of the composite materials could be a reason. The deviations indicate the importance of thermal characterization of the composite materials to obtain accurate latent heat values, which are essential for engineering design of thermal energy storage systems. The measured melting points of various formulations are also listed in Table 3. It is seen that the measured melting points agree within 3 °C. This suggests no significant confinement effect due to the diatomite microstructure on the salt properties. This is different from the observations of Nomura et al. who studied

### Table 2

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>N1</th>
<th>N2</th>
<th>N3</th>
<th>N4</th>
<th>N5</th>
<th>N6</th>
<th>N7</th>
<th>N8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite, wt.%</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>30</td>
<td>35</td>
<td>40</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>Na2SO4, wt.%</td>
<td>85</td>
<td>80</td>
<td>75</td>
<td>70</td>
<td>65</td>
<td>60</td>
<td>55</td>
<td>50</td>
</tr>
</tbody>
</table>

Visual observations of sintered samples:
- ♦ - pellets with serious deformation and leakage of the PCM;
- ● - pellets with a small amount of deformation and little leakage of the PCM;
- * - pellets with perfect appearance without deformation nor leakage.

3.4. Energy density of the composite materials

Evaluation of energy density of the composite materials requires the consideration of both latent heat and sensible heat. This is done by using the following equation for a temperature range between \(T_0\) and \(T_s\):

$$Q = \int_{T_0}^{T_s} C_{ss} dT + \delta \left( \int_{T_0}^{T_{fi}} C_{si} dT + \Delta H_{lf} + \int_{T_{fi}}^{T_s} C_{il} dT - \int_{T_0}^{T_{fi}} C_{il} dT \right)$$

where \(Q\) is the total thermal energy stored in a unit mass of the material, \(C_{ss}, C_{si}\) and \(C_{ll}\) are respectively the heat capacities of the shape stabilization material (diatomite), the PCM in solid state, and the PCM in liquid state, and \(T_0, T_s\) and \(T_{fi}\) denote respectively the lower bound temperature, the upper bound temperature and the melt point of the PCM. For calculating the energy density, accurate measurements of the heat capacity are crucial. Fig. 6 shows the measured heat capacity of the composite material containing 45% diatomite. The DSC-TG curve is also shown in the figure as an inset for comparison. The endothermic peak shown in the heat capacity curve at 878–906 °C agrees well with the DSC measurements. Curve-fitting of the measured heat capacity data over the two temperature ranges of 50–875 °C and

![SEM images of composite materials with 25% (a) and 45% (b) diatomite (10000×).](image-url)
908–1100 °C gives the following two polynomial expressions corresponding to the two temperature ranges:

\[
c_{p,m}^0 = 0.9104 + 4.7958 \times e^{-4T} + 7.0377 \times e^{-7T}^2 (R^2 = 0.9424)
\]

\[
c_{p,m}^0 = 1148.7786 - 3.5996T + 0.377 \times e^{-4T^2} - 1.3142 \times e^{-7T^3} (R^2 = 0.9873)
\]

where \( T \) is temperature. Heat capacity over 1000 °C was not determined because the composite material was found to have failed; see the TG curve in the inset of Fig. 5 where mass loss becomes increasingly serious when the temperature increases to over 1000 °C.

Using the heat capacity data discussed above, the energy densities of the composite materials are calculated. Illustrated in Fig. 7 is the calculated energy density of the composite material as a function of diatomite concentration over the temperature range of 700–900 °C. The inset in the figure shows the changes in energy density of the composite material containing 45% diatomite as temperature increases from 100 to 1000 °C with 100 °C intervals. The energy density is seen to decrease approximately linearly with increasing diatomite concentration. At a diatomite content of 15%, the energy density is as high as 676 kJ/kg. This decreases to 306 kJ/kg when the diatomite concentration increases to 50%.

As discussed earlier, deformation and leakage occur at a diatomite concentration below 40%, whereas a high diatomite concentration gives a low energy density. It is therefore concluded that the composite material containing 45% diatomite can be regarded as a close to the optimal formulation. In the following, an analysis is made on the inset in Fig. 7 for the optimal formulation. Below the melting temperature of the PCM, the energy density increases with increasing temperature mainly due to the sensible heat contribution except for the 200–300 °C temperature range where solid–solid phase change occurs.

A large increase occurs at the melting temperature range due to the latent heat contribution. At temperatures higher than 1000 °C, the energy density falls rapidly due to the failure of the material. These results suggest that the sodium sulfate based diatomite composite materials should be used at temperatures below approximately 980 °C, which is 20 °C below the failure temperature and should not be an issue for modern temperature control technologies. As the melting temperature of sulfate is approximately 880 °C, the composite materials should be used at above 890 °C (10 °C above the melting point) or achieving a high energy density.

4. Conclusions

This work aims to develop high temperature composite thermal energy storage materials. Sodium sulfate and diatomite are selected for the work. The following conclusions are obtained:

- Sodium sulfate and diatomite have an excellent chemical compatibility.
- The composite material containing approximately 45% diatomite gives an optimal formulation in terms of energy density, salt leakage and mechanical strength.
- The melting temperature of sodium sulfate in the composite materials is around 880 °C and no confinement effect is observed due to the nanoscale diatomite pore size. This indicates that the material should be used at temperatures over 890 °C to maximize the energy density.
- The composite materials are found to fail at temperatures above 1000 °C, suggesting that the materials should be used at temperatures below about 980 °C.
- The composite material with the optimal formulation has an energy density exceeding 360 kJ/kg for an operating temperature range of 700–900 °C.

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