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Micro encapsulated & form-stable phase change materials for high temperature thermal energy storage

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HIGHLIGHTS

- A new approach to synthesise a form-stable phase change material (FPCM).
- The FPCM contains chloride salt and diatomite.
- Micro encapsulation and sintering methods are combined to synthesise the FPCM.
- Chloride salt is well enclosed in the micro structure formed by diatomite.
- The microstructure maintains after 1000 heat-cold cycles.

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ABSTRACT

Chloride molten salts are promising candidates for high temperature thermal storage applications, owing to their energy storage density and thermal stability. Nevertheless, the main disadvantage of them is their corrosive behaviour with metal containers, which narrows down the range of applications. Encapsulation is considered a favourable method to prevent the corrosion. In this work, composite thermal storage materials consist of a phase change material (PCM) and a encapsulation material are studied, where the PCM is a mixture of sodium and potassium eutectic salts and the encapsulation material is diatomite. The composite materials which consist of PCMs & encapsulation materials are fabricated using a micro encapsulation method which is a combination of mixing and sintering. After applying the aforementioned method, it is observed that the PCMs are distributed homogeneously in the composite materials. With the help of XRD, it is found that the compounds stay unchanged after the encapsulation process, which indicates that the materials are compatible to each other. In this study, the composite material containing 70 wt% PCM exhibits the most favourable thermal energy storage properties, stability and capsule integrity as it is shown that the latent heat of the aforementioned composite material is observed 179.3 J/g and no significant decline or salt leakage is found after hundreds of heating-cooling cycles.

1. Introduction

Nowadays fossil fuels are still supplying about 80% of the total primary energy needs in the world [1]. However, the excessive use of fossil fuels have resulted in a shortage of traditional energy source and some severe environmental issues [2,3]. Therefore, the technologies of renewable energy and the waste heat recovery have attracted increasing attention [4–6]. Thermal energy storage (TES) technology which is capable of reducing the intermittency of renewable energy and decreasing the mismatch between energy supply and demand has been widely investigated and applied by researchers and engineers [7–9]. The synthesis of high-performance thermal energy storage materials (TESM) is one of the key technologies for thermal energy storage applications [10–14]. Recently, phase change thermal storage materials, especially micro encapsulated (MEPCM) and form-stable phase change energy storage materials (FPCM) exhibit rising potential in industrial applications [15–17] such as solar energy thermal storage [18–21], space heating energy storage using off-peak electricity [22,23], exhaust

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heat recovery [24,25] and cascaded latent heat storage (CLHS) system [26,27].

Molten salts such as chloride salts show considerable phase change enthalpy, chemical stability and are economically affordable, which makes them favourable candidates as high temperature energy storage material [28,29]. However in industrial applications, their corrosive behaviour and low heat transfer properties narrow down the range of application [30–33].

By enclosing PCMs in encapsulation materials or matrix materials, MEPCMs and FPCMs enhance the compatibility of PCMs and the container and minimize the risk of corrosion at high temperature. It also greatly enhances the heat transfer efficiency by enabling the direct contact between the heat storage material and heat transfer fluid (HTF). Numerous encapsulation and matrix materials can be used to synthesise MEPCMs or FPCMs working at different ranges of temperature. For instance, silicates, magnesium oxide, clay, diatomite, vermiculite, metals, polymers and expanded graphite can work as matrix materials to enclose PCMs such as paraffin waxes, fatty acids and hydrated salts, metals, nitrates, carbonates, chlorides, sulphates and their mixtures [34–41].

Karkri et al. [42] used in situ polymerization to synthesize MEPCMs that consist of paraffin wax as the PCMand melamine-formaldehyde resin as the encapsulation material. The average diameter of the spherical microcapsules is observed ~1.5 μm and the shell is ~1.5 μm. Sarkar et al. [43] introduced an in-situ polymerization procedure to synthesise microcapsules in which graphene underwent a heat treatment and epoxy resin formed the PCM and urea-formaldehyde polymer was the encapsulation material. The results indicated that the encapsulation process did not have any negative impact on the thermal properties of the PCM. Zhang et al. [44] used the in situ sol-gel process in inorganic salt water to synthesize $Na_2SO_4{\cdot}10H_2O@SiO_2$ solid microcapsules. It was discovered that the use of silica as encapsulation material in microencapsulation of hydrated salt can reduce the phase separation effectively.

Diatomite is a natural porous material which features considerable specific surface area, good adsorption performance [45–49], high temperature resistance and corrosion resistance. Diatomite has good wettability with molten salts and water. Therefore, it is often used as a matrix material to synthesise FPCMs. Karaman et al. [50] synthesised a FPCM with diatomite and polyethylene glycol. It has a phase change temperature at 27.7 °C and a latent heat of 87.09 J/g. It has ~50 wt% of PCM, and exhibits favourable chemical and physical stability in heating-cooling cycling experiments. Konuklu et al. [51] used impregnation process to prepared diatomite-based FPCM. The maximum ratio of PCM was 32% in their study. Deng et al. [52] synthesised a high temperature FPCM with KNO_3 and diatomite. After the mixing and sintering process, KNO_3 penetrated into the pores of diatomite and the mass fraction was ~65%. Qian et al. [53] researched a group of FPCMs containing diatomite and PCMs (polyethylene glycol, $LiNO_3$, and Na_2SO_4) via different processes which are a vacuum impregnation method and a facile mixing and sintering method. Qin et al. [54] used the diatomite as a matrix material and sodium sulphate as PCM to produce a FPCM for an application at 880 °C. The result shows that the FPCM with 45% mass percentage of diatomite had the best performance in energy density, package integrity and mechanical strength. Ge et al. [55] synthesised a 500 °C FPCM of using lithium and sodium carbonates, magnesium oxide and graphite. The FPCM showed good chemical compatibility with each other. Besides, with the addition of graphite, it showed a significant enhancement in the thermal conductivity.

In this study, a binary eutectic chloride salts and diatomite are used to synthesise a group of novel FPCMs. The novel FPCMs exhibit favourable thermoproperties as thermal energy storage materials. In the synthesis procedure for the FPCMs, for the first time, we combine mixing and sintering methods to enclose salts in fine diatomite particles.

Table 1
Chemical compositions of the diatomite wt%.

Composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO
Content	≥85	< 5	≤1.5	< 0.4	< 0.5

This method is scalable for industrial production. The materials are promising for high temperature heat storage applications such as solar thermal power generation, peak shaving of electrical power grids, decentralized energy systems, and waste heat recovery owing to their favourable thermophysical properties and non-corrosive behaviour.

2. Experiments

2.1. Raw materials

All raw materials used in this study are solid at ambient temperature. Diatomite is provided by JJS MINERALS CO. LIMITED, UK and its chemical composition is shown in Table1. One can see that silica (> 85%) and alumina (< 5%) are two main components of diatomite and others account for < 10%. In the material preparation phase, diatomite was calcined to get rid of organic impurities and in the process its porous structure is maintained (Fig. 1). The specific surface area of diatomite is 66.29 m^2/g which was measured with an Autosorb-1 device (Quantanchrome, USA) based on Brunauer–Emmett–Teller (BET) theory. Because of the existence of capillary adsorption force, this porous microstructure can further ensure that the molten salts were enclosed at high temperature.

The NaCl and KCl used in this study are both analytic grade and purchased from Sigma-aldrich Company Limited, UK. Fig. 2(a) shows the melting point of NaCl-KCl binary eutectic system is 657 °C where the mole ratio of NaCl:KCl was 1:1.02. Fig. 2(b) shows the heating and cooling DSC curves of the binary eutectic system are in the temperature range 300–750 °C. Phase transition was observed at a temperature of 655 °C in both heating and cooling processes. The peak temperature and latent heat are 665 °C and 259.6 J/g, respectively, in the solid-liquid transition and 650 °C and 249.3 J/g in the liquid-solid transition.

2.2. Fabrication of NaCl-KCl/diatomite composites

The mass fraction of the components is shown in Table 2.

- Preparation of eutectic salt

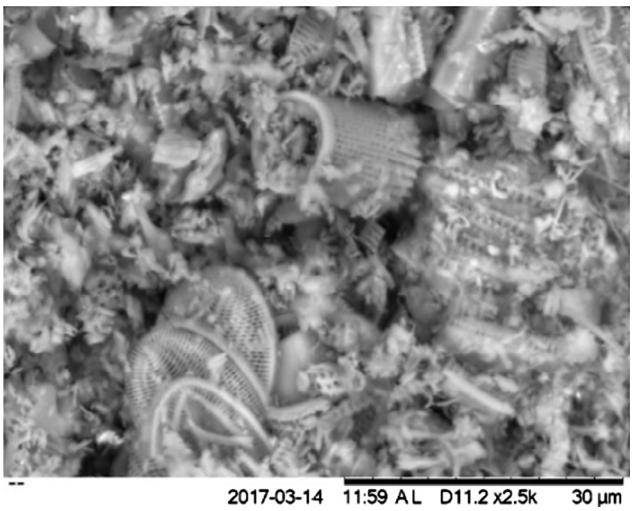

Fig. 1. Microstructure of the diatomite.