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Preparation, characterization and thermal properties of binary nitrate salts/expanded graphite as composite phase change material

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ABSTRACT

The binary nitrate salts/expanded graphite (EG) composite phase change material (PCM) were prepared via adding different mass rate of EG to binary nitrate salts consisting of $NaNO_3$ and KNO_3 (6:4) by aqueous solution method adopting ultrasonic. The morphology and chemical composition of EG and the composite PCM were characterized and investigated by X-ray diffraction (XRD), scan electron microscope (SEM), energy dispersive spectrometer (EDS), transmission electron microscope (TEM), respectively. Laser thermal conductivity instrument and differential scanning calorimeter (DSC) were employed to measure thermo physical properties. Drawing the conclusion from investigation, that EG had enhanced thermal conductivity coefficient which largely increased to 4.884 W/(m K) and reduced total latent heat by mostly 11.0%. The morphology and phase structure results indicated that EG were well dispersed into and physically combined with molten salts. In general, the prepared composite PCM could be a suitable phase change material for thermal energy storage.

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1. Introduction

Since serious shortage of energy resource and tremendous requirement for renewable energy, phase change material (PCM) with advantageous thermal properties has been applied to satisfy the increasing demand [1–5]. Depending on the characteristics of high latent heat, high specific heat and high thermal conductivity and so on [6,7], PCM has played an important role in various fields extensively [8–10].

In recent decades, several inorganic PCM and their mixtures have been investigated for thermal energy storage [11–13]. Due to its better thermal properties, molten salts were usually used as direct heat transfer medium in industrial applications [14–16]. Various nitrate salts and their composite have attracted tremendous researcher's concern. The mixtures consisting of KNO_3, $LiNO_3$ and $Ca(NO_3)_2$ with excellent thermal properties were proved to be a promising PCM [17]. Iverson et al. [18] concluded that temperature did not have a significant effect on mechanical properties through analyzing the thermal and mechanical properties of several nitrate salts in common use.

Recently, researches have focused on improving the thermo physical properties of heat transfer and energy storage medium. The usage of different additives is a usual method to obtain better heat efficiency of molten salts. A kind of inorganic compound with the chlorides has given a rise to the thermal conductivities of multi-component molten salts composed of potassium nitrate, sodium nitrite and sodium nitrate [19].

According to the excellent thermal and mechanical properties, graphite and EG have been particularly chosen for improving thermal conductivity of conventional PCM. Rao et al. [20] had prepared paraffin/graphite composite phase change materials and demonstrated that the total latent heat value decreased as the increasing mass rate of graphite. EG/paraffin nanocomposites were obtained by dispersing EG into paraffin via intensive ultrasonic irradiation without dispersants. Owing to the distinctive thermal properties of EG, the thermal conductivity of composite increased to 1.04 times higher than that of pure paraffin [21]. Kim et al. [22] had prepared the paraffin/xGnP composite PCM by stirring xGnP in liquid paraffin. An almost linear relationship was concluded between thermal conductivity and mass fraction of xGnP. Meanwhile, EG have gained spread application in paraffin [23,24] and other organics [25,26] for energy storage systems.

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As EG has benefited the organic on thermal properties, great efforts have been spent on the mixture of EG and inorganic. Martin et al. [27] had prepared the binary salt consisting of 70 wt.% $NaNO_3$ and 30 wt.% KNO_3 and demonstrated that the melting temperature ranged from 223 °C to 262 °C and the enthalpy was about 118 ± 2 kJ/kg. At room temperature, the apparent conductivities of KNO_3/$NaNO_3$-graphite made by cold-compression were up to 20 W/(m K), which was 20 times higher than that of binary salts [28,29]. Xiao et al. [30] had reported that the usage of EG to nitrates had a improvement on thermal conductivity by about 30–40% and a reduction on latent heat per mass mixture by nearly 5–18%.

In present paper, we report a simple and convenient method to prepare the nitrate salts/EG composite PCM by solution method with ultrasonic, different from the conventional preparation method. The binary nitrate salts were prepared by statically heating $NaNO_3$ and KNO_3 at mass ratio of 6:4 to completely melt. The ultrasonic had played a role of breaking EG into nanoscale slices and dispersing them into nitrates. The physical combined composite PCM was proved to have excellent latent heat and high thermal conductivity.

2. Experimental

2.1. Materials

Potassium nitrate and sodium nitrate were obtained from samples with A.R. grade and no further purification. Deionized water and graphite intercalation compounds [31] were self-restraint.

2.2. Preparation

After being dried at 100 °C, graphite intercalation compounds were expanded through a rapid heating in microwave ovens as reported in our previous work [31]. The expanded graphite was prepared while the bright flame was out.

Potassium nitrate and sodium nitrate were put into an air oven and dried at 120 °C for 24 h respectively and then mixed at the mass ratio of 6:4 uniformly. A mixture of binary nitrates salts was placed into a crucible and then heated at 350 °C for 30 min statically in order to melt completely. Afterwards, the crucible was gradually cooled down to room temperature. The molten salts were obtained. Grinding the molten salts slowly and dissolved it in a breaker by deionized water gradually. Then, EG was added into the previous solution slowly under continuous stirring at different mass rate. After the EG soaking into the solution, the solution was stirred by the strong ultrasonic homogeneous instrument (SCIENTZ-IID) with a power of 800 W for 1.0 h. Then, the breaker was put into a drying oven and dried at 100 °C for 24 h. By grinding the dried composite PCM, sample was obtained. Before drying of the solutions, one was filtered and washed using deionized water until the stripped graphite flakes (SGFs) were enough visible. SGFs were obtained after drying as mentioned.

2.3. Characterization and determination of thermal properties

X-ray diffraction (XRD; DMAX-Ultima IV, Rigaku Corporation, Japan) was employed to identify the microstructure and chemical composition of EG, SFGs and the composite PCM. The morphology and chemical composition of composite PCM were investigated by scan electron microscope (SEM; S3400N, Hitachi, Japan) with an energy dispersive X-ray spectroscopy detector, field emission scanning electron microscopy (FE-SEM; S-4800, Hitachi, Japan) (EDS; EX-250, HORIBA, Japan) at room temperature. The morphology of SGFs was investigated with a high resolution transmission electron microscope (HRTEM; JEM-2010HR, Jeol, Japan). Thermal conductivity of binary nitrate salts and binary nitrate salts/EG composite PCM was measured by employing a laser heat conductive instrument (Germany, NETZSCH, LFA 447) at room temperature. The phase change temperature and latent heat of the nitrates and nitrates/EG composite PCM were both measured by differential scanning calorimetry (DSC; DSC-204, NETZSCH, Germany) under a nitrogen atmosphere. The data were collected with a scan rate of 10 °C min^{-1} from room temperature to 260 °C.

3. Results and discussion

3.1. Stripped graphite flakes

The morphologies of EG and SGFs were observed by SEM as shown in Fig. 1. As can be seen from Fig. 1a, EG has a 3D worm-like architecture within size of 150 μm. The high-magnification SEM photograph (Fig. 1b) of SGFs shows that EG altered to slices in nanoscale after the ultrasonic.

The TEM photographs of SGFs from different angles were shown in Fig. 2. As represented in Fig. 2a, SGFs were flat and semitransparent slices with some wrinkles and folds. It could be observed that its dimension was between 8 and 25 nm which corresponded to observation of SEM photograph in Fig. 1b. As observed in Fig. 2b, the folds with lamellar structure were slices as given in Fig. 1b.

The phase structure of EG and SGFs were characterized by XRD as shown in Fig. 3. The sharp and intensive diffraction peaks at 26.3°, 56.0° correspond to EG and SGFs, respectively. A third diffraction peak of SGFs at 45.0° appeared particularly because ultrasonic made structure of graphite flake into disorder.

3.2. The composite PCM

The SEM images of binary molten salts and composite PCM samples were shown in Fig. 4. As shown in Fig. 4a, the $NaNO_3$–KNO_3 eutectic crystal was gray milky substance which looked like smooth block. The images in Fig. 4b–e correspond to samples with EG at mass rates of 0.5, 1.0, 1.5, 2.0%, respectively. Judging from the images, we might draw the conclusion that SGFs were well dispersed in eutectic crystal with foliated and angular structure.

The phase structure of molten salts and composite PCM samples were characterized by XRD at room temperature as shown in Fig. 5. The peaks at 26.3°, 56.0° correspond to SGFs. However, the weak feature peak of SGFs centered at 45.0° completely disappears after the composite PCM composed. The peaks at 23.0°, 28.5°, 38.0° correspond to potassium nitrate and the peaks at 31.5°, 46.0°, 47.5° correspond to sodium nitrate, respectively. Obviously, potassium nitrate and sodium nitrate were the main crystal phases as identified in Fig. 5(a). Further, the position of peaks was without excursion which proved that the phase structure of nitrate crystal were no chemical reaction. Due to the little additive of EG, its presentation was unobvious in the composite PCM.

The chemical composition of the prepared composite PCM was further determined by EDX analysis attached to the SEM. The EDX spectrum (Fig. 6b and c) sustains that the composite PCM (Fig. 6a) consists of C, N, O, Na and K elements. The strong N, O, Na and K signal originates from binary nitrates, while the C signal comes from the EG. What's more, the difference of percentage content of C in the two samples (Fig. 6b and c) was caused by mutual interference of C and K element belonging to low atomic sequence and the little quality of test samples, etc. According to the above analysis, it is unambiguously demonstrated that EG had been successfully combined into binary nitrate crystal.

The images of map scanning in Fig. 7b–f correspond to C, N, K, Na, and O elements attached to the SEM (Fig. 7a), respectively. The dispersion of every element in samples could be easily judged.

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