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A novel process for preparing molten salt/expanded graphite composite phase change blocks with good uniformity and small volume expansion

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ABSTRACT

Herein a novel process was explored for preparing molten salt/expanded graphite (EG) composite phase change material (PCM) blocks, which involves mixing a solid molten salt with EG thoroughly, compressing the mixture into a block with a designed shape and then heating the block to a temperature above the melting point of the molten salt followed by cooling. An $MgCl_2$-KCl eutectic salt was used as the PCM, and its EG-based composite PCM block was prepared by this process, in which the optimal mass fraction of the eutectic was determined to be around 85%. The microstructure of the $MgCl_2$-KCl/EG composite PCM block containing 85% the eutectic shows a uniform distribution of the molten salt. The composite PCM block has a melting point of 424.14 °C and a solidification point of 418.39 °C, and its latent heat values are 161.37 J/g for melting and 160.28 J/g for solidification. Compared with the eutectic salt, the composite PCM block exhibits a reduction in supercooling by 3.7 °C and an enhancement in thermal conductivity by 11-fold. It has been verified that the composite PCM block possesses excellent thermal reliability. Furthermore, the composite PCM block has been compared with the one prepared by the conventional method (first adsorption and then compression). It is found that the composite PCM block fabricated by the novel process exhibits better uniformity and smaller volume expansion than the one obtained from the conventional method. The $MgCl_2$-KCl/EG composite block shows great promise in high-temperature thermal energy storage systems, and this novel process is very suitable for preparing molten salt/EG composite PCM blocks.

1. Introduction

Latent thermal energy storage (LTES) based on phase change materials (PCMs) as the working media is the most important technology for storing heat, owing to its high energy storage densities and nearly isothermal operating characteristics [1,2]. Since the efficiency of LTES systems is largely dependent on the properties of PCMs, the PCMs with large latent heat, high thermal conductivity, good reliability and low cost are highly desirable for the systems. Generally, according to application fields, PCMs can be classified into three major categories: low, medium and high-temperature [3–5]. Molten salts usually exhibit high phase change temperatures and possess the characteristics of large latent heat capacity, low vapor pressure, good thermal stability and commercial availability, thereby having important applications in solar power generation, waste heat recovery, etc [6–8]. However, molten salts suffer from some intrinsic drawbacks such as low thermal conductivity, corrosion and liquid leakage during phase transition, which greatly restrict their applicability in the high-temperature LTES systems [9].

Preparation of a composite is an effective route for overcoming the shortcomings of a PCM along with improving its applicability [10]. The composition technologies mainly include encapsulation of a PCM into a spherical shell [11] and combination of a PCM with supporting materials [12–15]. Compared with the former one that needs complicated preparation process and thus suffers from high cost, the later technology has the advantages of simpler preparation process and lower cost along with a diversity of supporting matrices. Especially, using porous supporting materials to absorb PCMs, not only can resolve the liquid leakage of the PCMs through the adsorption of the carriers, but also has the function of adjusting the thermal conductivity of the obtained composite PCMs by selecting the carriers having different thermal conductivity [16–18]. Since Zhang et al. [19] reported the paraffin/expanded graphite (EG) composite PCM in 2006, EG has been combined with various organic PCMs to prepare their EG-based composites. And the obtained EG-based PCMs have been revealed to be form stable and exhibit excellent thermal reliability along with enhanced thermal conductivity at a cost of a reduction in latent heat only by around 10% [20–22]. These good characteristics of the EG-

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based composite PCMs are attributed to the merits of EG, which include large pore volume, high thermal conductivity and good compatibility with organics [23,24].

Recently, an increasing attention has been paid on the EG-based composite PCMs containing inorganic PCMs such as hydrate salts [25] and molten salts [26,27]. It has been reported that, various molten salts, such as $LiNO_3$-KCl [26], KNO_3-$NaNO_3$ [28,29] and NaCl-$CaCl_2$ [30], can combine with EG to obtain the composite PCMs with form stability and enhanced thermal conductivity, suggesting that the shortcomings of the molten salts can be effectively overcome by the combination with EG. Generally, the process used for preparing the molten salt/EG composite PCMs involves the melting of the molten salts and the subsequent adsorption of EG [26,30] or the dissolving of the molten salts into water to obtain their solutions followed by the adsorption of EG and drying [28]. Note that the uniformity of the obtained composite PCMs is largely dependent on the absorbability of EG for those molten salts. However, different from the organic PCMs that have good compatibility with EG, the molten salts are hydrophilic, making them more difficult to be adsorbed into EG. Consequently, the molten salt/EG composites prepared by this process cannot reach the uniform distribution of the molten salts into EG [25,31,32]. In addition, when applied the EG-based composite PCMs in LTES systems, they usually need to be compressed into blocks with specific shapes, with the purposes of making the composite PCMs fit into the application situations along with increasing their thermal conductivities and volumetric thermal storage densities [33,34]. Unfortunately, volume expansion has been always found on the composite PCM blocks containing the molten salts after they experienced one or several heating-cooling cycles, [35,36] which could be attributed to their high working temperatures. As a result, it is required to reserve some space in a heat storage unit for allowing the volume expansion of a PCM block used in it, thereby leading to a low usage ratio for the effective volume of the unit. Apparently, it is highly necessary to explore a novel process for preparing molten salt/EG composite PCM blocks with good uniformity as well as small volume expansion.

In the current work, a novel process is presented out for preparing the molten salt/EG-based composite PCM blocks. First, a solid molten salt is thoroughly mixed with EG. Then, the resultant mixture is compressed into a block with a designed shape according to its application situation. Finally, the obtained block is heated to a temperature above the melting point of the molten salt and kept for several hours to make the PCM melt completely. After cooling, the obtained sample is the molten salt/EG-based composite PCM block. Specifically, an $MgCl_2$-KCl eutectic salt was chosen as the molten salt PCM to combine with EG. The $MgCl_2$-KCl/EG composite blocks with different mass fractions of the eutectic were prepared by this mixing-compression-heating process, followed by a liquid leakage test on them for determining the optimal mass fraction of the eutectic in its EG-based composite. Then, the microstructure and thermal properties of the $MgCl_2$-KCl/EG composite block with the optimal mass fraction were characterized, and its thermal reliability was evaluated. Furthermore, the conventional method was also employed to prepare the $MgCl_2$-KCl/EG composite PCM with the optimal mass fraction of the eutectic, followed by compressing it into a block with the same shape and packing density as those of the one obtained from the novel process. And then the uniformity and volume expansion of the two blocks fabricated by the two processes were compared. It is shown that, the $MgCl_2$-KCl/EG composite PCM block fabricated by the novel process, not only possesses good thermal characteristics and excellent thermal reliability, but also exhibits better uniformity and smaller volume expansion than the one obtained from the conventional method. It is suggested that this novel process is propitious to prepare the molten salt/EG composite PCM blocks with good uniformity and small volume expansion.

2. Experimental section

2.1. Materials

Magnesium chloride and potassium chloride (AR, > 99% in purity) were purchased from Shanghai Aladdin Chemical Reagent Co, Ltd. Expandable graphite powder with an expandable volume of 300 mL/g was purchased from Qingdao Furuite Graphite Co, Ltd., China, which granularity was mesh 100. EG was prepared from the expandable graphite powder by the microwave method [37].

2.2. Sample preparation

2.2.1. Preparation of $MgCl_2$-KCl eutectic salt

An $MgCl_2$-KCl eutectic with a phase change temperature of around 423 °C was selected as the PCM, in which the molar fractions of $MgCl_2$ and KCl were 0.315 and 0.685, respectively [38]. In a typical preparation, magnesium chloride and potassium chloride powders were thoroughly mixed, followed by being heated to 500 °C and held for 3 h to obtain a uniform mixture. After cooling down to ambient temperature, the solidified salt mixture was ground, followed by being placed in a glove box before use.

2.2.2. Preparation of $MgCl_2$-KCl/EG composite PCM blocks

The procedures for preparing the $MgCl_2$-KCl/EG composite PCM block by the novel mixing-compression-heating process are illustrated in Fig. 1. First, the solid $MgCl_2$-KCl eutectic was mixed with the EG using a high-speed mixer. Second, the resultant mixture was compressed into a round block (40 mm in diameter, 15 mm in thickness) at a packing density of 1.2 g/cm^3 using a tablet machine, followed by being weighed (m_1). Then, the block was placed into a watch-glass, followed by being heated to 500 °C and kept for 3 h in a muffle oven. After cooling down, the obtained $MgCl_2$-KCl/EG composite PCM block was weighed (m_2). For determining the optimal mass fraction of the eutectic in its EG-based composite, three composite blocks with the eutectic mass fractions of 80%, 85% and 88% were prepared, respectively, followed by a liquid leakage test. The test was carried out by careful examinations on the three watch-glasses for placing the three composite blocks, as shown in Fig. 2, with the purpose of finding out if there are any traces of the $MgCl_2$-KCl eutectic left on them. It is found that there are some of the white $MgCl_2$-KCl eutectic salt in the watch-glass for placing the composite block containing 88% the eutectic. Moreover, a reduction ratio in weight has been calculated based on $(m_1-m_2)/m_1 \times 100\%$. It is shown that the weight reduction ratios of the composite blocks with the different eutectic mass fractions are 0.26% for 80%, 0.72% for 85% and 2.52% for 88%. Based on the above results, it can be inferred that the optimal mass fraction of the $MgCl_2$-KCl eutectic in its EG-based composite should be less than 88%. Therefore, in the current work, the one containing 85% the eutectic is taken as the $MgCl_2$-KCl/EG composite PCM block, which exhibits little leakage of the eutectic salt in its watch-glass (Fig. 2) as well as a low weight reduction ratio by 0.72%.

For comparison purpose, the conventional method was also employed to prepare the $MgCl_2$–KCl/EG composite PCM block containing 85% the eutectic. First, the eutectic was added into a crucible containing the EG. Then, the crucible was heated to 500 °C and kept for 3 h under continuous stirring. After cooling down, the sample was grinded to obtain the $MgCl_2$–KCl/EG composite PCM. Finally, the obtained composite PCM was pressed into a round block with the same shape and packing density as those of the one fabricated by the novel process.

2.3. Characterizations

The microstructures of EG and the $MgCl_2$-KCl/EG composite PCM block were observed using a scanning electron microscope (SEM, LEO1530VP, Zeiss, Germany).