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Preparation and characterizations of heat storage material combining porous metal with molten salt①

WANG Hua(王 华), HE Fang(何 方), DAI Yong-nian(戴永年), HU Jian-hang(胡建杭)
(Faculty of Materials and Metallurgical Engineering,
Kunming University of Science and Technology, Kunming 650093, China)

Abstract: A new type of heat storage materials combining high temperature molten salts phases change latent heat thermal storage materials, PCM with porous metals sensible heat thermal storage materials was developed. The process was expressed as following: firstly, it is necessary to heat up the molten salts phases change materials to molten; and then the porous metals are put into the molten bath; after being held for 1－3 h, the composite heat thermal storage materials lumps are taken out of the molten bath and cooled to atmospheric temperature; the last step is to electrodeposit a layer metal coat on the surface of the material lumps. The new type of heat storage material integrates the advantages of both solid sensible heat thermal storage materials and high temperature phases change latent heat thermal storage materials. The metal-base heat storage materials enjoy some favorable characteristics such as higher heat charge-discharge rate, higher heat storage density and better mechanical strength.

Key words: composite heat storage material; porous metal-base; PCM; thermal characteristics
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1 INTRODUCTION

Generally speaking, the heat storage technology is divided into two types, i. e. sensible heat thermal storage and latent heat thermal storage[1－3]. Sensible heat thermal storage technology is to use the heat absorption capacity of the ceramic materials to store the heat energy into the ceramic beads, and to use the heat transformed and stored under the condition of high or low temperature[4]. In the past few decades, the sensible heat thermal storage materials were widely applied owing to their good chemical and mechanical stability, excellent safety and heat conductivity[5]. But their disadvantages are as clear as their advantages. Their heat storage amount per unit mass or volume is relatively smaller, and their temperature change is remarkable during the heat charge-discharge process. In other words, it is difficult for them to operate at a certain temperature range. In contrast, latent heat thermal storage technology is to utilize the phase change, solid to liquid in most case, of materials to store up heat energy and eventually to recycle industrial waste heat or solar energy[6, 7]. Phase change heat storage materials also have good chemical stability, fine safety and large heat storage quantity per unit mass or volume. And more, they can charge-discharge heat around their phases change point. But the heat conductivity of the phase change material for latent heat thermal storage (PCM) can become deformable or even worse when the phases change taking place, especially on the surface of solid-liquid[8]. So, it is one of the key project in heat storage materials development to integrate the advantages of solid sensible heat thermal storage materials and phase change latent heat thermal storage materials, and to overcome their disadvantage. We developed successfully a new type of composite heat storage material combing high temperature molten salt PCM with porous nickel[9, 10]. As supposed, this new type of material is integrating the advantages of both kinds of individual heat storage materials, and overcoming their disadvantages. As results, the new composite material enjoys some favorable characteristics, such as high heat charge-discharge rate, high heat storage density and high strength. This article reports the preparation process and thermal characteristics of the new type heat storage material.

2 EXPERIMENTAL

The composite materials were prepared in a Muffle furnace, in which the PCM were heated up to molten. The molten salts system includes LiF-NaF-KF, Li_2CO_3-Na_2CO_3, NaCl-$MgCl_2$ and LiOH-LiCl

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Correspondence: WANG Hua, Professor; Tel: +86-871-5144174; E-mail: wanghuaheat@hotmail.com

etc. The melting point and phase change latent thermal energy of molten salts system can be determined simultaneously through DSC thermoanalyzer. When the PCM were molten out, the porous metals were put into the molten bath aiming to make the PCM combine into the metal-base. In order the porous nickel and aluminum to be obtained easily, the two types of typical porous metals were employed as base materials in the experiments. To guarantee the two kinds of materials combine completely, the temperature were usually controlled within 50 − 200 ℃ over the melting-point of the PCM. In addition, the holding time can be adjusted from 0.5 to 3 h according to particular needs. It is necessary to point out that the porous ratio of metal-base need to be determined at beginning of the experiments. When the composite heat storage materials were ready, we examined their characteristics, such as SEM morphology and heat storage density. The technology of electrodeposition process was proposed in Refs. [11, 12]. The experimental flow chart is shown in Fig. 1.

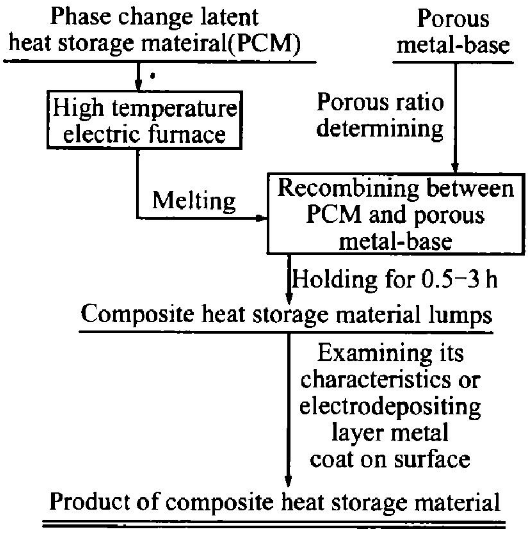

Fig. 1 Schematic of experimental process

3 RESULTS AND DISCUSSION

Macrostructures of the composite heat storage material combining porous nickel-base with molten salts PCM are shown in Fig. 2. According to various needs, the type of composite heat storage material can be prepared as cuboid or spheriform.

Fig. 3 displays the effect of compounding time on the volume fraction of PCM in the composite heat storage materials. As shown in Fig. 3, the volume fraction of PCM increases with increasing the combining time at the beginning of compounding process. As compounding process is going on, the effect of compounding time on the volume fraction of PCM becomes unconspicuous. Fig. 3 shows that the volume fraction of PCM reaches about 77% after combining for 1.5 h, 79% for 2 h and 80% for 3 h, respectively. After combining for 2 h, the volume fraction of PCM in composite heat storage material is inclined to a maximum value. So, when preparing composite heat storage material, the optimum combining time is 2 h.

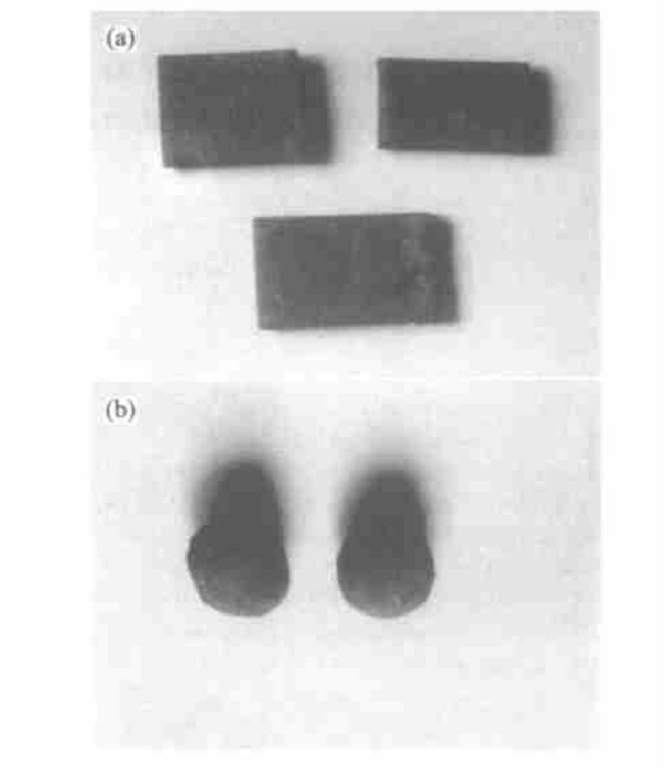

Fig. 2 Macrostructures of new type of composite heat storage material

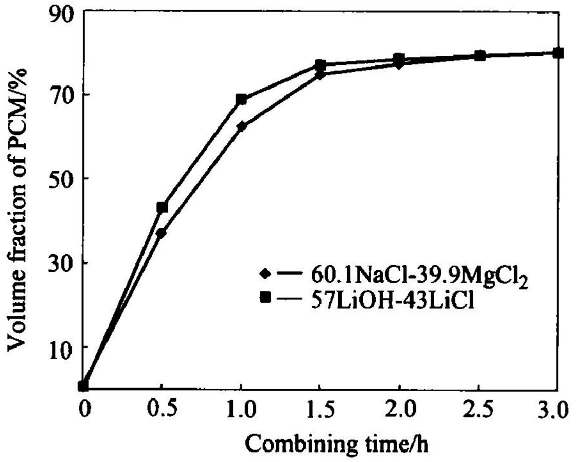

Fig. 3 Relationship of volume fraction of PCM in composite material with combining time(porous nickel is used as base)

The compounding parameters of composite are listed in Table 1. As presented in Table 1, the practical volume fraction of PCM in composite heat storage material are very close to the theoretical values 2 h later. It is evident that the combining action proceeded fully between the metal-base and the molten PCM. Take 46.5LiF-11.5NaF-42.0KF and nickel-base as an example, mass fraction of PCM reaches 81.3%

Table 1 Compounding parameters of composite heat storage material

PCM	Melting point of PCM, T_m/K	Latent heat of PCM, $\triangle H/(kJ\cdot kg^{-1})$	Practical mass fraction of PCM in composite heat storage material/ %	Theoretical mass fraction of PCM in composite heat storage material/ %	Porous metal-base	Combining time/ h
46.5LiF-11.5NaF-42.0KF	727	400	81.3	82.1	Ni	2
			79.6	83.3	Al	2
60.1NaCl-39.9MgCl$_2$	723	293	81.2	84.5	Ni	2
57LiOH-43LiCl	530	290	78.4	82.0	Ni	2
			80.7	81.8	Al	2

when combining time is 2 h, while the theoretical mass fraction is 82.1% in this case. It is necessary to point out that theoretical mass fraction of PCM is obtained by calculating the density of PCM and the porous ratio of the metal-base.

The SEM micrographs of heat storage material combining PCM, 60Na_2CO_3-40Li_2CO_3, with porous nickel-base are shown in Fig. 4. As shown in Fig. 4, apparently the framework texture is nickel-base. And the PCM is packed in the hole of the porous nickel-base. If the combining actions proceed completely, most of the hole in nickel-base will be filled with PCM. During heat charge-discharge process, the solid and liquid phase change of PCM will be repeated. Due to the capillary phenomenon, the molten PCM cannot leak out of the nickel skeleton. This type of heat storage material enjoys a favorable advantage of high-speed thermalenergy charge-discharge, owing to metal-base has excellent heat conductivity compared with ceramic materials. The metal fibers play an important role in enhancing heat transfer process.

The thermal storage density of the composite heat storage material is much higher than that of traditional sensible heat thermal storage material, such as ceramic and metal. Fig. 5 demonstrates the effect of temperature on heat storage density of two types of composite heat storage materials. From Fig. 5, it can be seen that the heat storage

density of composite materials increases with in-

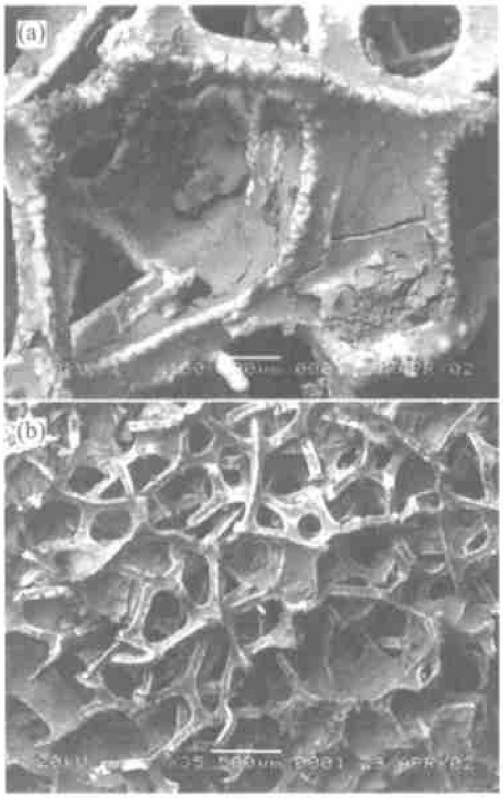

Fig. 4 SEM micrographs of porous nickel-base composite heat storage material

(a) —Higher magnification; (b) —Lower magnification

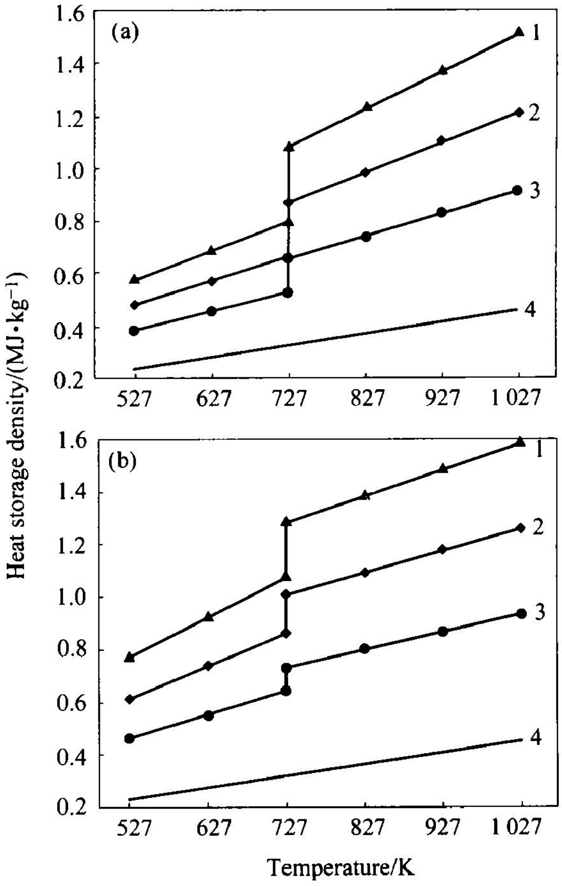

Fig. 5 Relation between temperature and heat storage density of heat storage materials

(a) —Ni+ 146.5LiF-11.5NaF-42.0KF;

(b) —Ni+ (60.1NaCl-39.9MgCl$_2$)

1—Ni+ 70% PCM; 2—Ni+ 50% PCM;

3—Ni+ 30% PCM; 4—Ni+ 0% PCM

creasing volume fraction of PCM and temperature. It is worth noting that the relation between temperature and heat storage density is linear before and after the PCM melting point 727 K. At 727 K, if the PCM is undergoing solid-liquid phases change, the thermal storage density of composite material will "jump" to a higher level. This may be explained by the fact that PCM have considerably big phase change latent thermal energy. Thus this new type of composite heat storage material will have better to be used above the melting point of PCM. The smoothed line of Fig. 5 (a) shows the heat storage density of pure nickel. Compared with other curves, it can be observed that PCM enhance the heat storage density of materials significantly. From Fig. 5(b) the same observations can be obtained.

4 CONCLUSIONS

A type of composite heat storage material is developed through combining PCM latent heat thermal storage material with porous metal-base sensible heat thermal storage material. The combining action proceeds completely between the metal-base and the molten PCM. As expected, the metal-base heat storage materials integrate the advantages of solid sensible heat thermal storage materials and PCM latent heat thermal storage materials. Compared with traditional sensible heat storage material, such as ceramic and metals, the heat storage density of this type of composite heat storage material is significantly enhanced through combining PCM with porous metal base, due to the PCM possessing large phase change latent heat energy.

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