Molten Salts/Porous-Nickel-Matrix Composite as Phase Change Material for Effective Use of High Temperature Waste Heat*

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Abstract: A new supported phase change material (PCM) made of molten salts impregnated by capillary forces in a porous-nickel matrix is presented. The preparation of molten salts/porous-nickel matrix PCMs was mainly discussed. Structures and properties of these materials were studied by X-ray diffraction (XRD) analysis, scanning electronic microscopy (SEM) observation and differential scanning calorimetry (DSC) analysis. The optimum composite time was 2~3 hours. The optimum composite temperature was 50~100 ℃ above melting point of the molten salt. Heat storage density of PCMs was also discussed.

Key words: high temperature; composite phase change material (PCM); thermal energy storage; porous nickel matrix; molten salt
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1 Introduction

Thermal energy storage is very important in fluctuant energy recovery and can meet the requirement of the difference of waste heat availability and utilization periods. There are three basic thermal energy storage methods: sensible heat, latent heat and chemical energy. In phase change energy storage, the storage or extraction of thermal energy is carried out by phase change materials (PCMs) during its phase transition. According to the type of phase change, phase change thermal storage can be classified as: solid-solid, solid-liquid, liquid-gas, solid-gas. The liquid-gas and solid-gas PCMs usually have high heat of phase transition, however, due to the large volume change during its phase transition, they are seldom chosen as PCM for practical use[1]. The solid-liquid PCMs were mainly discussed in the paper. A phase change material (PCM) is able to absorb or release large quantities of latent heat at a fairly constant temperature during its phase transition, resulting in less volume to store the energy required by the system. In addition, the temperature remains nearly constant during the phase change, which is beneficial for both the load and the collector.

For these advantages, the research of phase change materials (PCMs) has attracted much attention in recent years, but mainly focused on low temperatures below 500 K. A significant number of authors have based their work on organic materials such as alkanes, waxes or paraffins[2-7]. Within inorganic materials, the research focused on low temperature hydrated salt, such as $CaCl_2 \cdot 6H_2O$, $NaSO_4 \cdot 10H_2O$[8-9]. A few of work has been conducted on PCMs of high temperature. Capsulated PCMs of high temperature was chiefly discussed, composite PCMs of high temperature was seldom concerned. This paper presents a new supported phase change material (PCM) made of molten salts impregnated by capillary forces in a porous nickel matrix for effective use of high temperature waste heat.

The objective of this study is to investigate the feasibility of the employed five kinds of molten salts impregnated by capillary forces in a porous nickel matrix as composite PCM for effective use of high temperature waste heat. The preparation, structures and properties of these materials will be characterized.

2 Experiment

2.1 Materials

Five kinds of high temperature molten salt were chosen as PCM, Table 1 provides thermal properties of five PCMs used in the experiment. Porous-nickel was chosen as matrix, area density of nickel is 420 ± 30 g/m^2.

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Tab. 1 Thermal Properties of PCM

PCM	LiOH	Li_2CO_3	NaCl	K_2CO_3	Na_2CO_3
Melting point/K	744	993	1073	1170	1127
Latent heat/(kJ·kg^{-1})	910.1	606.0	477.3	235.8	275.7

2.2 Experimental process and design

First, molten salts (PCM) were heated by vacuum electric furnace to a temperature higher than its melting point. Then, put the porous-nickel immerged in molten salts, and let molten salts in liquid form penetrated into porous-nickel matrix in solid state in vacuum condition. After a period of time, take out the composite material and let it cool down in vacuum condition. Second, dryness of composite PCM and the calculation of percentage of phase change material in composite materials proceeded.

The structure of the prepared PCM is analyzed via scanning electronic microscope (SEM) and its latent heat is given by DSC method. Fig. 1 shows the photographs of different shape of molten salts/porous-nickel matrix composite PCM.

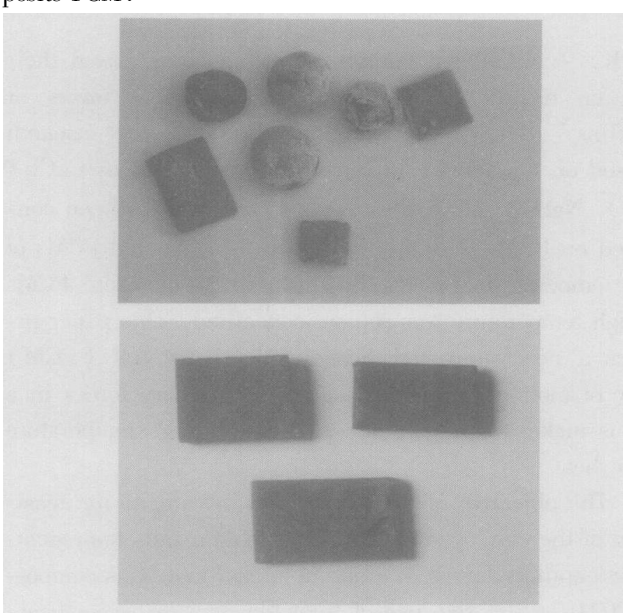

Fig 1 Photographs of different configuration of molten salts/porous-nickel-matrix composite PCM

3 Results and discussion

3.1 Analysis

3.1.1 SEM analysis Fig. 2 shows SEM photographs of composite phase change material with Ni—Li_2CO_3. From the figure, we can see that the molten salt — Li_2CO_3 has been divided into numerous tiny cells by the nickel matrix. The size of cell varies from 200 μm to several millimeter, and there are some cavities in the tiny cells, thus will reduce the thermal conductivity of composite PCM, but these cavities benefit for the expansion of the molten salt when it melts.

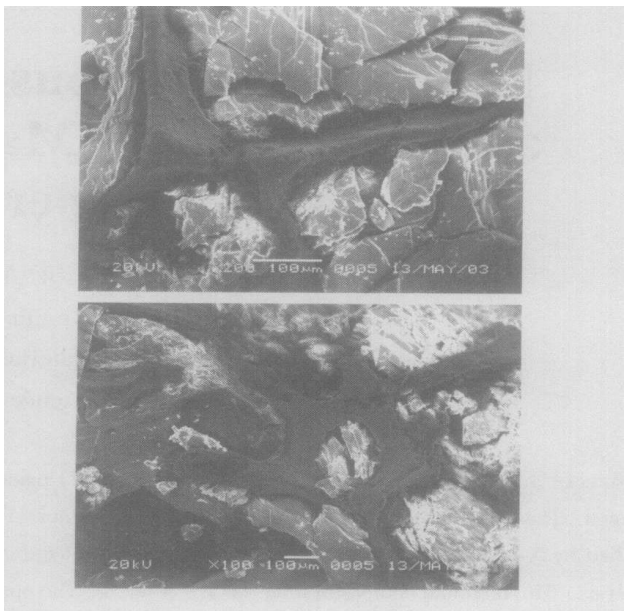

Fig 2 SEM photographs of composite phase change material with Ni—Li_2CO_3

3.1.2 XRD analysis The composite PCMs were investigated by X-ray diffraction (XRD). The XRD chart of an sample made of Li_2CO_3 impregnated by capillary forces in a porous-nickel matrix was shown in Fig. 3. The XRD peaks were identified to Ni, Li_2CO_3 and NiO. These results indicate that a little of nickel was oxidated. This will reduce the thermal conductivity of the composite material. But this kind of composite PCM was also the candidate of high heat storage density.

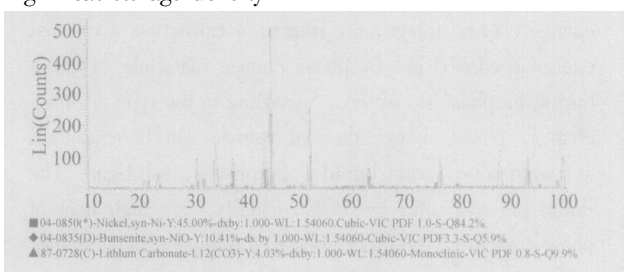

Fig 3 X-ray diffraction pattern of composite PCM with combination of Li_2CO_3 and nickel

3.2 Determination of composite time

Thermal energy storage density was influenced by the percentage of phase change material in composite materials. Commonly, the higher percentage was, the higher thermal energy storage density would be. Fig. 4 shows the percentage of phase change material in composite materials is increasing with composite time obviously before certain time point, after that point the composite time does little help to the increase. Such as, the percentage of Li_2CO_3 composite with Ni at 800 ℃ is 54.9% at half an hour, 86.5% at two hours and 86.6% at three hours. Overtime help to get higher percentage, but it went against preparation. In the experiment the optimum time is 2-3 hours.

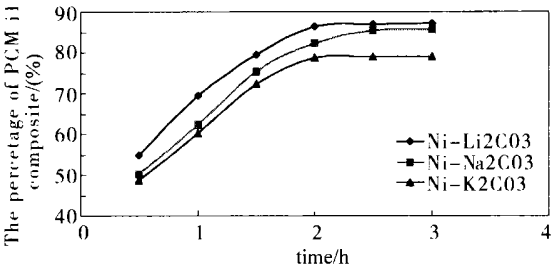

Fig 4　Percentage of phase change material in composite materials

3.3　Determination of optimum composite temperature

Fig. 5 and Fig. 6 show TG—DSC curves of Ni-Li_2CO_3, Ni-Na_2CO_3 composite PCM, respectively. From TG analysis, the loss of weight of composite PCM is various with the different molten salt after its phase transition. Forexample, the loss of weight of Ni-Li_2CO_3 composite PCM reaches to 2.05% at 833 ℃ (melting point of Li_2CO_3 is 732.5 ℃), but when the temperature rises to 1 000 ℃, data amounts to 10.07%. While the loss of weight of Ni-Na_2CO_3 composite PCM reaches to 0.37% when the temperature rises to 1000 ℃ (melting point of Na_2CO_3 is 853.9 ℃). Increasing the composite temperature helps to preparation process, but loss of weight of composite PCM also increases. Balancing these two aspects, the optimum composite temperature is 50 ~ 100 ℃ above melting point of molten salt, according to experiment and TG—DSC analysis.

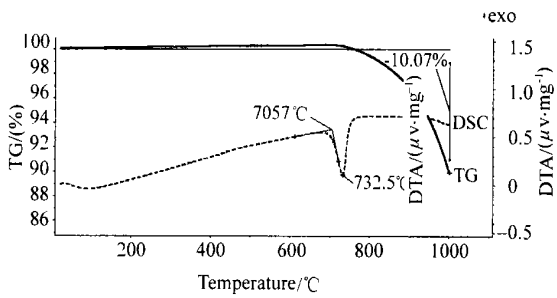

Fig 5　TG—DSC curves of Ni— Li_2CO_3 composite PCM

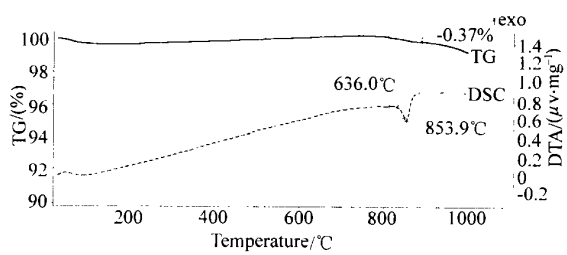

Fig 6　TG—DSC curves of Ni— Na_2CO_3 composite PCM

3.4　Thermal energy storage density

Thermal storage density is an important parameter of composite PCM, the comparison of thermal storage density of Ni, Ni-Li_2CO_3 and Li_2CO_3 is listed in Fig. 7. From Fig. 7, we can see that thermal storage density increases sharply when the application temperature is over its melting point. It indicates the application temperature of composite PCM may not be too high or too low, otherwise the characteristic of high thermal storage density of composite PCM cannot reveal.

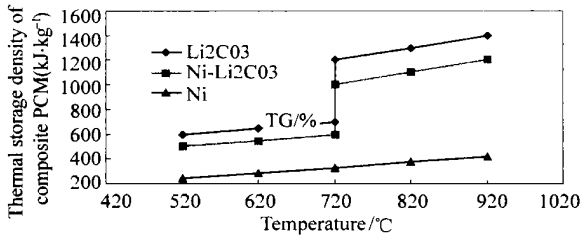

Fig 7　Effect of temperature on heat storage density

4　Conclusions

Experiments were carried out to prepare the composite PCM of excellence performance. The following results were obtained:

(1) The optimum composite time was 2 ~ 3 hours and the percentage of PCM in the composite material is very high over 75%.

(2) The optimum composite temperature was 50 ~ 100 ℃ above melting point of the molten salt.

(3) The application temperature of composite PCM may not be too high or too low, otherwise the characteristic of high thermal storage density of composite PCM cannot reveal.

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高温余热回收用熔融盐/多孔镍基复合相变蓄热材料

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摘 要: 提出了一种由多孔镍基熔浸熔融盐制备而成的新型复合相变蓄热材料, 重点研究了该材料的制备。并采用 X—射线衍射分析、扫描电镜和差热差重分析, 研究了复合蓄热材料的性能和结构。结果表明: 最佳的复合时间 2~3 h; 最佳的复合温度为高于熔点 50~100 ℃。

关键词: 高温; 复合相变材料; 热能贮存; 多孔镍基; 熔融盐

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