Study on the influence of glass encapsulating on the hygroscopicity of high temperature phase change heat storage materials

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Abstract. In this paper, Na₂CO₃-K₂CO₃ / MgO phase change composite was coated on the surface of glass by spray plating, which solved the problem of absorbing moisture and pulverizing of molten salt / MgO phase change thermal storage material in high humidity environment, and reduced the absorbing moisture and pulverizing rate from 31% to 19% without affecting the latent heat of phase change thermal storage material.

1. Introduction

Nowadays, with the great growths in the economy, the energy demand and consumption have increased enormously, and the fossil fuels still provide 80% of the world’s energy supply[1]. However excessive exploitation of fossil fuels energy will lead to energy shortage and environmental pollution[2]. Therefore, it is urgent to find an alternative to fossil energy and the development, and utilization of new energy and improving the efficiency of energy use have become the focus of research and development in various countries[3]. At present, thermal energy storage (TES) technology occupies a very important position in the research of new energy development and utilization around the world. The phase change material (PCM) is one of the key technologies for thermal energy storage[4-6]. It can store and release a large amount of energy through two-phase transition[7-10]. Recently, molten salts phase change materials have attracted the attention of researchers all over the world for their advantages of wide range of application temperature, high latent heat and low cost[11-12]. However, their hygroscopicity leads to narrowing of application scope in practical applications[13].

In this study, the carbonate phase-change composite material is taken as the research object, and the surface of the material is sealed by glass powder spray plating, so that the moisture in the air is isolated from the PCM, which plays a role of moisture-proof.
2. Experimental description

2.1. Raw materials
In this study, the $K_2CO_3$-$Na_2CO_3$ eutectic salt is used as heat storage medium. The MgO is used as matrix material. The $K_2CO_3$, $Na_2CO_3$ and MgO are provided by Global Energy Interconnection Research Institute co. Ltd (Beijing, China), and glass powder is provided by University of Science and Technology Beijing (Beijing, China). The softening temperature of glass powder is about 550 °C.

2.2. Preparation of eutectic salt
Fig.1 shows the phase diagram of $Na_2CO_3$-$K_2CO_3$ eutectic salt. The phase diagram shows that the transformation temperature is 717 °C when the mass ratio of $Na_2CO_3$: $K_2CO_3$ is 1:1. Firstly, $Na_2CO_3$ and $K_2CO_3$ were mixed according to the mass ratio of 1:1. Then deionized water was injected to make the mixture completely dissolved, and the mixture was placed in the oven and dried at 120 °C for 72 hours. Then it was crushed to less than 0.5mm with a crusher.

![Figure 1. The phase diagram of Na₂CO₃–K₂CO₃ eutectic salt][14]

2.3. Preparation of $Na_2CO_3$ and $K_2CO_3$ eutectic Salt/MgO composites
For preparing PCM with different proportions of coated molten salt particles and MgO, the above powders were weighed at 51.5:48.5 (1.5% encapsulation) and 53:47 (3% encapsulation) proportions. And mixed the powders in a ball mill for 1 hour. Then weighed 30g of mixed powder and put it into a 50 mm diameter steel mould. The green body was prepared at 40 Mpa pressure for 2 minutes. The sintering temperature of green body was 720 °C and the holding time was 2 hours. The PCM sample is shown in Fig. 2.

![Figure 2. The molten salt / ceramic phase change thermal storage material sample][18]

2.4. Encapsulation by spraying method
The glass powder and anhydrous ethanol were mixed in a mass ratio of 1:4, 2:4 And 3:4. The evenly mixed mixture was placed in a spray pot. Then it was evenly sprayed on the surface of the sample. The
sample was placed in an oven and dried at 60 °C for 2 hours. After that, the dried sample was sintered at 720 °C for 2 hours. The results are shown in Fig. 3.

![Figure 3](image)

Figure 3. The results of different concentration of glass powder after spraying and sintering (a. 3:4 concentration of glass powder solution spraying; b. 2:4 concentration of glass powder solution spraying; c. 1:4 concentration of glass powder solution spraying)

2.5. Characterization

The thermal storage performance of the PCM was measured using a differential scanning calorimeter (DSC) and a thermal gravity analyzer (STA449F5, NETZSCH, Germany) under N₂ atmosphere. The heating rate was 10k/min and the temperature range was 30°C~750°C. Hygroscopicity of the sample was tested in a EW1070 humidity chamber (ESPEC, China). The humidity test was carried out at 28°C and 80% relative humidity for 96 hours.

3. Results and discussion

3.1. Characterization hygroscopicity test of the composite PCMs

The morphology characteristics of the samples after humidity test are shown in Fig. 4. Fig. 4 (a) shows the morphology of the original sample after 96 hours in 80% relative humidity environment, and the composite has begun to show serious moisture absorption phenomenon. Fig. 4 (b) and Fig. 4 (c) show the morphology of the samples after spraying the encapsulating with the ratio of glass powder to absolute ethanol of 1:4 and 2:4 under the humidity of 80%RH for 96 hours, and the surface of the materials appears cracking and falling off. Even so, there is no obvious moisture absorption phenomenon. Fig. 4 (d) shows the morphology of the sample after spraying the encapsulating with the ratio of glass powder to absolute ethanol of 3:4 in 80% relative humidity environment for 96 hours. It keeps the same look without moisture absorption cracking.

Table 1 and Fig. 5 show the weight gain rates of the samples with different concentration spraying in the same humidity environment. From table 1, it can be seen that the weight of the original sample increases by 31.4% after 96 hours, while the weight gain of the sealed sample is only 19.1%. As shown in Fig. 5, it can be seen that the moisture absorption of the sealed sample is significantly lower than that of the unsealed sample.

![Figure 4](image)

Figure 4. The morphology of the samples with different concentration spraying in 28°C and 80%RH environment for 96 hours (a. without spraying; b. 1:4 concentration of glass powder solution spraying; c. 2:4 concentration of glass powder solution spraying; d. 3:4 concentration of glass powder solution spraying)
Table 1. The weight gain rates of the samples with different concentration spraying in the same humidity environment (28℃ and 80%RH)

|        | None | Glass:ethanol 1:4 | Glass:ethanol 2:4 | Glass:ethanol 3:4 |
|--------|------|------------------|------------------|------------------|
| 0h     | 0%   | 0%               | 0%               | 0%               |
| 24h    | 15.2%| 10.1%            | 9.7%             | 7.3%             |
| 48h    | 20.3%| 13.7%            | 13.1%            | 12.6%            |
| 72h    | 26.5%| 17.4%            | 16.8%            | 15.3%            |
| 96h    | 31.4%| 25.6%            | 21.4%            | 19.1%            |

3.2. Latent heat of molten salt / ceramic composite PCMs

Fig. 6 shows the phase change latent heat of the samples. Fig. 6 (a) shows the phase change latent heat of the unsealed samples, and Fig. 6 (b) shows the phase change latent heat of the sealed samples. It can be seen that the phase change latent heat and the phase change temperatures of the different samples are basically the same. Therefore, the phase change enthalpy of the phase change thermal storage material is not affected by the spraying treatment.

4. Conclusions

In this study, the surface of the molten salt / MgO composite phase change heat storage material was encapsulated by spraying, to reduce the water absorption. The following conclusions are drawn:
(1) The coating with the ratio of 3:4 of glass powder and anhydrous ethanol can effectively reduce the moisture absorption and pulverization of the composite. When it is placed in 28°C and 80%RH environment for 96 hours, the moisture absorption rate of the composite is much lower than that of the composite without encapsulation, and there is no pulverization on the surface.

(2) The encapsulating of PCMs with glass powder has no significant effect on the latent heat of PCMs.

Acknowledgement
The work was supported by the technology projects of state grid corporation of China. (The key technologies for improving thermophysical properties of high temperature phase change heat storage materials, No. SGGR0000DLJS1800085)

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