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Effect of humidity environment on properties of molten salt phase change materials

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Abstract. Phase change materials (PCMs) are promising alternative materials for a variety of thermal energy storage and related applications. In this work the effect of environmental humidity on properties of molten salt phase change materials was studied by putting different PCMs in different humidity. The results of differential scanning calorimeter (DSC) analysis showed that humidity environment has little effect on the latent heat and onset melting point of these PCMs. SEM micrographs illustrated the effects of water vapor on surface morphology of different phase change materials. The results of thermal constant analysis suggested that humidity affects the thermal conductivity of some salts. But this effect is basically invariable, and will not change with the increase of humidity.

1. Introduction

The diminishing natural resources and global climate change are currently two of the most important challenges in the world, which have affected our ways of living and working. Thermal energy storage (TES) plays an important role in increasing energy efficiency and energy saving. In these applications, TES system often serves as a warehouse to hold and transfer thermal energy by a Heat Transfer Fluid. And the most suitable material for filling the warehouse is PCMs. Phase change often refers to the transformation of solid, liquid or gas phase, the energy utilized to change from one to the other phase is referred to as latent energy. Basically, PCMs are of great use to store energy in a specific temperature range, which absorb heat in an endothermic process when the temperature rises, and changes phase from one to another. According to the different types of phase change, different initial states of PCMs are selected, namely: liquid-gas, solid-gas, solid-solid and solid–liquid [1].

In order to meet the needs of mass production, PCMs should meet these major requirements [3, 4]: suitable melting point, high heat of fusion, high thermal conductivity, good thermal and chemical stability, insignificant overcooling during solidification, availability and cheapness.

The low cost and high heat of fusion of inorganic salts like chlorides, carbonates are attracting the attention of researchers [5, 6]. The melting temperature and heat capacity of these salts increases in the following order: nitrates, chlorides, carbonates and fluorides [7]. Though fluoride salts seems to have the highest performance, they are the least attractive because of its expensive price and corrosiveness.

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Carbonate salts are economical along with a large latent heat, which are suitable for PCMs [8]. There have been a lot of researches on the physical and chemical properties of carbonate salts, such as density, viscosity, thermal conductivity and thermal stability.

In the practical application, the PCMs will face with many extreme environments. However, few people have studied the influence of extreme environment on the properties of PCMs. This work studies the effect of environmental humidity on properties of PCMs. We chose some common carbonates: Na_2CO_3, Li_2CO_3 and Na_2CO_3-K_2CO_3 eutectic salt, and placed them in different humidity within the same temperature. We focus on the latent heat, thermal conductivity and surface structure of these PCMs, try to find out the relationship between moisture resistance and salt type.

2. Experimental section

2.1. Sample preparation

Before the experiment, The raw material will be dried for 10 hours at 120°C to remove moisture, which contains K_2CO_3 (purity ≥ 99%), Na_2CO_3 (purity ≥ 99%), Li_2CO_3 (purity ≥ 99%) and MgO (purity ≥ 99%). For the fabrication of eutectic salts PCMs, eutectic salts needed to be synthesized first. Firstly, the raw materials of Na_2CO_3 and K_2CO_3 were mixed by ball milling in the weight proportion of Na_2CO_3: K_2CO_3 = 52:48 for 3h, the mass ratio was at the eutectic point of the Na_2CO_3-K_2CO_3 binary system determined from the phase diagram generated by FactSage software 7.2. Secondly, the mixed salts was put in a crucible and melted in a muffle furnace at 750°C for 2h (with the heating rate 6°C /min). After the mixture was naturally cooled to room temperature, it was pulverized to powder by a crusher .Then the eutectic salts and MgO were mixed by ball milling in the weight proportion of salt: MgO = 55:45 for 3h. In this step, the powder preparation needed for the experiment is completed. Next, the powders were pressed into circular sheets with a diameter of 5cm by a hydraulic machine, the pressure was 40 MPa and holding time was 60s. Finally, these circular sheets were sintered in a muffle furnace at 720°C for 2h (with the heating rate 2°C /min).

As for the fabrication of Na_2CO_3 and Li_2CO_3 PCMs, the steps are basically the same in addition to the preparation of eutectic salt. The final sintering temperature of Li_2CO_3 PCMs and Na_2CO_3 PCMs are 680°C and 840°C.

2.2. Humidity experiment

The experiment was carried out in a humidity chamber which can regulate temperature and humidity separately. In this work, the samples were tested for 360h under four humidity conditions, which are 50RH%, 60 RH%, 70 RH% and 80 RH%(error≤2%) respectively. And the temperature remained 25°C during the process.

2.3. Characterization

Simultaneous thermal analyzer (TG-DSC, STA 449 F5 Jupiter, NETZSCH) was used to study the onset melting temperature and latent heat of the samples. The measurements were done under a flow of nitrogen (the nitrogen flow velocity was 20mL/min) at a flowrate of 10 °C/min, and the termination temperature was generally higher than the melting point of salt at least 50°C to obtain complete latent heat of phase change. Thermal constant analyzer (TPS 2200, Hot disk) was used to measure thermal conductivity (ordinary temperature) of the samples. The morphologies of these PCMs were observed by scanning electron microscope (TM4000, Hitachi) to find effect of humidity experiment on microstructure of the samples.

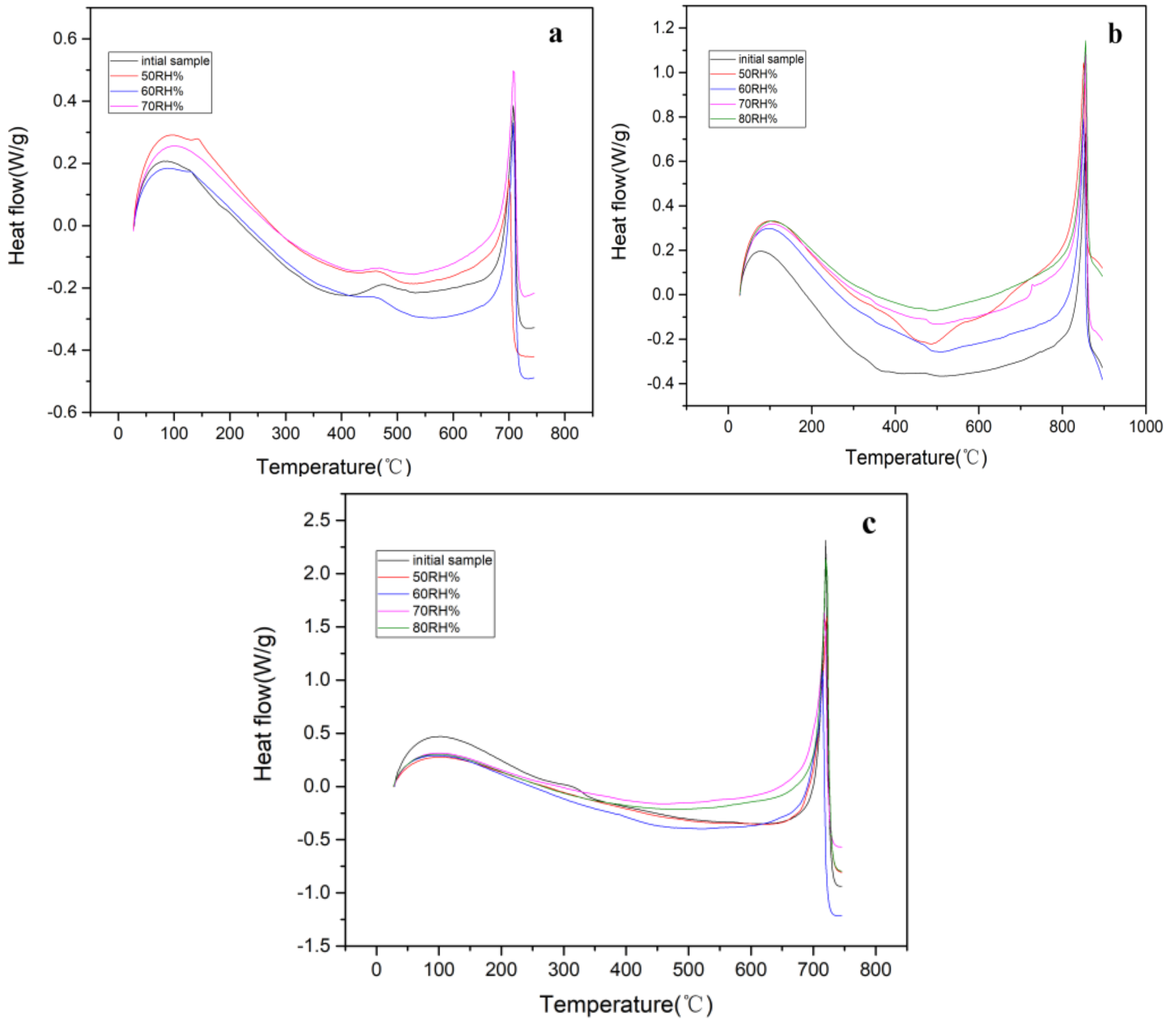

Figure 1. DSC curves of Na_2CO_3-K_2CO_3 eutectic salt PCMs (a), Na_2CO_3 PCMs (b) and Li_2CO_3 PCMs(c) after different humidity experiment

3. Results and discussion

3.1. Latent heat

Figure 2 shows the DSC curve of samples which have been tested in different humidity and Initial samples obtained from STA in a N_2 atmosphere. Among these samples, the sample of the Na_2CO_3-K_2CO_3 eutectic salt PCMs was completely destroyed at about 96h in the 80RH% experiment, so the measurement was not carried out on this sample. The location of the peaks in each picture is quite consistent, which indicates that the heat of fusion and onset melting point of the samples are basically the same. The latent heat was determined by the area of the endothermic peak in the curve and onset point is evaluated by the intersection of the tangent at the left start of the endothermic peak and the tangent at the maximum slope, which were both calculated by software Proteus Analysis (NETZSCH-Proteus-61).

Table.1 shows the calculated results, which suggests that the latent heat and onset melting point of the sample have not changed after different humidity experiments. From these results, we concluded that the humidity environment has little effect on the latent heat and onset melting point of these PCMs before it was seriously destroyed.

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Table 1 Latent heat and onset point of Na_2CO_3-K_2CO_3 eutectic salt PCMs, Na_2CO_3 PCMs and Li_2CO_3 PCMs after different humidity experiment.

Relative humidity	Na_2CO_3-K_2CO_3		Li_2CO_3		Na_2CO_3	
	Latent heat(J/g)	Onset point(°C)	Latent heat(J/g)	Onset point(°C)	Latent heat(J/g)	Onset point(°C)
Initial sample	79.93	691.3	265.1	707.9	125.6	839.4
50RH%	79.80	689.4	265.6	706.2	126.3	838.6
60RH%	79.92	693.2	265.7	704.5	126.1	840.6
70RH%	79.88	693.6	265.4	706.6	127.2	841.1
80RH%	-	-	265.6	708.6	126.5	840.8

3.2. Microstructure of the samples

Figure 2 shows the microstructure of the initial sample and the samples after 50RH%, 60 RH%, 70 RH% humidity experiments of Na_2CO_3-K_2CO_3 eutectic salt PCMs. The particle size of the sample surface increased under the influence of humidity environment, and the increase of particle size is more obvious with the increase of humidity, which indicated that the growth rate of sample particles accelerated with the increase of humidity. And this result also explained why the whole morphology of samples was destroyed under 80RH% environment.

Figure 3 and Figure 4 shows the microstructure of the initial sample and the samples after 50RH%, 60 RH%, 70 RH% humidity experiments of Na_2CO_3 PCMs and Li_2CO_3 PCMs respectively. The humidity environment had little effect on the surface morphology of Na_2CO_3 PCMs, and the morphology of the samples has not changed significantly with the increase of humidity. As for Li_2CO_3 PCMs, the increase of humidity environment had no effect on its surface morphology.

It can be concluded that the resistance of different salts to water vapor is different in PCMs with these results. Among these samples, the surface morphology of Na_2CO_3-K_2CO_3 eutectic salts PCM changed significantly in high humidity environment while that of Na_2CO_3 PCMs changed little. And there is hardly any transform in Li_2CO_3 PCM.Figure 3 SEM images of Na_2CO_3 PCMs after different humidity experiment (a: initial sample, b: 50RH%, c: 60RH%, d: 70RH%)

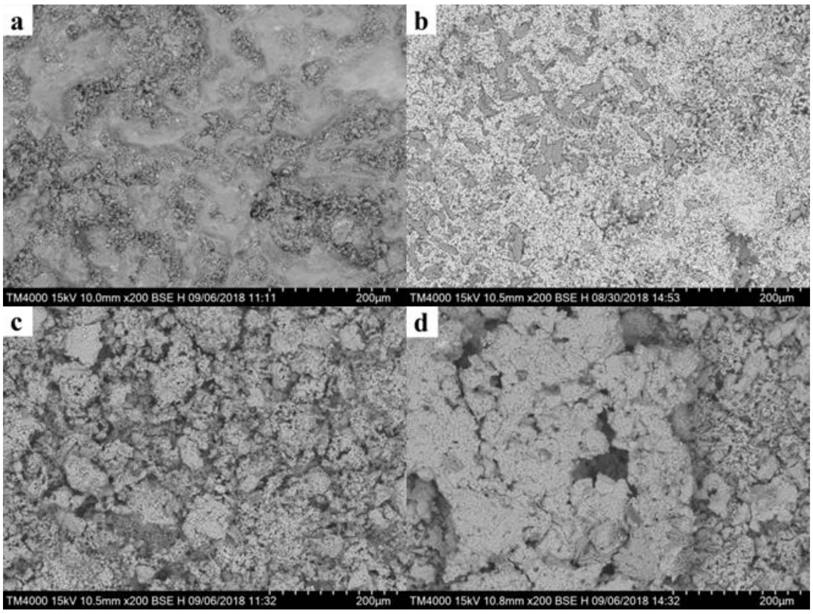

Figure 2. SEM images of Na_2CO_3-K_2CO_3 eutectic salt PCMs after different humidity experiment (a: initial sample, b: 50RH%, c: 60RH%, d: 70RH%)

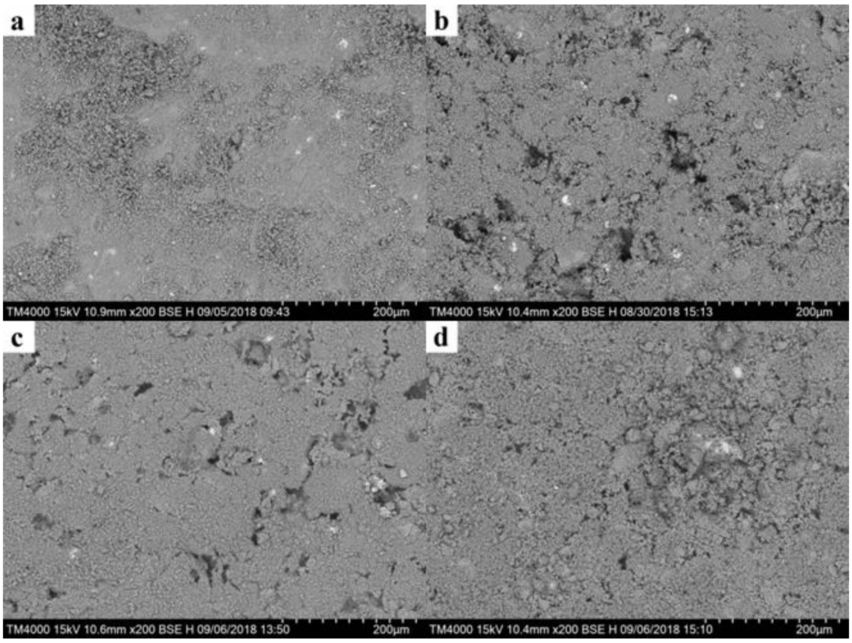

Figure 3. SEM images of Na_2CO_3 PCMs after different humidity experiment (a: initial sample, b: 50RH%, c: 60RH%, d: 70RH%

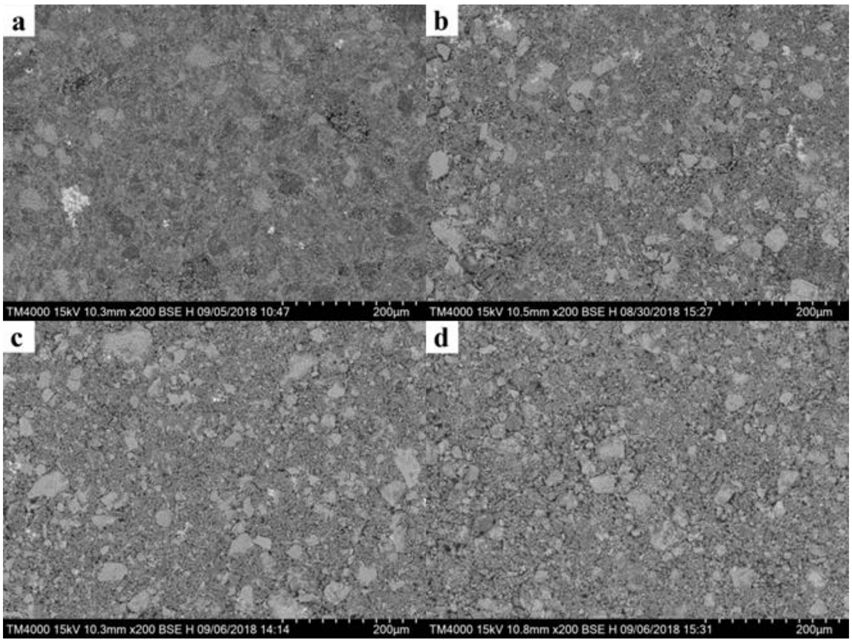

Figure 4. SEM images of Li_2CO_3 PCMs after different humidity experiment (a: initial sample, b: 50RH%, c: 60RH%, d: 70RH%)

Table 2. Thermal conductivity of Na_2CO_3-K_2CO_3 eutectic salt PCMs, Na_2CO_3 PCMs and Li_2CO_3 PCMs after different humidity experiment.

Relative humidity	Thermal conductivity($W\cdot m^{-1}\cdot K^{-1}$)		
	Na_2CO_3-K_2CO_3	Li_2CO_3	Na_2CO_3
Initial sample	2.015	2.987	1.785
50RH%	1.832	3.001	1.706
60RH%	1.778	3.037	1.754
70RH%	1.803	2.994	1.712
80RH%	-	3.072	1.678

3.3. Thermal conductivity

The thermal conductivity of these samples was influenced by many factors, Table 2 shows the thermal conductivity of these samples after different humidity experiment which was measured in room temperature (25°C). Firstly, it can be concluded that the thermal conductivity of samples is greatly affected by the type of salt, the conductivity of Li_2CO_3 sample was about 3 $W\cdot m^{-1}\cdot K^{-1}$ while that of Na_2CO_3 sample is only about 1.7 $W\cdot m^{-1}\cdot K^{-1}$. Meanwhile, the thermal conductivity of Na_2CO_3-K_2CO_3 sample decreased slightly after the experiment, which indicates that the humidity affects the thermal conductivity of some salts. But this effect is basically invariable, and will not change with the increase of humidity.

4. Conclusions

In this paper, we report a study on the effect of humidity environment on properties of molten salt PCMs. The focus is on the elucidation of the influence of humid environment on the thermal properties of different PCMs. The results show that the humidity environment has little effect on the latent heat and onset melting point of these PCMs. The resistance of different salts to water vapor is different in PCMs, among these samples, the surface morphology of Li_2CO_3 sample is least affected by humidity, and that of Na_2CO_3-K_2CO_3 eutectic salt sample is most affected by humidity. As for thermal constant analysis, it suggests that the humidity affects the thermal conductivity of some salts. But this effect is basically invariable, and will not change with the increase of humidity. The research results could provide guidance for matters needing attention in the application of PCMs in daily life

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