Investigations on thermal properties of Metal-doped Na$_2$CO$_3$/MgO composites for thermal energy storage

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Abstract. The Na$_2$CO$_3$/MgO composites doped with metal particles, such as Cu, Al, Fe, etc. were prepared. Their synthesis, phase composition, chemical compatibility and thermal properties were investigated. The XRD results show that Na$_2$CO$_3$ and MgO have good chemical compatibility. The density of the sample can be increased with doping Cu powders. The onset temperature and the melting point of samples increase with doping Al powder, while those properties with doping Cu powder decrease. With the increase of the content of Na$_2$CO$_3$ in the sample, the onset temperature and the melting point show an increasing trend. But both the latent heat and the thermal conductivity are shown to be decreased in comparison to Na$_2$CO$_3$/MgO composites. Since the samples are sintered in air, the metal powders doped in the PCMs can be oxidized inevitably. Based on these results, it can be inferred that the deterioration of the thermal properties have close relations with the oxidation of metal powders.

1. Introduction

In recent years, the extensive interest has been growing on phase change materials (PCMs) applied as a storage medium due to their high energy storage densities and nearly isothermal operating characteristics[1-5]. Latent thermal energy storage has wide applications in many fields, such as in the field of solar energy utilization, industrial waste heat utilization, electric peak-shaving and energy conservation of buildings[6-11]. PCMs plays an important role in latent thermal energy storage and has great development prospects. In order to alleviate the global energy crisis, there is an urgent need to develop PCMs.

In composite phase change thermal storage materials, PCMs such as paraffin, salts or metals are usually used as latent heat storage materials, while polymer or ceramic-based materials serve as a supporting material, which can prevent the leakage of PCMs by maintaining their microporous structure[12]. The poor formability, low volume density, weak thermal stability, strong corrosion behavior at high temperature and low thermal conductivity, etc. are common problems of PCMs, so use PCMs directly for practical applications is not easy. Doping technique is the most common way to improve the thermal properties of PCMs. Since the metal-powder has strongly thermal conductivity, it is expected to enhance the thermal conductivity of PCMs by doping minor metal-powder into PCMs[13-15].
In this study, we study the preparation process and the change of thermal properties of \( \text{Na}_2\text{CO}_3/\text{MgO} \) composite PCMs with added \( \text{Cu}, \text{Al}, \text{Fe} \). \( \text{Na}_2\text{CO}_3 \) serves as the phase change material, while \( \text{MgO} \) is used as a ceramic-based supporting material, metal powders \( \text{Cu}, \text{Al}, \text{Fe} \) were selected as dopants. Chemical compatibility and microstructure of the phase change thermal storage materials were characterized by X-ray diffraction (XRD). The thermal stability and thermal energy storage of phase change thermal storage materials were determined using differential scanning calorimeter and thermal gravity analyzer (DSC/DTA-TG). Thermal conductivity was measured by thermal property analyzer.

2. Experimental

2.1. Materials
\( \text{Na}_2\text{CO}_3 \) (99.27%) was supplied by Tianjin Bo-hua Yong-li Chemical Co. Ltd, served as the phase change heat storage material. \( \text{MgO} \) (96.20%) was used as the supporting material to provide a network structure for the phase change material. \( \text{MgO} \) was purchased from Weifang Li-he Powder Technology Co. Ltd. Metal powders \( \text{Cu}, \text{Al}, \text{Fe} \) was chose as the dopant. Metal powder particle size is less than 40μm, and purity of >99% were purchased from Nangong Xindun alloys spraying Co. Ltd.

2.2. Preparation of composite PCMs
The raw materials were dried in an oven for 4h to remove water. The nominal compositions of \( \text{Na}_2\text{CO}_3/\text{MgO} \) were mixed with different weight ratios in a ball mill for 120min. The mixed raw materials were aged in 5% water and ground in a mortar for 20 minutes. Then set the mixture in a mold (50mm in diameter). Slices were prepared by compressing the \( \text{Na}_2\text{CO}_3/\text{MgO} \) mixture in a tablet machine with 25MPa pressure for 2min. The prepared slices were sintered in a furnace at 830°C under air atmosphere for 2h to form composite PCMs with \( \text{Na}_2\text{CO}_3/\text{MgO} \) weight ratios of 50:50, 55:45 and 60:40.

To study the thermal properties of composite PCMs, metal powders, such as \( \text{Cu}, \text{Al}, \text{Fe} \) with 5wt.% were added to the initial mixture of \( \text{Na}_2\text{CO}_3/\text{MgO} \) followed by the same treatment described above. Thermal properties was measured by differential scanning calorimeter and thermal gravity analyzer and thermal property analyzer.

2.3. Characterization and thermal properties of composite PCMs
X-ray diffraction (XRD) measurements were carried out by Bruker D8 advance (Cu Kα/40kV/40mA). The thermal stability of composite PCMs was measured using a differential scanning calorimeter and a thermal gravity analyzer (STA 449 F5 Jupiter, NETZSCH) under Ar atmosphere. The measurements were performed using 10-20 mg samples in a \text{Al}_2\text{O}_3 \) crucible with the heating rate of 10°C/min from 25 to 900°C. Measurement of specific heat capacity with platinum rhodium crucible with the same heating rate from 25 to 800°C. The results of measurement were collected and processed through NETZSCH-Proteus software. The thermal conductivity of \( \text{Na}_2\text{CO}_3/\text{MgO} \) and the \( \text{Na}_2\text{CO}_3/\text{MgO} \) composite with added metal powders \( \text{Cu}, \text{Al}, \text{Fe} \) were measured using Thermal constant analyzer (TPS2200, Hot Disk). The thermal conductivity is measured by plate method, and based on the experimental need we can set different voltages and currents by the controllable power transformer and determined. The results were collected and processed by software Hot Disk Thermal Analyser 7.3.

3. Results and discussion
The samples sintered at 830°C are shown in Figure1. The XRD pattern for the \( \text{Na}_2\text{CO}_3/\text{MgO} \) composite PCMs (\( \text{Na}_2\text{CO}_3/\text{MgO} =50:50 \), weight ratio) is shown in Figure 2. The peaks of \( \text{Na}_2\text{CO}_3 \) (PDF Card-04-011-4108) and \( \text{MgO} \) (PDF Card- 00-004-0829) appear in the XRD pattern, and there are no other peaks. The results indicate that \( \text{Na}_2\text{CO}_3 \) and \( \text{MgO} \) have good chemical compatibility, and there is no chemical reaction between them during the preparation of composite PCMs.
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Figure 1. Digital photo of the sintered at 830°C samples.

Figure 2. X-ray diffraction patterns of Na$_2$CO$_3$/MgO PCMs.

The density and the thermal conductivity of the samples sintered at high temperature of 830°C are shown in table 1 and table 2, respectively. To visually analyze the relationship between the content of the dopants and their density and thermal conductivity, the figures are plotted, as shown in Figure 3 and Figure 4, respectively.

Table 1. The density of the samples after sintering at 830°C(g/cm$^3$).

| Na$_2$CO$_3$:MgO | 0% | 5%Al | 5%Fe | 5%Cu |
|------------------|----|------|------|------|
| 50:50            | 1.822 | 1.758 | 1.793 | 2.139 |
| 55:45            | 1.867 | 1.756 | 1.755 | 2.195 |
| 60:40            | 1.972 | 1.808 | 1.745 | 2.345 |

Table 2. Thermal conductivity of the samples(W/mK).

| Na$_2$CO$_3$:MgO | 0% | 5%Al | 5%Fe | 5%Cu |
|------------------|----|------|------|------|
| 50:50            | 1.751 | 1.690 | 1.717 | 1.532 |
| 55:45            | 1.788 | 1.478 | 1.425 | 1.524 |
| 60:40            | 1.759 | 1.419 | 1.263 | 1.630 |
Figure 3. Density of different proportions of Na$_2$CO$_3$/MgO.

From Figure 3 it shows with the increase of Na$_2$CO$_3$ content, except the samples doped with Fe, the rest samples showed an upward trend. The samples doped with Cu powders have the highest density, while the samples doped with Al powder have the lowest density. It indicates the addition of the Cu powder can increase the density of Na$_2$CO$_3$/MgO samples. The results show that the increase of the density of the sample with doping Cu powder is due to the high density of Cu powder itself and the low melting point of Cu. Cu powder melts at high temperature to make the sample more dense and promote densification.

In Figure 4, with the increase of Na$_2$CO$_3$ content, the thermal conductivity of the samples doped with Al and Fe powders shows a downward trend. But for the samples doped with metal powder Cu, the reverse result is obtained. Its curve is almost level at first and then goes up slowly. The results shown in Figure 3 and Figure 4 suggest Cu is the effective additive.

The phase change latent heat and the specific heat capacities of all the samples are shown in Table 3 and Table 4, respectively. The dependence of phase change latent heat and specific heat capacity upon Na$_2$CO$_3$/MgO ratios are shown in Figure 5 and Figure 6, respectively.

| Table 3. Phase change latent heat of Na$_2$CO$_3$/MgO composite (J/g). |
|-----------------------------|----------------|----------------|----------------|----------------|
| Na$_2$CO$_3$: MgO          | 0%             | 5% Al          | 5% Fe          | 5% Cu          |
| 50:50                       | 106            | 88.91          | 86.42          | 80.41          |
| 55:45                       | 118.3          | 102.2          | 99.82          | 97.46          |
| 60:40                       | 125.8          | 110.2          | 103.5          | 95.48          |

| Table 4. Specific heat capacity of Na$_2$CO$_3$/MgO composite (J/(g*K)). |
|-----------------------------|----------------|----------------|----------------|----------------|
| Na$_2$CO$_3$: MgO          | 0%             | 5% Al          | 5% Fe          | 5% Cu          |
| 50:50                       | 1.298          | 1.203          | 1.439          | 1.325          |
| 55:45                       | 1.213          | 1.271          | 1.250          | 1.165          |
| 60:40                       | 1.265          | 1.173          | 1.318          | 1.178          |
Figure 5. Phase change latent heat of Na$_2$CO$_3$/MgO composite.

Figure 6. Specific heat capacity of Na$_2$CO$_3$/MgO composite.

Figure 5 shows all the additives can decrease the latent heat value. But adding Fe powder can enhance the specific heat capacity of the sample obviously. For composites with a weight ratio of 50:50, the enhance of the specific heat capacity is most obvious. It is speculated that the reaction of metal powders Fe, Cu and Al during high temperature sintering may lead to the increase and decrease of specific heat capacity of the samples.

The DSC curve of the samples of different components is shown in the Figure 7(a), Figure 7(b) and Figure 7(c), respectively. The onset temperature and the melting point calculated by the DSC curve are shown in table 5 and table 6, respectively.

Figure 7(a). The DSC curve of Na$_2$CO$_3$/MgO composite PCMs at Na$_2$CO$_3$/MgO weight ratios of 50:50.

Figure 7(b). The DSC curve of Na$_2$CO$_3$/MgO composite PCMs at Na$_2$CO$_3$/MgO weight ratios of 55:45.

Figure 7(c). The DSC curve of Na$_2$CO$_3$/MgO composite PCMs at Na$_2$CO$_3$/MgO weight ratios of 60:40.
Figure 7(c) The DSC curve of Na$_2$CO$_3$/MgO composite PCMs at Na$_2$CO$_3$/MgO weight ratios of 60:40.

Table 5. The onset temperature of Na$_2$CO$_3$/MgO composite (°C).

| Na$_2$CO$_3$: MgO | 0%  | 5% Al | 5% Fe | 5% Cu |
|-------------------|-----|-------|-------|-------|
| 50:50             | 838.5 | 842.9 | 836.1 | 835.3 |
| 55:45             | 841.1 | 844.5 | 840.5 | 838.0 |
| 60:40             | 843.9 | 846.8 | 841.4 | 840.1 |

Table 6. Melting point of Na$_2$CO$_3$/MgO composite (°C).

| Na$_2$CO$_3$: MgO | 0%  | 5% Al | 5% Fe | 5% Cu |
|-------------------|-----|-------|-------|-------|
| 50:50             | 853.2 | 857.3 | 852.9 | 850.3 |
| 55:45             | 854.7 | 858.3 | 856.1 | 851.9 |
| 60:40             | 855.6 | 860.2 | 857.0 | 853.8 |

Tables 5 and 6 show that the onset temperature and the melting point of the sample with metal powder are about 840°C and 850°C, respectively. The onset temperature and the melting point of samples with Al powder have increased, while those with Cu powder have decreased. With the increase of the content of Na$_2$CO$_3$ in the sample, the onset temperature and the melting point show an increasing trend. It can be inferred that with the increase of Na$_2$CO$_3$ ratio, its melting point will gradually increase.

4. Conclusions

The Na$_2$CO$_3$/MgO composites doped with metal particles, such as Cu, Al, Fe, etc. were prepared. The densities of PCMs increase with doping metal powders. But both the latent heat and the thermal conductivity are shown to be decreased with respect to Na$_2$CO$_3$/MgO composites. Since PCMs is sintered in air, the metal powders doped in the PCMs can be oxidized inevitably. Based on these results, it can be inferred that the deterioration of the thermal properties have close relations with the oxidation of metal powders. Therefore, further research is still needed.
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