Effect of Mental-Doped on Thermal Properties of K$_2$CO$_3$-Na$_2$CO$_3$ eutectic salt/magnesium oxide Composites for Thermal Energy Storage

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Abstract. In this work, Na$_2$CO$_3$-K$_2$CO$_3$/MgO composites with MgO serving as supporting material and Na$_2$CO$_3$-K$_2$CO$_3$ eutectic salt acting as thermal absorbing materials were prepared by the form-stable technique. Besides, the possible effects of Cu, Fe and Al on the thermal properties of the composite were investigated. The thermal properties including phase composition, latent heat and thermal conductivity, etc. were measured using X-ray diffraction, differential scanning calorimetry, thermal constant analyzer and thermogravimetric analysis, etc. The X-ray diffraction results show that Na$_2$CO$_3$-K$_2$CO$_3$ and MgO have good chemical compatibility. The differential scanning calorimetry results show that the melting point of the Na$_2$CO$_3$-K$_2$CO$_3$/MgO composites is 707.5°C and its enthalpy of fusion is 67.98 J/g. The thermal constants analyzer results indicate that the addition of metal powder can improve the thermal conductivity of the sample, but the increase rate is not obvious because of its oxidation in the air, some even reduce the thermal conductivity.

1. Introduction

The world primary energy consumption is about 13.8 billion tons of oil equivalent, of which about 80% is provided by burning fossil fuels. Due to economic and thermal constraints and poor management, burning fossil fuels will discharge a lot of waste heat. Waste heat is usually unstable and randomly distributed [1]. On the other hand, the use of renewable energy is essential to reduce the consumption of fossil resources and part of the carbon dioxide that causes greenhouse effect [2-3]. However, intermittency is one of the main challenges of large-scale use of these renewable energy sources [4]. Thermal energy storage (TES) is recognized as one of the key technologies for energy supply in the future [5]. Latent heat energy storage with phase change materials (PCMs) is one of the most effective way for thermal energy storage [6]. This system is increasingly interesting in recent years because of the high-energy storage density and isothermal characteristics of PCMs [7]. A form-stable composite material containing molten salts and supporting material have been proposed for corrosion resistance, in which molten salts can be used as thermal storage materials [8]. The composite energy storage material (CESM), which is composed of inorganic salt and ceramic matrix, has a porous structure. The inorganic salt is distributed in the ultra-porous network of ceramic matrix. When the temperature is higher than the melting point of inorganic salt, the inorganic salt melts and absorbs the latent heat and does not flow out due to capillary tension [9]. The composite solves some inherent defects of traditional PCMs, such as supercooling, phase separation, vessel aging and corrosion [10]. However, form-stable composite material usually exhibits some intrinsic drawbacks such as low volume density, weak thermal stability and poor thermal conductivity (0.4-0.6 W·m$^{-1}$·K$^{-1}$) [5]. Doping
is the most common method to improve the thermal properties of PCMs. Metal powder has a strong thermal conductivity, adding a small amount of metal powder to PCMs is expected to improve the thermal conductivity of PCMs [11].

In this study, Na₂CO₃-K₂CO₃/MgO composites with MgO serving as supporting material, Na₂CO₃-K₂CO₃ eutectic salt acting as thermal absorbing materials and Cu, Fe, Al using as additive were prepared by the form-stable technique.

2. Experimental

2.1. Sample preparation

2.1.1 Preparation of Na₂CO₃-K₂CO₃ eutectic salts (ES). In order to prepare K₂CO₃-Na₂CO₃/MgO composites, the following ES was synthesized. Firstly, ball milling Na₂CO₃ and K₂CO₃ raw materials with the weight ratio of Na₂CO₃: K₂CO₃ = 52:48, stirring for 10h, and the mass ratio was the eutectic point of Na₂CO₃-K₂CO₃ binary system, which was determined by the phase diagram generated by Factsage software 7.2 (see Figure 1). At 393.15K, the two salts were pre-dried in vacuum furnace for at least 24 hours to remove water. The mixed salt was then melted in a muffle furnace and equilibrated at 750°C for 2 hours to form ES (see Figure 2). The mixture was then cooled naturally to room temperature and crushed to powder with a pestle and mortar and stored in a sealed container. The SEM observation of the prepared eutectic salt was shown in Fig.3.

| Sample number | K₂CO₃ (wt.%) | Na₂CO₃ (wt.%) | MgO (wt.%) | Cu (wt.%) | Fe (wt.%) | Al (wt.%) |
|---------------|--------------|--------------|------------|-----------|-----------|-----------|
| Sample1       | 24           | 26           | 50         | 5         |           |           |
| Sample2       | 24           | 26           | 45         | 5         |           |           |
| Sample3       | 24           | 26           | 45         | 5         |           |           |
| Sample4       | 24           | 26           | 45         |           |           |           |

Figure 1. Phase diagram of Na₂CO₃-K₂CO₃ salt generated using Factsage 7.2

2.1.2 Preparation of ES /ceramic composites. ES/ceramic composites were prepared by press mix sintering. The specific composition of the composites was shown in Table 1. The mixture was then pressed into a 12.6 mm diameter stainless steel cylindrical mold by a hydraulic press to produce a circular sheet. The applied pressure is 8 tons and the holding time is 30 seconds. Finally, the sintering process was shown in Figure 4. The sintering temperature is set at 700°C, 720°C and 740°C. Considering the hygroscopicity of the samples, the samples were kept at 100°C and 510°C for half an hour respectively.
Figure 3. SEM observations on the prepared ES

Figure 4. Process of sintered process of ES/ceramic composites

2.2 Characterization

The morphology of PCMs was observed by scanning electron microscopy (SEM, TM4000, Hitachi). The thermophysical properties of PCMs, such as initial melting point, melting point, latent heat and specific heat, were measured by using a synchronous thermal analyzer (STA 449 F5, Netzsch). Use 10-20 mg of sample to measure in an alumina crucible with a heating rate of 10K/min at 25-800°C. The thermal conductivity of PCMs was measured by TPS 2200 thermal constant analyzer and hot disk method. XRD test was carried out with Bruker D8-advance.

3. Results and discussion

3.1 Determination of sintering temperature

The digital photo of sintered 700°C, 720°C and 740°C samples are shown in fig 5. As can be seen in fig. 5, the surface morphology at 720°C is the best. In order to better prove that the sintering temperature is 720°C, the density and thermal conductivity are tested, and the test results are shown in fig6 and fig7.
Figure 6. The density of sample 1, sample 2, sample 3 and sample 4 sintering at 700°C, 720°C, and 740°C
In fig. 6 and fig. 7, sample 1, sample 2, sample 3 and sample 4 are sintered at 720°C, and their density and thermal conductivity are the best.

3.2 XRD of the as-prepared samples
The XRD pattern for the Na2CO3-K2CO3/MgO composite PCMs (Na2CO3:K2CO3: MgO=50:50, wt.%) is shown in fig 8. It found that the PCMs are composed of ES and MgO, and there are no other peaks. The results indicate that ES and MgO have good chemical compatibility.

Figure 8. XRD patterns of (Na2CO3-K2CO3)/MgO PCMs

3.3 DSC of the ES/ceramic composites
Table 2. The experimental values of the samples

| System  | Onset temperature/°C | Melting point/°C | ΔHPCM/J/g |
|---------|----------------------|-----------------|-----------|
| Sample 1| 691                  | 707.5           | 67.78     |
| Sample 2| 683.1                | 703.6           | 60.34     |
| Sample 3| 692.1                | 702.9           | 66.75     |
| Sample 4| 691.7                | 706.5           | 52.36     |
Figure 9. DSC(a) and TG(b) curve of sample1, sample2, sample3 and sample4. DSC and TG curves of sample1, sample2, sample3 and sample4 were shown in Fig. 9. The corresponding melting temperature, onset temperature and the enthalpy of phase change measured in this work are listed in Table 2. Table 2 indicated both the onset temperatures and melting points of sample1, 2, 3 and 4 are almost the same. The enthalpy of phase change of sample4, sample 3 and samples 2 is 22.8%, 1.5% and 11% lower than sample 1, respectively. It is found from 3.2 that there is no reaction between ES and MgO. Fig9 (b) indicate that mass loss is seen in sample 4. So, the decrease of enthalpy of phase change of sample 4 is due to the reaction between aluminum and matrix.

4. Conclusions
Using Na₂CO₃-K₂CO₃ as phase change material, a novel composite was prepared by doping metal of Cu, Fe and Al into ES/ceramic composite. The obtained results revealed that Na₂CO₃-K₂CO₃ and MgO have good chemical compatibility, latent heat of phase transformation decreases due to the addition of Al and the addition of metal powder can improve the thermal conductivity of the sample, but the increase rate is not obvious because of its oxidation in the air, some even reduce the thermal conductivity.

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