Effect of SiO₂ on the thermal stability of carbonate/MgO composite for thermal energy storage

Y R Guo¹, Y Liu¹, G Q Zhang², Z F Deng², G Z Xu² and B R Li*¹

¹ Departments of School of Energy, Power and Mechanical Engineering, University of North China Electric Power University, Beijing, 102206, China
² State Key Lab of Advanced Power Transmission Technology, Global Energy Interconnection Research Institute, Beijing, 102209, China

Corresponding author and e-mail: B R Li, libr@ncepu.edu.cn

Abstract. In this paper, a novel carbonate/MgO composite for high temperature thermal storage was prepared by doping nano-SiO₂. Na₂CO₃-K₂CO₃ eutectic salt was used as the phase change material. The long-term stability of the samples was tested by holding at 750 °C for a period of time. The differential thermal analysis calorimeter, X-ray diffractometer and scanning electron microscope were employed to detected the possible influences of constant high temperature on thermal properties. The results showed that the doped nano-SiO₂ particles can restrain high temperature molten salt loss and improve the stability of the composite in both structure and thermal properties.

1. Introduction

Nowadays fossil fuels are still supplying about 80% of the total primary energy needs in the world [1]. However, the excessive use of fossil fuels has resulted in a shortage of traditional energy source and some severe environmental issues [2-3]. At present, there are two main ways to solve these problems. One way is to develop renewable energy sources actively to replace the traditional energy. Another is to reduce the waste of existing energy and maximize the use of existing resources. Thermal energy storage, which can effectively and efficiently absorb and store the process waste heat and the solar energy, and release when needed, has attracted widespread attention [4]. According to the storage mode, thermal energy storage can be divided into sensible heat storage, latent heat storage and chemical heat storage. Among them, latent heat storage mainly uses phase change materials to absorb a lot of heat in the process of phase change to achieve thermal energy storage [5]. Compared with the sensible heat storage and chemical heat storage, the latent heat storage possesses the advantage of high latent heat storage density and almost constant phase change temperature [6-8], which make it to be a more ideal way to store heat.

Recently, molten salts, which possess considerable phase change enthalpy and chemical stability, have been widely investigated as the favorable candidate of medium and high temperature phase change materials [9]. However, applications of molten salts as PCMs are often hampered by low thermal conductivity and chemical incompatibility (such as corrosion of containers) due to the poor thermal stability [10].

Researchers study the form-stable phase change materials to overcome the shortage of molten salts in using. Magnesium oxide, diatomite, α-alumina and mullite and porous materials were added to
improve the stability of phase change materials. Yi-feng Jiang et al studied the thermal stability of the eutectic Na₂SO₄-NaCl salt-ceramic composites. The researchers demonstrated that both Na₂SO₄-NaCl/α-alumina and Na₂SO₄-NaCl/mullite composites showed good thermal stability without crack after 20 thermal cycles in the temperature range of 550–680 °C in air [11]. Yu-shi Liu et al investigated the thermophysical properties of the Na₂SO₄·10H₂O-Na₂HPO₄·12H₂O eutectic hydrated salt/nano-α-Al₂O₃ composite phase change material. They found that the doping of nano-α-Al₂O₃ decreased the supercooling degree and increased the thermal conductivity of the phase change material. Moreover, 4.5wt% nano-α-Al₂O₃ modified eutectic hydrated salt had an excellent thermal stability after 200 melting-freezing cycles [12].

In this study, a novel composite phase change material is investigated. The composite is synthesized by using the eutectic Na₂CO₃-K₂CO₃ salts as phase change material, magnesium oxide as skeleton material and adding nano-SiO₂ dopant. The thermal properties, microstructure and phase composition of the composites were studied by means of differential scanning calorimeter, scanning electron microscope and X-ray diffractometer.

2. Materials and methods

2.1. Materials
Sodium carbonate (Na₂CO₃, purity>99%) and potassium carbonate (K₂CO₃, purity>99%), purchased from Tianjin Bo-hua Yong-li Chemical Co., Ltd. and Zibo Wu-hong Import and Export Co., Ltd., were used as phase change materials. Magnesium oxide (MgO, purity>99%), which was purchased from Weifang Li-he powder Technology Co., Ltd., was used as ceramic skeleton material. Nano-SiO₂ particles purchased from Beijing Jia An Heng Technology Co., Ltd. were added to improve the thermal properties.

2.2. Preparation of the samples
Firstly, the eutectic salt was fabricated based on the eutectic ratio of 52:48 for Na₂CO₃ and K₂CO₃. Secondly, the eutectic salt, MgO and nano-SiO₂ were mixed by the ratio of 55:45:0, 55:40:5, 55:38:7, 55:35:10, 55:32:13, 55:30:15 to get six kinds of homogeneous composite powders. Then, the composite powders were loaded into the compression mold and then the mole was put on the compression stage. The pressure applied on the mold was 30MPa and was maintained for 30s to obtain a disk-like sample with a diameter of 12.6mm. Finally, the samples were placed into the muffle furnace calcined at 750°C for 168h and the mass of the samples was recorded every 24h.

2.3. Characterization
The phase compositions were examined by X-ray diffraction (XRD, Bruker D8 Advance) using Cu Kα radiation and a scan speed of 6°/min. The morphology of the resultant samples was characterized by scanning electron microscopy (SU8000). The phase change properties were characterized by differential scanning calorimeter (DSC; STA449F5, Netzsch, Germany) in the nitrogen atmosphere with a heating rate of 10°C /min from 35°C to 750°C.

3. Result and discussion

3.1. The trend of the mass change of samples
The curves of the mass change of the samples varying with the holding time were shown in Fig.1. According to these curves, after being preserved heat at 750°C for 168h, the mass change of the samples with 0%, 5%, 7%, 10%, 13%, 15% nano-SiO₂ was 40.2%, 32.1%, 28.3%, 31.9%, 22.9%, 23.4%, respectively. In other words, the mass change of samples with nano-SiO₂ was less than the sample without nano-SiO₂ after being preserved heat at 750°C for 168h. In addition, the mass change of the sample with 13% nano-SiO₂ was less than other samples after holding at 750°C for 168h. Therefore, the doping of nano-SiO₂ can reduce the mass loss of the samples to a certain extent.
3.2. XRD patterns of nano-SiO$_2$ and samples with and without nano-SiO$_2$

The XRD patterns of nano-SiO$_2$ before and after being calcined at 750°C were shown in Fig. 2. According to the patterns, it can be concluded that the nano-SiO$_2$ doping in the samples was amorphous phase and no crystal transformation occurred during sintering.

![XRD patterns of nano-SiO$_2$ before and after being calcined at 750°C.](image1)

**Figure 2.** XRD patterns of nano-SiO$_2$ before and after being calcined at 750°C.

![XRD patterns of the samples with different content of nano-SiO$_2$.](image2)

**Figure 3.** XRD patterns of the samples with different content of nano-SiO$_2$.

Fig. 3 showed the XRD patterns of the samples with different content of nano-SiO$_2$. It was clear that KNaCO$_3$ and MgO were the main phases for all of the samples. But the diffraction peaks of Na$_2$MgSiO$_4$ couldn’t be found only in the samples with no SiO$_2$ addition. This phenomenon demonstrated the possible reactions among Na$_2$CO$_3$, MgO and SiO$_2$. The diffraction peak intensities of Na$_2$MgSiO$_4$ increased gradually with the increasing content of nano-SiO$_2$, indicating the increasing amount of Na$_2$MgSiO$_4$ as the contents of nano-SiO$_2$ varied from 0% to 13%. But, further increasing
the content of nano-SiO$_2$ from 13% to 15% showed limit effects on the diffraction peak intensities of Na$_2$MgSiO$_4$.

3.3. DSC of the original samples and samples after being preserved heat at 750°C for 168h

Both the samples without exposing to constant high temperature and samples after being preserved heat at 750°C for 168h were measured using the differential scanning calorimeter to investigate the effect of the doping nano-SiO$_2$ on the thermal properties and the thermal stability of the samples.

![DSC curves of the samples](image)

**Figure 4.** DSC curves of the samples without exposing to constant high temperature (a) and the samples after being preserved heat at 750°C for 168 hours (b).

The DSC curves of the samples were illustrated in Fig.4. It can be seen that the endothermic peak is found to be changed greatly with the doped amount of SiO$_2$.

![Melting temperature and enthalpy](image)

**Figure 5.** Melting temperature and enthalpy of the original samples and the samples after being preserved heat at 750°C for 168h hours.

Depending upon the curves shown in Fig.4, the melting temperatures of the samples in this work was calculated based on the intersection point between the extension line of the front baseline and the tangent at the maximum slop of the frontiers of the peak. The calculated results were shown in Fig.5.
It can be seen from the Fig.5 that no obvious change was found in the melting temperature before and after calcinations. But, there was obvious reduction in phase latent value. For example, after holding at 750°C for 168h, the results in Fig.5 showed that the reduction in the enthalpy for the samples with nano-SiO$_2$ for 0%, 5%, 7%, 10%, 13%, 15% was 34.52J/g, 22.53J/g, 19.00J/g, 30.75J/g, 23.89J/g, 26.38J/g, respectively. In comparison with the SiO$_2$ doped samples, the sample without SiO$_2$ addition showed a higher reduction in the enthalpy, suggesting the doped SiO$_2$ can improve the thermal stability by restraining the molten salt loss. This result was consistent with that shown in Fig.1.

Since the microstructures of samples usually have close relations with thermal properties, the cross-section morphologies of the samples were observed by SEM and the results were shown in Fig.6. Fig.6 indicated SiO$_2$ can alter the microstructures of the composites significantly. This might be one reason for explaining the previous DSC results.

![Figure 6. SEM of samples with different content of nano-SiO$_2$](image)

4. Conclusions
The effect of SiO$_2$ on the thermal stability of the samples was evaluated. The DSC results suggested that SiO$_2$ addition showed no obvious influences on the melting points. But they would reduce the phase transition enthalpy. The reduction of the latent heat in samples with nano-SiO$_2$ addition was lower than that of sample without nano-SiO$_2$. These results demonstrated that the carbonate/MgO composites can restrain the molten salt loss and improve the thermal stability by doping SiO$_2$ when exposing to constant high temperature for long time.

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).

References
[1] Guo Q, Wang T 2015 J. Thermochim. Acta 613 66
[2] Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S 2004 J. Energy Convers. Manage. 45 1597.
[3] Kenisarin MM 2010 J. Renew. Sustain. Energy Rev. 14 955
[4] A. Safari, R. Saidur, F.A. Sulaiman, Y. Xu, J. Dong 2017 J. Renew. Sustain. Energy Rev. 70 905
[5] Yaxue Lin, Yuting Jia, Guruprasad Alva, Guiyin Fang 2018 *J. Renew. Sustain. Energy Rev.* **82** 2730

[6] Z. Khan, A. Ghafoor 2016 *J. Energy Convers. Manag.* **115** 132

[7] Z.N. Meng, P. Zhang 2017 *J. Appl. Energy* **190** 524

[8] G.X. Ma, S. Liu, S.L. Xie, Y. Jing, Q.Y. Zhang, J.H. Sun, Y.Z. Jia 2017 *J. Appl. Therm. Eng.* **111** 1052

[9] Tian H, Wang W, Ding J, Wei X, Huang C 2016 *J. Sol. Energy Mater. Sol. Cells* **149** 187

[10] Guanghui L, Geng Q, Zhu J 2018 *J. Appl. Energy* **217** 212

[11] Yifeng J, Yanping S, Rhys D.Jacob 2018 *J. Sol. Energy Mater. Sol. Cells* **178** 74

[12] Yushi L, Yingzi Y 2017 *J. Sol. Energy Mater. Sol. Cells* **160** 18