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Effect of in-situ synthesized nano-MgO on thermal properties of $NaNO_3$-KNO_3

Yi Huang[a], Xiaomin Cheng[a,b,*], Yuanyuan Li[a], Guoming Yu[b], Kai Xu[a], Ge Li[a]

[a] School of Materials Science and Engineering, Wuhan University of Technology, China
[b] School of Mechanical and Electrical Engineering, Huanggang Normal University, Huanggang 438000, Hubei, China

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ABSTRACT

Nitrate molten salt has been proved promising heat storage materials with good thermophysical properties in concentrating solar power station. Increasing specific heat capacity of molten salt can help enhance its thermal storage capacity. In this paper, the effect of nano-MgO on specific heat capacity of $NaNO_3$-KNO_3 is investigated. MgO nanoparticles are synthesized by using in-situ method based on the high temperature decomposition reaction of $Mg(OH)_2$ in solar salt. Materials characteristic analyses using field emission scanning electron microscope (FE-SEM) show that modified salt induces to form needle-like structure. Field emission transmission electron microscope (FE-TEM) was used to obtain the microstructure images of nano-MgO. The diameter of spherical MgO nanoparticlesare about 50–200 nm. The length and width of needle-like nano-MgO are 50–200 nm and 5–30 nm, respectively. In addition, the specific heat capacity of molten salt was measured by differential scanning calorimeter (DSC). Results show that the specific heat capacity of the modified salt is significantly enhanced while the latent heat is slightly decreased. After the samples calcined at 600°C for 1 h, the specific heat capacity is increased by 118.6% in solid state when adding 14.8 wt.% Mg $(OH)_2$, and increased by 168.1% in liquid state when adding 10.4 wt.% Mg $(OH)_2$, respectively. This work discussed the enhancement mechanism of the specific heat capacity is not only related to the MgO nanoparticles, but also the semi-solid layer formed at their surface.

1. Introduction

The non-continuity of solar energy in time and space makes solar heat storage technology more and more important. Solar thermal power plants use heat accumulators to generate electricity. Compared to wind power generation devices and photovoltaic power devices, concentration solar thermal power generation devices are better to meet the energy needs because of thermal storage system (Brosseau et al., 2005; Kearney et al., 2004; Herrmann et al., 2004). The molten salt materials used in the heat storage system can improve the heat storage efficiency to a certain extent. Alkali metal nitrate has extraordinary thermophysical properties, which makes it a potential thermal storage material for solar power applications. However, the lower specific heat capacity of the molten salt greatly impedes their application. Increasing the specific heat capacity of molten salt will largely reduce storage volume, which is to say, with same storage volume, more energy could be stored. Current studies show that the specific heat capacity of molten salt can be raised up by adding nanoparticles to the structure.

In the solar energy storage system, the specific heat capacity is an important thermal performance parameter which can be directly connected with the ability of heat storage and heat exchange. In recent years, people have begun to pay attention to the enhancement of specific heat capacity of nano-fluid. Riazi et al. (2016) found that the addition of trace amounts of nanoparticles into inorganic salts can significantly increase the specific heat capacity of inorganic salts. Chieruzzi et al. (2015) added SiO_2 nanoparticles into the potassium nitrate to improve the specific heat capacity of molten salt to varying degrees. Dudda and Shin (2013), Tiznobaik and Shin (2013) studied the addition of different sizes of nano-SiO_2 into molten salt. The specific heat capacity of nanomaterials were enhanced by evenly 25%. Ho and Pan (2014) investigated the addition of different concentrations of Al_2O_3 nanoparticles in the Hitec salt, results in the enhancement of specific heat, with its most when adding 0.063 wt.%. And Hani (Tiznobaik and Shin, 2013; Ho and Pan, 2014; Tiznobaik et al., 2015) and another study (Shin and Banerjee, 2014) tended to believe that the dendritic structure formed in the inorganic salt is the main reason for the increase of specific heat capacity. Shin and Banerjee (2011) proposed three models to explain the abnormal increase in specific heat.

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* Corresponding author at: School of Materials Science and Engineering, Wuhan University of Technology, China.
E-mail addresses: hy2011@whut.edu.cn (Y. Huang), chengxm@whut.edu.cn (X. Cheng), yyli@whut.edu.cn (Y. Li), yu9595@163.com (G. Yu), xukai19930323@sina.com (K. Xu), lige1018@whut.edu.cn (G. Li).

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However, there is no clear explanation for that so far.

Although there is no clear explanation for the increase in specific heat of molten salt by adding nanoparticles, the preparation of them indeed plays the key role there. There are many methods for the synthesis of nanoparticles, such as sol–gel method (Cui et al., 2016; Nassar et al., 2017), solution combustion synthesis method (Krishna et al., 2017; de Andrade et al., 2006), molten salt method (Lasfargues et al., 2016; Luo et al., 2017) and chemical reduction method (Jiang et al., 2007, 2006).

In-situ method has many advantages that the process is simple and raw materials are cheap. There are some people studying this method to improve molten salt specific heat capacity. In this paper, we apply the in-situ method to synthesize nano-sized magnesium oxide particles in molten salt, which very few researchers (Lasfargues et al., 2016; Luo et al., 2017) have reported previously, and none of them has used magnesium hydroxide as the precursor. Furthermore, in this paper, it is the first time to discuss the effect of holding temperature and the concentration of precursor on the specific heat capacity of solar salt. The latent heat of modified solar salt is also discussed.

2. Experimental

2.1. Modified solar salt preparation

Sodium nitrate, potassium nitrate and magnesium hydroxide (Analytical Reagent, Sinopharm Chemical Reagent Co., Ltd, China) were purchased. Base salt with $NaNO_3$ and KNO_3 were obtained solar salt at a mass ratio of 60–40%. All chemical is analytical grade.

All raw materials were put into a vacuum drier set at 110 °C for 24 h before preparation. Certain amounts of magnesium hydroxide precursor were added to solar salt according to the mass ratios shown in Table 1.

Samples were grinded in the agate mortar for 20 min. After that, the mixture was transferred into ceramic crucibles and put into a furnace for 1 h. In order to ensure the generation of magnesium oxide and avoid the degeneration of solar salt (Zhu et al., 2015), the temperatures were set at 400 °C, 500 °C, 600 °C, respectively, which were higher than the decomposition temperature of magnesium hydroxide (380 °C) and lower than the decomposition temperature of solar salt (above 600 °C). The decomposition reaction formula of magnesium hydroxide is as follows:

$$Mg(OH)_2 \xrightarrow{380^{\circ}C} MgO + H_2O \tag{1}$$

After heated at different temperatures for 1 h, the crucibles were taken out, and the as-prepared samples were poured onto the stainless steel to crystallize at a rapid cooling rate. After cooling, the samples were transformed into ceramic crucibles to grinding and mixing about 45 min. The process is shown in the Fig. 1.

In addition, MgO nanoparticles were obtained through three steps. First, modified salt was washed by water for two times, with centrifugal separation after each time of washing. Second, the nanoparticles were ultrasound dispersed. Third, the nanoparticles were dried.

2.2. Experiment instruments

The specific heat capacity (Cp) of all samples was measured by Differential Scanning Calorimeter (aluminum crucible, Pyris 1 DSC, PerkinElmer, USA). It was subjected to the following thermal cycle in a constant stream of nitrogen: held at 130 °C for 10 min, heating from 130 °C to 300 °C at a heating rate of 10 K per minute.

The surface morphology of the samples was observed by Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss Ultra Plus, Germany) with Energy Dispersive X-ray (EDX) for the analysis of elements.

Field Emission Transmission Electron Microscopy (FE-TEM, JEM2100F, Japan) was used to observe MgO nanoparticles.

X-ray Diffraction (XRD, D8 Advance, Germany) with Cu Kα radiation ($\gamma = 1.5405$) was performed to identify the composition of samples after in-situ preparation.

Fourier Transform Infrared Spectrometer (FT-IR, Nicolet 6700, USA) was used to measure the functional group among the modified salt, MgO nanoparticles and binary salt.

3. Results and discussions

3.1. Components of modified salt

XRD aims to analyze the components of salt. The component of $0^{\#}$ sample, $1^{\#}$ sample and $6^{\#}$ sample were performed in Fig. 2(a). MgO nanoparticles after treating $6^{\#}$ sample were also measured in Fig. 2(b). MgO nanoparticles appear in $6^{\#}$ sample. However, nano-MgO can't be seen from the curve of $1^{\#}$ sample because of accuracy of XRD. Strong diffraction peaks at 29.38°, 31.89° and 38.95° (2θ) are seen due to the feature peaks (1 0 4), (0 0 6) and (1 1 3) of $NaNO_3$ (R-3c, JCPDS, No. 71-1558), respectively. Diffraction peaks of KNO_3 (Pmcn, JCPDS, No. 71-1558) are located at 23.55°, 29.41° and 41.16° (2θ), corresponding to the feature peaks (1 1 1), (0 1 2) and (2 2 1) respectively. Diffraction peaks at 36.96°, 42.94° and 62.35° (2θ) are seen due to the feature peaks (1 1 1), (2 0 0) and (2 2 0) of MgO (Fm-3m, JPDS No. 75-1525). There is no other phase that was found except MgO, $NaNO_3$ and KNO_3. It is that the contents of them, or other phases are too small to detected.

3.2. The structure of modified salt

3.2.1. Different holding temperature

Generally, the property of a material is largely related to the microstructure of the material. Microstructure of the material can be observed by FE-SEM. Fig. 3(a) shows the SEM image of $0^{\#}$ sample (without precursor). It can be seen that the surface of the nitrate material is flat, and there are some holes existing on the surface. Base salt corners are smooth, and the structure of the material is uniform. Moreover, most of the inorganic salt is angular. Fig. 3(b) represents the SEM image of $8^{\#}$ sample. It should be note that the nanoparticles are spherical grain and have some agglomerations. The size of the particles is between 50 nm and 200 nm. The SEM image of $7^{\#}$ sample is obtained

Table 1
Mass ratios of each component used in the preparation of molten salt.

	Percentage of precursor (wt.%)	Precursor ($Mg(OH)_2$)(g)	Percentage of MgO (wt.%)	$NaNO_3$(g)	KNO_3(g)	Temperature (°C)
$0^{\#}$	0	0	0	3.000	2.000	600
$1^{\#}$	1.4	0.073	1	3.000	2.000	600
$2^{\#}$	2.8	0.145	2	3.000	2.000	600
$3^{\#}$	4.1	0.217	3	3.000	2.000	600
$4^{\#}$	5.5	0.289	5	3.000	2.000	600
$5^{\#}$	10.4	0.578	10	3.000	2.000	600
$6^{\#}$	14.8	0.867	15	3.000	2.000	600
$7^{\#}$	14.8	0.867	15	3.000	2.000	500
$8^{\#}$	14.8	0.867	15	3.000	2.000	400