NOVEL NANO-SIO$_2$/ NANO$_3$-KNO$_3$/ EXPANDED GRAPHITE COMPOSITE HEAT STORAGE MATERIAL WITH HIGH SPECIFIC HEAT CAPACITY AND LARGE THERMAL CONDUCTIVITY

Qiang Yu[1], Yuanwei Lu[1*], Xiaopan Zhang[1], Yuting Wu[1]

1 Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Ministry of Education of China, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China.

Corresponding Author, Tel.: +86 10 67396543; Fax: +86 10 67392774. E-mail: luyuanwei@bjut.edu.cn

ABSTRACT

Binary nitrate (NaNO$_3$-KNO$_3$)/expanded graphite (EG)/ nano-SiO$_2$ composite heat storage materials, used as high-temperature thermal energy storage materials, were prepared by mechanical dispersion method, and the effects of EG and nano-SiO$_2$ additives on thermal properties of compound salts were investigated by SEM (scanning electron microscope), STA (Simultaneous Thermal Analysis) and LFA (Laser Flash Apparatus). The results showed that the specific heat capacity of the composites increased first and then decreased with the increase of EG mass fraction. When the mass fraction of EG was 15%, the specific heat of the composite was 3.92J/(g·K), which was 2.58 times higher than that of pure binary nitrate, and the thermal conductivity of the composite was 8.46W/(m·K), which was 16.2 times higher than that of pure binary nitrate. Compared with NaNO$_3$-KNO$_3$/EG(15%wt) composite, the average specific heat capacity and thermal conductivity of the NaNO$_3$-KNO$_3$/EG(15%wt)/nano-SiO$_2$ composite material increased by 15.98% and 42.91% respectively. The preparation process was simple, and the NaNO$_3$-KNO$_3$/EG/nano-SiO$_2$ composite had a broad application prospect in high-temperature energy storage system.

Keywords: binary nitrate; nanoparticles; expanded graphite; specific heat; thermal conductivity

NONMENCLATURE

Abbreviations	
EG	Expanded Graphite

SEM	scanning electron microscope
STA	Simultaneous Thermal Analysis
LFA	Laser Flash Apparatus
XRD	X-ray diffractometer
Symbols	
Cp	Specific heat capacity J/(g·K)
λ	thermal conductivity W/(m·K)

1. INTRODUCTION

Thermal storage is a key-link technology in solar thermal power generation system. It can not only solve the problems that solar energy technology is facing, such as time intermittence and instability, but also utilize low-temperature waste heat more effectively. Molten salts are considered as ideal media for heat storage and transfer with the desirable features including low cost, broad operating temperature, good thermal/chemical stability, low vapor pressure [1]. However, As heat transfer and storage medium, the thermal conductivity of molten salt is less than 1 W/(m K) and specific heat is than 2 kJ/(kg K), which will not only prolong the heat storage and discharge time of the system, but also increase the complexity of the heat exchange system and reduce the thermal efficiency of the system.

Expanded graphite has excellent thermochemical properties, high porosity and high thermal conductivity [2], which can greatly enhance the thermal conductivity of molten salt. Acem [3] prepared KNO$_3$-NaNO$_3$/EG composite heat storage material by cold pressing method. It was found that the thermal conductivity of

the sample increased by 15%-20%. Aktay [4] added expanded graphite into melted KNO_3-$NaNO_3$ salts through impregnation method and the thermal conductivity of the composites was increased five times. As mentioned above, EG could greatly improve the thermal conductivity of the composite materials. On the other hand, it has become a research hotpot that adding nanoparticles into molten salts to improve the specific heat and the thermal storage performance of heat storage materials. Tiznobaik [5] dispersed SiO_2 nanoparticles into Li_2CO_3-K_2CO_3, and found the specific heat of the composites increased by 25% after adding SiO_2 nanoparticles. Shin [6] found that adding Al nanoparticles into binary carbonate could lead to a 32% increase in the specific heat.

On the basis of previous research, expanded graphite and nanoparticles have been demonstrated available to improve the thermal conductivity and the specific heat of heat storage materials. However, there are hardly any works that concern both thermal conductivity and specific heat. So it is highly necessary to improve the thermal conductivity and specific heat of the materials at the same time. In this paper, nano-SiO_2/$NaNO_3$-KNO_3 was used as thermal storage material and expanded graphite with different content (5%, 10%, 15% and 20%) as matrix material. A nano-SiO_2/$NaNO_3$-KNO_3/EG composite heat storage material with stable shape was prepared by mechanical dispersion method. The thermo-physical properties were measured to evaluate its potential application, including latent heat, specific heat capacity and thermal conductivity.

2. EXPERIMENTAL SECTION

2.1 Reagents and materials

Potassium nitrate and sodium nitrate (AR, ＞99% in purity) were purchased from Beijing Chemical Plant. The silica nanoparticles (average diameter 20nm, specific surface area 143 m^2/g, spherical) supplied by Beijing Deco Island Gold Technology Co., Ltd., China. EG powder was purchased from Qingdao Furuite Graphite Co, Ltd., China, which expandable volume was 300 mL/g and granularity was mesh 80.

2.2 Sample preparation

In this study, An $NaNO_3$-KNO_3 eutectic was selected as the heat storage materials, in which the molar fractions of $NaNO_3$ and KNO_3 were 6 and 4, respectively. Potassium nitrate and sodium nitrate powders were thoroughly mixed, followed by being heated to 400 °C in muffle furnace and held for 12 h to obtain a uniform mixture. The binary nitrate and SiO_2 nanoparticles (the mass of SiO_2 nanoparticles accounts for 1% of the total mass of binary nitrate and SiO_2 nanoparticles) were weighed and stirring in a constant temperature salt tank at 400 C. The stirring speed is 750 r/min and the stirring time is 15 min [7]. Then, adding different mass ratios EG, stirring until the liquid nano-molten salt completely enters the micropore of EG, and cooling. Finally, the bulk sample was ground to powder, which is to prepare nano-SiO_2/$NaNO_3$-KNO_3/EG composite material. The composite material was compressed into a cylinder block at the pressure of 10MPa using a tablet machine. Then, the sample was heated to 400 °C and held for 3 h, then cooling down to ambient temperature.

2.3 Characterization and measurement

The microstructures of composites were observed using a scanning electron microscope (SEM, SU8020, Hitachi, Japan). The crystalline phases of composites were characterized by an X-ray diffractometer (XRD, D8-ADVANCE, BRUKER/AXS, Germany). The latent heat and specific heat capacity were measured using the Simultaneous Thermal Analysis (STA-449F3, NETZSCH,) with a standard automated procedure (ASTM E1269). The thermal conductivity of composites were characterized by Laser Flash Apparatus (LFA-45, NETZSCH), which uses the laser flash method.

2.4 Results and discussion

2.4.1 Characterization of microstructure

The morphologies of EG, $NaNO_3$-KNO_3/15wt% EG and nano-SiO_2/$NaNO_3$-KNO_3/15wt% EG composites were shown in Figure 1. Expanded graphite in Figure 1(a-b) showed worm-like structure with abundant pore and large volume. Adding nitrate, nitrate was evenly distributed in the channel, middle layer and inner space of EG, as shown in Figure 1 (c-d). After adding SiO_2 nanoparticles, a uniform and high density network structure was formed on the surface of the composite, which effectively increased the specific surface area of molten salt, as shown in Figure 1 (e).

Figure 2 showed XRD patterns of EG(c), the $NaNO_3$-KNO_3 (b) eutectic salt and the nano-SiO_2/$NaNO_3$-KNO_3/EG (a) composites block. EG showed two diffraction peaks located at 26.381° and 54.542°. The phase of the prepared $NaNO_3$-KNO_3 mixed salt was $NaNO_3$ and KNO_3, and no other substances were found, as shown in Figure 2(b). The positions of strong diffraction peaks of nano-SiO_2/$NaNO_3$-KNO_3/EG composites correspond to those of $NaNO_3$-KNO_3 and

EG, which indicates that there was only physical mixing between $NaNO_3$-KNO_3 and EG, and no chemical reaction occurs, as shown in Figure 2(a). The diffraction peak of SiO_2 was not obvious on the XRD curve because of its small addition.
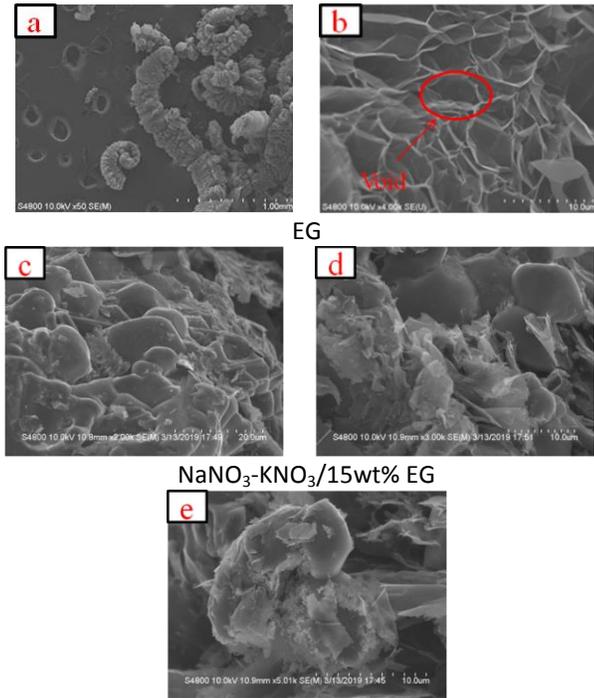

EG

NaNO₃-KNO₃/15wt% EG

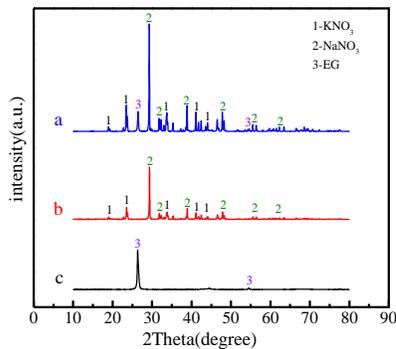Nano-SiO₂/NaNO₃-KNO₃/15wt% EG

Fig 1 SEM images of composites

Fig 2 XRD patterns of EG (c) and $NaNO_3$-KNO_3 eutectic salt (b) and nano-SiO_2/$NaNO_3$-KNO_3/15wt%EG (a) composite

2.4.2 *Thermophysical properties of composites*

Specific heat capacity of composites varied with temperature were presented in Figure 3. When the mass fraction of EG was 10%, 15% and 20%, the average specific heat of $NaNO_3$-KNO_3/EG composites was 3.35 J/(g K), 3.38 J/(g K) and 3.05 J/(g K), respectively, which were higher than that of binary nitrates. When the mass fraction of EG was 10%, 15% and 20%, the average specific heat of nano-SiO_2/$NaNO_3$-KNO_3/EG composite was 3.73 J/(g K), 3.92 J/(g K) and 3.75 J/(g K), respectively. Under the same mass fraction of EG, the average specific heat of nano-SiO_2/$NaNO_3$-KNO_3/EG

composite was higher than that of $NaNO_3$-KNO_3/EG composite. It could be observed by SEM that the surface of SiO_2/$NaNO_3$-KNO_3/EG sample was almost uniformly distributed and forming a high density network structure, which was the key factor to improve the specific heat of composites.
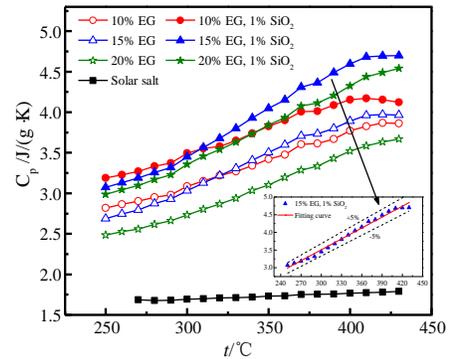

Fig 3 Specific heat capacity of composites

The DSC curves of composites varied with temperature were presented in Figure 4. By analyzing the DSC curves, the melting latent heat of samples with different EG mass fractions was shown in Table 1.
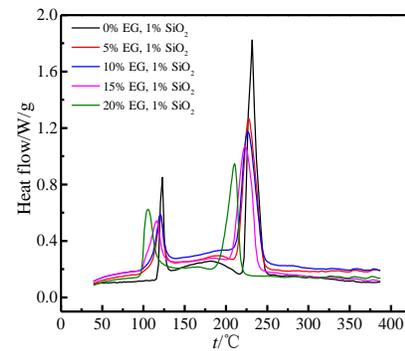

Fig 4 DSC curves of binary eutectic nitrate and composites

Table 1 Melting Point and Latent Heat of Composites

w (wt%)	melting point (℃)	Latent heat measurements (J/g)
0	220.8	113
5	214.7	100.3
10	213.7	91.07
15	208.4	87.62
20	194.2	58.51

Figure 4 showed that there were two phase transition peaks in each DSC curve. The first phase transition peak was formed by solid-solid phase transformation of binary nitrate and the second phase transition peak was formed by solid-liquid phase transformation of binary nitrate because of the stable thermochemical properties of EG in the high temperature. Figure 4 also showed that the peak of phase transition peak decreases with the increase of EG mass fraction in solid-liquid phase transition. Table 1 showed that the phase

3 Copyright © 2019 ICAE

change latent heat of binary eutectic nitrate was 113 J/g. With the increased of EG mass fraction, the phase change latent heat of the composites was decreases. This was because only binary nitrate had latent heat in composites. EG was solid at high temperature, and it did not make any contribution to the latent heat of composites.

The thermal conductivities of composites with different EG content were shown in Figure 5. The thermal conductivity of the composites could be improved by adding expanded graphite, and the thermal conductivity increases with the increase of EG mass fraction. Meanwhile, the thermal conductivity of the composites could continue improved by adding SiO_2 nanoparticles. From the microscopic point of view, Due to good thermal conducting and uniform distribution of EG, composites formed excellent heat transfer network. In addition, the porous structure of expanded graphite provided a larger contact area between molten salt and EG, which leaded to higher heat transfer. After adding SiO_2 nanoparticles, the surface of composites would form a network of nanostructures. The continuous growth of nanostructures and the high surface area of nanoparticles would form channels for heat transfer and increased the overall thermal conductivity of composites.
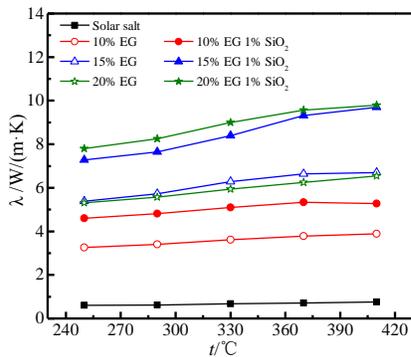

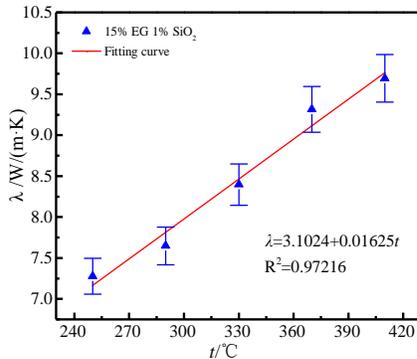Fig 5 Thermal conductivity of composites.

Fig 6 Fitting curve of thermal conductivity and temperature.

The corresponding relational equations between the thermal conductivity and temperature of nano-

$SiO_2/NaNO_3$-KNO_3/15wt% EG composite could be approximately concluded as follows:

$$\lambda = 3.1024 + 0.01625 \times T \quad 250°C \leq T \leq 430°C \quad (1)$$

As showed in Figure 6, the thermal conductivity of the composites was linear with temperature and increased with the rising temperature.

2.5 Conclusions

(1) The average specific heat capacity of $NaNO_3$-KNO_3/15wt% EG composite was 3.38 times that of nitrate. The specific heat of the composites could continue to increase by adding SiO_2 nanoparticles.

(2) Expanded graphite could improve the thermal conductivity of composites. The thermal conductivity increased with the increased of EG mass fraction. The thermal conductivity of the composites could continue to increase by adding SiO_2 nanoparticles.

REFERENCE

[1] Wang T, Mantha D, Reddy RG. Novel low melting point quaternary eutectic system for solar thermal energy storage. Appl. Energy. 2013; 102:1422-1429.

[2]Zhang Q, Wang H, Ling Z, Fang X, Zhang Z. RT100/expand Graphite Composite Phase Change Material with Excellent Structure Stability, Photo-Thermal Performance and Good Thermal Reliability. Sol. Energy Mater. Sol. Cells. 2015; 140:158-166.

[3] Acem Z, Lopez J, Barrio EPD. $KNO_3/NaNO_3$ – Graphite materials for thermal energy storage at high temperature: Part I. – Elaboration methods and thermal properties. Appl. Therm. Eng. 2010; 30(13): 1580-1585.

[4] Aktay KSDC, Tamme R, Müller-Steinhagen H. Thermal Conductivity of High-Temperature Multicomponent Materials with Phase Change. Int. J. Thermophys. 2008; 29(2): 678-692.

[5] Tiznobaik H, Shin D. Enhanced specific heat capacity of high-temperature molten salt-based nanofluids. Int. J. Heat Mass Transfer. 2013; 57(2): 542-548.

[6] Shin D, Banerjee D. Specific heat of nanofluids synthesized by dispersing alumina nanoparticles in alkali salt eutectic. Int. J. Heat Mass Transfer. 2014; 74(5): 210-214.

[7] Song WL, Lu YW, Wu YT. Effect of SiO_2 nanoparticles on specific heat capacity of low-melting-point eutectic quaternary nitrate salt. Sol. Energy Mater. Sol. Cells. 2018; 179:66-71.