

Energy storage materials MgO-Hitec molten salt composite by electromagnetic heating In-situ preparation

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ABSTRACT

Molten salt can be effectively improved its specific heat capacity doped with nanoparticles. In this paper, the influence of different contents of MgO on the specific heat capacity of Hitec ($\text{KNO}_3\text{-NaNO}_2\text{-NaNO}_3$) is investigated. MgO-Hitec is synthesized with electromagnetic heating to rapidly increase the temperature of the nucleation method, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as the magnesium source. The specific heat capacity of the composite molten salt fluid was measured with a differential scanning calorimeter (DSC). X-ray diffraction (XRD), nanoparticle size analyzer and scanning electron microscope (SEM) were used to characterize the MgO-Hitec molten salt synthesized in situ. The results show that the specific heat capacity of 2.5% MgO-Hitec fluid is $1.737 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, which is 23% higher than the $1.429 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ of Hitec-based salt. The average grain size of the synthesized MgO is $\sim 40 \text{ nm}$, the average particle size is less than 250 nm , and there is a certain degree of aggregation of MgO in the newly synthesized composite salt. The heat storage density is the largest up to $9.87 \times 10^5 \text{ kJ} \cdot \text{m}^{-3}$. The composite molten salt is suitable for solar energy transfer and heat storage materials.

Keywords: In-situ synthesis; MgO-Hitec composite molten salt; heat storage

1. INTRODUCTION

Energy and the environment are the two major themes of human development [1]. Solar salt is currently the main heat transfer and storage medium in solar thermal power generation [2]. While another common nitrate, Hitec, is expected to be commercially used in molten salt system in solar thermal power generation, because its specific heat capacity is relatively high. However, small, low thermal conductivity, which limits

its wide application in solar thermal power stations to a certain extent.

Nanomaterials have surface effects, quantum effects and quantum tunneling effects [3], which can regulate the properties of materials from the perspective of atoms and molecules [4]. Therefore, researchers introduced nano-fluid into molten salt to improve its specific heat capacity and thermal conductivity, namely, nano-fluid enhanced heat transfer technology [5]. At present, the preparation of molten salt nanofluids can be divided into two categories: one-step method and two-step method. In the one-step method, nanoparticles are directly synthesized in situ in molten salt system, and nanoparticles generated in situ can be better dispersed in molten salt. Luo et al [6] obtained nano molten salt fluid by ball milling binary nitrate ($\text{KNO}_3\text{-NaNO}_3$) and copper acetate, and found that the specific heat capacity was significantly improved. The two-step method has been studied more. The two-step method is to obtain nanoparticles first, and then use physical means to disperse them in the prepared molten salt. Song et al [7] used a high-temperature melting method to disperse nano- SiO_2 into quaternary nitrate and found that its specific heat capacity was improved. Shin et al [8] compared the performance difference between the one-step method and the two-step method by adding SiO_2 to the molten salt. Compared with the traditional two-step method, the one-step method is more economical. There is little difference in footwork. In-situ synthesis can reduce the agglomeration of nanoparticles and greatly increase the specific heat capacity of molten salt composites.

Based on the above studies, in this paper, magnesium oxide nanoparticles (MgO) were generated

in situ by electromagnetic heating and rapid temperature nucleation in Hitec. Molten salt nanofluid composites with MgO content of 2.5W %, 3.5W % and 4.5W % were prepared by changing different synthesis paths. The molten salt nano-fluid was analyzed by differential scanning calorimeter (DSC), scanning electron microscope (SEM), X-ray diffractometer (XRD) and nano-particle size analyzer. The experimental results show that the specific heat capacity and heat storage performance of molten salt nano-fluid are significantly improved.

2. EXPERIMENT

Potassium nitrate (analyzable, Guangzhou Chemical Reagent Factory), sodium nitrate (analyzable, Chengdu Cologne Chemical Co., LTD.) and sodium nitrite (analyzable, Tianjin Damao Chemical Reagent Factory) were placed in a drying oven at 120°C for 24 hours. The dry single salt, according to the mass ratio ($\text{KNO}_3:\text{NaNO}_3:\text{NaNO}_2=53:7:40$) mixed evenly, using static melting method in 300°C muffle furnace heat preservation 3-4 hours, so that it forms a homogeneous liquid, cooling to room temperature to get Hitec ternary nitric acid molten salt, after grinding bags into the dryer for standby.

MgO-Hitec composite molten salt was prepared by hydrolyzing $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in Hitec molten salt in situ. Three in situ generation methods were used.

Spray method ①: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (analytical purity, Tianjin Damao Chemical Reagent Factory) weighed in proportion is made into a concentrated aqueous solution, sprayed on the Hitec solid surface, and dried at 120°C to disperse the magnesium in Hitec as much as possible. After being kept in a muffle furnace at 500°C for 3 hours, it was cooled and crushed. The prepared sample was recorded as MgO-HS.

Electromagnetic method ②: A certain proportion of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solid was mixed evenly with Hitec, and the samples were rapidly hydrolyzed and nucleated by 600W electromagnetic discontinuous heating (heating for 6 seconds and stopping for 4 seconds) for half an hour. The samples were then heated and crystallized in a muffle furnace at 500°C for 5h. The samples were recorded as MgO-HO.

Electromagnetic method ③: Repeat ② discontinuous heating at 600W for half an hour, then transfer it to a muffle furnace at 500°C to heat and

crystallize for 6 hours. The sample is marked as MgO-HT.

For comparison, the mechanical mixing method ④ was also used for preparation. The purchased nano-MgO (50nm, Shanghai Maclean Biochemical Technology Co., Ltd.) was directly mixed into the Hitec melt by mechanical stirring, and the muffle furnace was kept at 500°C for 3 hours. The sample was recorded as MgO-HD.

The MgO-Hitec samples were synthesized by the method ③, the MgO content was 2.5%, 3.5%, 4.5%, and the suffixes were -2.5, -3.5, -4.5, namely MgO-HT-2.5, MgO-HT-3.5, MgO-HT-4.5.

3. RESULTS AND DISCUSSION

3.1 Specific heat capacity of MgO-Hitec composite molten salt fluid

The measurement result of the specific heat capacity of the MgO-Hitec composite molten salt fluid is shown in Figure 1. Figure 1 (a) shows the 2.5% MgO content MgO prepared by spray method ① (MgO-HS), electromagnetic method ② (MgO-HO), electromagnetic method ③ (MgO-HT) and mechanical mixing method ④ (MgO-HD) - Specific heat capacity of Hitec composite molten salt fluid. It can be seen from Figure 1(a) that the specific heat capacity of the MgO-HD-2.5 composite molten salt fluid prepared by the mechanical mixing method ④ decreases with the increase of temperature. The main reason is that the MgO particles cannot be completely suspended in Hitec. Because the agglomeration particles are too large to settle at the bottom of the crucible or float on the surface of the molten base salt, the measurement results of its specific heat capacity are not stable. In order to make the nanoparticles and the molten salt mix more uniformly, the spray method ① is used to mix the magnesium chloride hexahydrate and the Hitec salt as evenly as possible, and the high temperature hydrolysis forms the MgO-HS-2.5 composite molten salt, although its specific heat capacity is compared with that of MgO-HD-2.5 has increased, but will also decrease with the increase of temperature, but compared with the specific heat capacity of Hitec-based salt, there is no significant increase. The specific heat of MgO-HO-2.5 prepared by electromagnetic method ② is similar to that of MgO-HS-2.5 prepared by spray method ①. The

specific heat capacity of the composite molten salt MgO-HT-2.5 fluid prepared by electromagnetic method ③ is significantly higher than the specific heat capacity of the first three and Hitec-based salts. Figure 1(b) shows samples MgO-HT-2.5, MgO-HT-3.5 and MgO-HT-4.5 prepared by electromagnetic method ③ with MgO content of 2.5%, 3.5% and 4.5%. It can be found that their specific heat capacity has increased, among which the increase of MgO-HT-2.5 is the most significant, and its specific heat capacity reached $1.737 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$, which is comparable to the $1.429 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ of the base salt. Than that, an increase of 23%.

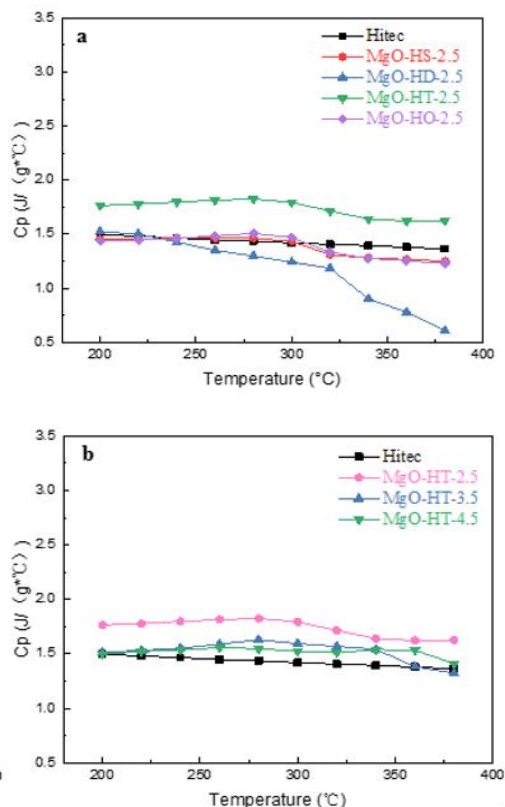


Figure.1 (a) Preparation method and (b) Influence of MgO content on specific heat capacity of the prepared MgO-Hitec composite molten salt

3.2 Characterization of MgO-Hitec composite molten salt materials

3.2.1 XRD phase analysis of MgO-Hitec composite molten salt materials

The XRD patterns in Figure 2(a) reveal that MgO is present in the MgO-Hitec composite molten salt. There is no other phase that was found except MgO, KNO_3 , NaNO_3 , NaNO_2 , the characteristic diffraction peaks of MgO are consistent with the card 77-2364 of the JCPDS-ICDD database. It can be seen from Figure

2(b) that the characteristic peak of MgO with 2θ between 40° - 50° is relatively strong. Based on its half-height width estimated by Scherer [9], the average crystal size of MgO is 40 nm. Figure 2(a) has no obvious diffraction peak of $\text{Mg}(\text{OH})_2$, which is different from the XRD result of Yinyue [10] after MgO generated in situ in the chloride salt. In addition to MgO, Yinyue's [10] XRD measurement results also contain $\text{Mg}(\text{OH})_2$. The reason may be that when MgO is separated with distilled water, MgO reacts with H_2O . The MgO-Hitec composite molten salt was prepared at a high temperature of 500°C , so $\text{Mg}(\text{OH})_2$ was not detected in its XRD.

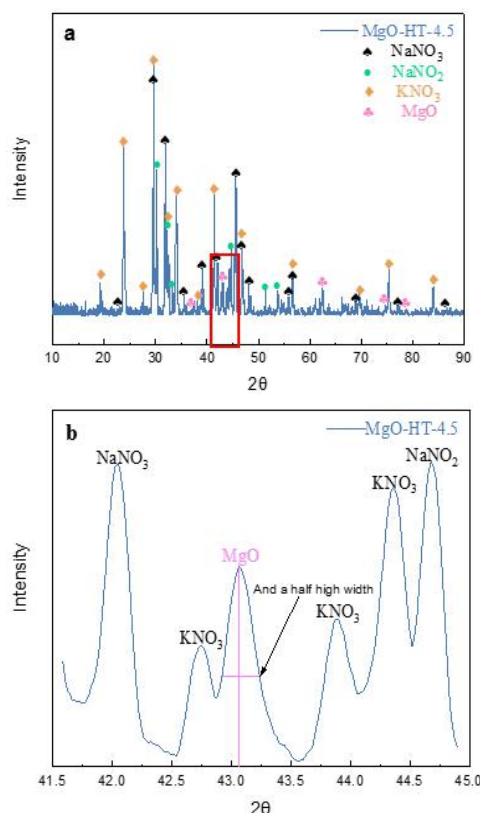


Figure.2 (a) XRD patterns of the composite molten salt MgO-HT-4.5 and (b) the main peak of MgO

3.2.2 Microstructure of MgO-Hitec composite molten salt

The scanning electron microscope (SEM) of the composite molten salt MgO-HT is shown in Figure 4. It can be seen from Figure 4(a) that a large number of MgO particles are generated in the base salt. From Figure 4(b) and Figure 4(c), it can be found that MgO is more evenly distributed in the middle of the salt and there is a certain degree of polymerization, which may be due to the precursor $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ mixed with potassium nitrate solid particles, which are largely formed in the process of local hydrolysis. The particles

thus temporarily aggregate into clusters, and further research will be conducted on the degree of dispersion after long-term heat storage.

3.3 Analysis of heat storage performance

Energy storage density is the most important data in heat transfer and storage applications. It is an important means to evaluate the energy storage advantages and disadvantages of materials and the thermal efficiency of the system. It determines the heat storage capacity of energy storage materials per unit volume and the heat transfer Heat transfer efficiency. The energy storage density per unit volume can be calculated according to the specific heat, density and working temperature range of the sample [12], and its calculation formula is shown in Equation 1.

$$E=Cp \int_{T_1}^{T_2} \rho (T) dT \quad (1)$$

Where E is the energy storage density of the material, T_1 and T_2 are the material's 50°C higher than the melting temperature and the working temperature of the material on the line; in this paper, the specific heat capacity of the material in the energy storage density is the average value of the specific heat capacity of the material, and the density function is taken from this group The density function of Qin Bo [11], the parameters and calculated values are shown in Table 1. It can be seen that in the MgO-HT series composite molten salt prepared by the electromagnetic method ③, when the addition amount of MgO is 2.5%, the storage The energy density reaches $9.87 \times 10^5 \text{ kJ} \cdot \text{m}^{-3}$, which is 23% higher than the $8.03 \times 10^5 \text{ kJ} \cdot \text{m}^{-3}$ of Hitec base salt. This means that 23% more heat can be stored under the same heat storage volume. It can be seen that it is very suitable as a molten salt heat transfer and storage material.

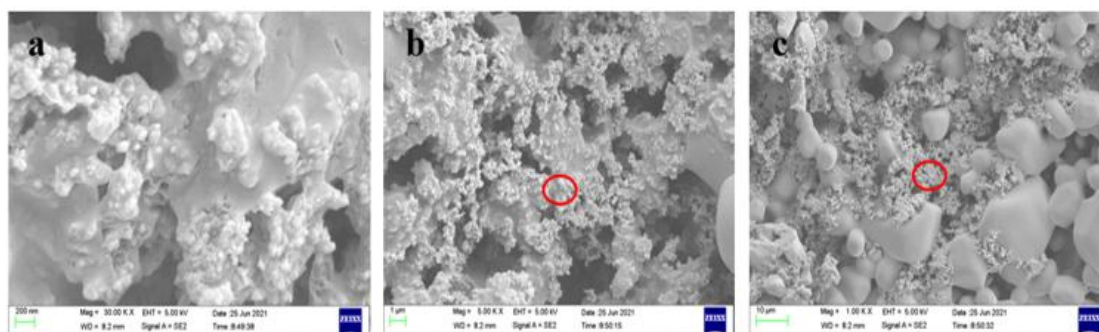


Figure.4 Scanning electron micrographs of composite molten salt MgO-HT-2.5 (a, b, c)

Table 1 Calculation data and results of energy storage density of composite molten salt MgO-HT

sample	$C_p(\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1})$	$\rho(\text{g} \cdot \text{cm}^{-3})$	$T_1(\text{K})$	$T_2(\text{K})$	$E(\times 10^5 \text{ kJ} \cdot \text{m}^{-3})$	Improve the rate of
Hitec	1.429	$\rho=2.09-7.54 \times 10^{-4}T$	465.15	773.15	8.03	--
2.5%	1.737	$\rho=2.11-7.68 \times 10^{-4}T$	465.15	773.15	9.87	23%
3.5%	1.522	$\rho=2.10-6.93 \times 10^{-4}T$	465.15	773.15	8.72	8%
4.5%	1.518	$\rho=2.13-7.64 \times 10^{-4}T$	465.15	773.15	8.70	8%

4 CONCLUSION

In this paper, the MgO-Hitec composite molten salt nanofluid was prepared by different methods. The specific heat capacity was measured and the composite molten salt was characterized. The following conclusions were obtained:

(1) Nanoparticles synthesized in situ have small particle size and can form stable homogeneous suspended solution with

molten salt without obvious settlement. MgO particles generated in situ can form stable suspended fluid in molten salt fluid.

(2) The specific heat capacity of MgO-Hitec composite molten salt nanocomposites has been significantly improved, and the increase rate is up to 23%. This molten salt nanofluid composite is suitable for high temperature heat transfer and storage.

(3) After 20h constant temperature, the mass of molten salt nanofluid does not change significantly, and it has a wide stable operating temperature range and high energy storage density. Therefore, it is suitable for solar energy transmission and heat storage materials

ACKNOWLEDGMENTS

For this study the authors acknowledge the support of the National Natural Science Foundation of China (No. 52036011).

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