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Experimental study on the specific heat and stability of molten salt nanofluids prepared by high-temperature melting

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ABSTRACT

Molten salt is an important heat storage and heat transfer medium in solar thermal power generation technology due to its high heat capacity, wide working temperature range, and low cost. Adding nanoparticles (usually by the two-step method with ultrasonic dispersion) can increase the specific heat of molten salt. Thus, the molten salt nanofluids can increase the heat capacity and decrease the heat storage cost of a solar thermal power generation system. However, nanoparticles are easy to agglomerate in the molten salt; moreover, after agglomeration, the performance of molten salt nanofluids is degraded. A two-step method with high-temperature melting in preparing molten salt nanofluids is proposed in this paper. Molten salt nanofluids were prepared by high-temperature melting. The base solution was a low-melting point molten salt and the nanoparticles were SiO_2 with a diameter of 20 nm. The specific heat was measured and the nanoparticle dispersity was analyzed. The stability of the molten salt nanofluids was studied, and the results were compared with those prepared by ultrasonic dispersion. The average specific heat of molten salt nanofluids prepared by high-temperature melting was 1.789 J/(g·K), which was close to that of molten salt nanofluids prepared by ultrasonic dispersion and 16.4% higher than that of pure molten salt. The molten salt nanofluids prepared by ultrasonic dispersion showed poor thermal stability under high-temperature conditions, and the average specific heat decreased by 8.5% after only 200 h. The thermal stability of molten salt nanofluids prepared by high-temperature melting showed a highly stable performance in long-time experiments. The variation of specific heat was less than 5% after 2000 h under the same high-temperature experimental condition. The molten salt nanofluids obtained by high-temperature melting showed better stability and long performance than those obtained by ultrasonic dispersion. Therefore, the two-step method with high-temperature melting is stable and reliable for preparing molten salt nanofluids.

1. Introduction

Facing the reality of energy depletion and environmental deterioration, the development and utilization of new energy and renewable energy are of great strategic significance. Solar thermal power, which is one of the most promising renewable energy power generation technologies, can generate high quality electrical energy and achieve large-scale heat storage without generating pollution [1–3]. Molten salts have become a potential heat transfer and storage medium in solar thermal power because of the following advantages: wide temperature range, high heat capacity, low cost, pollution-free [4,5]. Moreover, specific heat is one of the important thermophysical parameters of molten salt. Improving the specific heat of molten salt can play a key role in improving the heat storage capacity and reducing the heat storage cost of solar thermal power generation systems.

One way to increase the specific heat capacity of molten salt is by adding nanoparticles into molten salts to make molten salt nanofluids. Ramaprasath [6] added nano-SiO_2 with different sizes (5, 10, 30, and 60 nm) into HitecXL salt and studied the characteristics of the specific heat of the molten salt nanofluids. The results showed that adding 5, 10, 30, and 60 nm SiO_2 increased the specific heat of molten salt nanofluids by 28%, 34%, 19%, and 30%, respectively. Tiznobaik et al. [7] obtained nanofluid materials by dispersing four different sizes of SiO_2 nanoparticles in binary carbonate salt. Adding nanoparticles enhanced the specific heat of the original dibasic carbonates by 25%. Jo and Banerjee [8] analyzed the effect of nanoparticle dispersion on the specific heat

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capacity of molten carbonate salts and observed the enhancement in the specific heat capacity from the molten salt nanofluids with more homogeneous dispersion of the nanoparticles. Shin et al. [9] found that the thermal conductivity of the prepared carbonate nanocomposites was increased from 37% to 47% and the specific heat capacity increased from 5% to 15%. Ho and Pan [10] added different proportions of Al_2O_3 nanoparticles on the basis of HITEC salt and studied the optimized characteristics of the specific heat of molten salt. The optimal concentration of Al_2O_3 nanoparticles was 0.063 wt%. Zhao and Wu [11,12] found that multi-walled carbon nanotubes and nano-gold particles improved the thermophysical properties of the molten salts, which mainly depended on the small size effect of nanoparticles, dispersion degree, and morphological features. Interfacial thermal resistance is the main factor that influences the thermophysical properties of two-phase composites.

Properties of molten salt nanofluids, especially stability, are closely related to the preparation method. The one-step and two-step methods are the two main techniques for producing nanofluids [13]. The one-step technique combines the production and dispersion of nanoparticles in the base fluid into a single step. Variations of this technique exist. In the one-step direct evaporation, one of the most common one-step techniques, the nanofluid is produced by the solidification of the nanoparticles, which are initially in the gaseous phase when inside the base fluid. The one-step direct evaporation approach was developed by Akoh et al. [14] and is called the Vacuum Evaporation onto a Running Oil Substrate technique. The original idea of this method was to produce nanoparticles, but subsequently separating the particles from the fluids to produce dry nanoparticles was difficult. Another one step is laser ablation, which has been used to produce alumina nanofluids [15]. Zhu et al. [16] used a one-step pure chemical synthesis to prepare nanofluids of copper nanoparticles dispersed in ethylene glycol. The main advantage of the one-step method is its low agglomeration of nanoparticles, which improves nanofluid stability. The costs for drying and dispersion can be reduced using this method. The major disadvantages of this method are: (a) the method is impossible to scale up due to high production cost, and (b) it is only compatible with low vapor pressure base fluids [17,18].

The two-step method is the most widely used method for preparing nanofluids [19]. In the first step, nanomaterials, such as nanoparticles, nanofibers, or nanotubes, are produced in the form of dry powders. During the second step, the produced nanomaterials are directly dispersed into the given base fluid with the help of dispersing devices, such as a magnetic stirrer [20,21] and homogenizer [22], or using ultrasonic devices, like an ultrasonic bath and ultrasonic processor [23–25]. Currently, the limitation of this method is the possible particle sedimentation and aggregation with respect to time. Moreover, this limitation is due to the high surface energy of the particles, van der Waals attraction between particles, and gravitational forces [26]. Nanofluid aggregation has detrimental effects on specific heat improvement because each experiment showed that a high amount of aggregation leads to a minimal increase in specific heat and using surfactants yields maximal increase in specific heat [27]. Ho and Pan investigated the specific heat of molten HITEC salt loaded with Al_2O_3 nanoparticles and found that increasing the concentration above 0.023 wt% will cause particle aggregation and may reduce the specific heat capacity because of the reduced the interfacial area [28].

Stabilizing nanofluids remains a technical challenge due to the presence of van der Waals attractive forces, which promote aggregate formation. Without proper stabilization techniques, nanofluids will tend to form clusters and agglomerates and thermal performance will continuously decline [29,30]. Producing stable and durable nanofluids is crucial to ensure optimal thermal properties for the nanofluids [31]. This current study presents a two-step method with high-temperature melting in preparing molten salt nanofluids to improve the stability of molten salt nanofluids and provide the possibility of large-scale use of molten salt nanofluids in engineering. High-temperature melting disperses nanoparticles into liquid molten salt by mechanical stirring under high-temperature conditions. The method mainly disperses the nanoparticles in the medium by means of external mechanical forces, such as shearing force or impact force. During this process, the nanoparticles are dispersed in the molten salt base liquid, which will promote the formation of an electrical double layer on the surface of the nanoparticles, so that the nanoparticles are charged and nanoparticles are not easily agglomerated under the mutual repulsion of the same charge. The present study prepared molten salt nanofluids using high-temperature melting. The specific heat of molten salt nanofluids was measured. The microstructure of molten salt nanofluids was observed by a scanning electron microscope (SEM), and the dispersion performance of nanoparticles was also analyzed. The stability of molten salt nanofluids was experimentally studied. The abovementioned results were all compared with molten salt nanofluids prepared by ultrasonic dispersion, and the pros and cons of high-temperature melting and ultrasonic dispersion are presented.

2. Molten salt nanofluid preparation

The authors developed a low-melting point quaternary-mixed nitrate, $Ca(NO_3)_2$-KNO_3-$NaNO_3$-$LiNO_3$ (2:6:1:2 in mass ratio), and the study showed that the low-melting point molten salt works fine for solar thermal power generation. This molten salt has a melting point of approximately 85.4 °C and a maximum operating temperature of 600 °C. When the temperature is below 300 °C, the thermal conductivity is 0.53 W/(m·K) and the specific heat is 1.519 kJ/(kg·K). Moreover, the risk of blockage of this molten salt is greatly reduced and the corrosion to the pipeline is decreased, as shown by analysis of the experiment results on the convective heat transfer and long-term stability of the molten salt [32]. In this study, the above low-melting point molten salt was used as the base solution and weighted 9.9 g. Furthermore, SiO_2 nanoparticles are the frequently used nanoparticles for preparing nanofluids, and SiO_2 nanoparticles with a diameter of 20 nm and weight of 0.1 g were chosen in this study. The mass fraction of SiO_2 nanoparticles in molten salt nanofluids was 1 wt%. Molten salt nanofluids were prepared using ultrasonic dispersion and high-temperature melting, respectively. The differences between the two methods are: 1) In ultrasonic dispersion, the molten salt and nanoparticles are dissolved in deionized water; for high-temperature melting, the molten salt and nanoparticles are mixed directly under high temperature. 2) The molten salt nanofluids prepared by ultrasonic dispersion are ultrasonically shaken; the molten salt nanofluids prepared by high-temperature melting are stirred with a magnetic stirring bar. 3) The molten salt nanofluids prepared by ultrasonic dispersion are placed in an air-blowing thermostatic oven to dry the water. The molten salt nanofluids prepared by high-temperature melting does not require this step. The concrete steps for the two methods are discussed in the subsections below:

2.1. Ultrasonic dispersion

(1) Low-melting point molten salt and SiO_2 nanoparticles were weighed and mixed and then dissolved in deionized water.
(2) Molten salt nanofluids were ultrasonically shaken. The ultrasonic oscillation frequency was 45 Hz and the time was 50 min
(3) Molten salt nanofluid samples were obtained by placing the abovementioned molten salt nanofluids in an air-blowing thermostatic oven to dry the water.

Three sets of samples were prepared according to the above procedures to test repeatability: Sample S1, Sample S2, and Sample S3.

2.2. High-temperature melting

(1) Low-melting point molten salt and SiO_2 nanoparticles were