International Journal of Thermal Sciences 91 (2015) 142–145

Contents lists available at ScienceDirect

International Journal of Thermal Sciences

journal homepage: www.elsevier.com/locate/ijts

Experimental investigation of the specific heat of a nitrate–alumina nanofluid for solar thermal energy storage systems

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ARTICLE INFO

Article history:
Received 11 March 2014
Received in revised form
15 January 2015
Accepted 16 January 2015
Available online 16 February 2015

Keywords:
Nanofluid
Specific heat
Thermal energy storage

ABSTRACT

We measured the change in specific heat of nitrate salt–alumina nanoparticle nanofluids at low nanoparticle concentration (less than 2% by mass) to understand how adding small amounts of nanoparticles affected this property. Alumina nanoparticles were dispersed in a eutectic of sodium nitrate and potassium nitrate (60:40 mole fraction) to create nanofluids using a two-step method. Neutron activation analysis was used to measure the actual mass fraction of the alumina nanoparticles in the nanofluids. The nominal mass fraction was always larger than the actual mass fraction, with differences up to 41%. The specific heat was measured using a modulated differential scanning calorimeter (MDSC). The results showed that there exists a parabolic relation between specific heat and mass fraction of alumina nanoparticles (maximum 30.6% enhancement at 0.78% actual mass fraction of alumina nanoparticles). The measurement uncertainty for the specific heat values was less than 4%. The stability of the specific heat values of the nanofluids was also examined; we found the nanoparticle concentration with the highest specific heat value shifted from 0.78% to 0.3% when the same samples were tested after one and two months.

1. Introduction

More efforts are being made to better use various sources of renewable energy, such as wind, hydroelectric power and solar. The main reasons for this effort are increasing energy demand, cost of traditional energy sources, and concerns with environmental contamination. For the past twenty years, solar energy has been considered to be one of the most promising renewable energy sources.

Thermal energy storage (TES) systems allow us to store the excess thermal energy collected during sunshine hours for later use during night hours or cloudy days. The most commonly used method of thermal energy storage is the sensible heat method, such as solar heating systems and night storage heaters. Compared to this method, the latent heat thermal energy storage system provides a much higher energy storage density with a smaller temperature change. However, due to its huge power scale, current thermal energy storage systems have very high costs.

Nitrate eutectics are one of the most widely used thermal energy storage materials in TES systems. Compared with water, which has a specific heat of 4.2 J/g K at room temperature, nitrate eutectic has a low specific heat of 1.55 J/g K. To enhance the utility of nitrate salts as a TES material, the thermal properties require improvement.

Since Choi and Eastman [1] proposed a new term called nanofluids, which are fluids with nanoparticles suspended in them, many experiments showed enhancement of the specific heats of nanofluids compared with the corresponding base fluids. Nelson [2] showed that the specific heat of a nanofluid was enhanced by as much as 50% by adding 0.6% mass fraction of exfoliated graphite nanoparticles in polyalphaolefin. Malik [3] demonstrated a 5.5% specific heat improvement with 10% mass fraction of Al_2O_3 and nitrate composite materials compared with the pure nitrate eutectic. Shin and Banerjee [4,5] measured the specific heat of Silica–Carbonate nanofluid and Silica–Chloride nanofluid. The experimental results showed a 19–24% enhancement of the specific heat of Silica–Carbonate nanofluid and 14.5% for Silica–Chloride nanofluid at a 1% mass fraction of SiO_2 nanoparticle in both. Betts [6] found that the specific heat of nanofluid with

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http://dx.doi.org/10.1016/j.ijthermalsci.2015.01.012

addition of 1% mass fraction of Al_2O_3 nanoparticle and 1% SiO_2 nanoparticle into nitrate eutectic were increased by 19% and 20%, respectively. Shankar [7] found the specific heat of the carbonate eutectic with alumina nanoparticles is enhanced even at very low concentration of the nanoparticles in the nanomaterial. However, contradictory investigations in the literature demonstrated degeneration in the specific heat of the fluids with the addition of nanoparticle. Both Zhou and Ni [8] and Namburu et al. [9] reported that the specific heat of their fluids decreased as the volumetric concentration of nanoparticles increased.

Because of this disagreement on the effects of nanoparticles, the primary objective of this study is to determine the effect of nanoparticle concentration on the thermophysical properties of a nitrate–alumina nanofluid. In this paper, the two-step method will be described in the nanofluid fabrication section, followed by the introduction of neutron activation analysis (NAA) and modulated differential scanning calorimeter (MDSC) in the experiments section. Then, the results will be presented and discussed and finally conclusions will be made.

2. Nanofluid fabrication

We used the two-step method to prepare the nitrate–alumina nanofluid. The Al_2O_3 nanoparticles have an average particle size of 40 nm and the nitrate eutectic was composed of high purity Sodium nitrate and Potassium nitrate salts (60:40 for mole fraction).

The protocol of the two-step method is as follows: The Al_2O_3 nanoparticle is mixed with nitrate for a specific mass fraction (in this case, the nominal mass fractions of Al_2O_3 nanoparticle are 0.125%, 0.25%, 0.5%, 0.75%, 1%, 1.5% and 2%). Then this mixture is dissolved in distilled water. The water solution is then mixed by an ultrasonic mixer for 2 h to obtain a homogeneous dispersion of the nanoparticles. Finally, the water in the solution evaporates on a hot plate at a temperature of 90 °C. The dried salt is then mechanically removed from the pan and stored in an argon glove box until it is used for MDSC measurements.

3. Experiments

Neutron activation analysis (NAA) was used to measure the actual Al_2O_3 nanoparticle mass fraction in the nanofluid fabricated by the two-step method. To measure the specific heat, we used a modulated differential scanning calorimeter (MDSC). After the sample was first tested, stability tests were conducted one and two months later, respectively.

3.1. Neutron activation analysis (NAA)

We used neutron activation analysis to determine the actual mass fraction of Al_2O_3 nanoparticle in the nanofluid. The analysis is based on neutron activation, requiring a source of neutrons. Due to the bombardment with neutrons, the aluminum in the sample creates a radioactive isotope, which decays and emits measureable radiation in the form of gamma rays. Then we can analyze the spectra of the emissions of gamma rays to determine the concentration of aluminum in the sample.

$$Al^{27} + n^1 \rightarrow Al^{28*} \quad \text{(Radioactive isotope of aluminum)}$$

$$Al^{28*} \rightarrow Al^{28} + \gamma \quad \text{(Radiation)}$$

The results of the tests give us the percentage of aluminum in the nitrate–aluminum nanofluid. From this, the mass fraction of the Al_2O_3 nanoparticles can be calculated from the elemental percentage concentration, using the formula:

$$\varphi_{Al_2O_3} = \frac{102}{54}\varphi_{Al} \tag{1}$$

3.2. Modulated differential scanning calorimeter (MDSC)

Differential scanning calorimetry (DSC) is an invaluable method of thermal analysis in the material sciences. More details are described in ASTM E1269, the standard test method for determining specific heat capacity by DSC [10]. In this study, the specific heats were measured using modulated differential scanning calorimetry, which is a recently developed extension of DSC. It uses a sinusoidal temperature oscillation instead of the traditional linear ramp, which provides the heat capacity of the sample and the heat flow at the same time.

In this investigation, the measurement is started at room temperature. The sample is then heated at the rate of 40 °C/min to 450 °C and cooled to 250 °C. The crucibles are then held at 250 °C for 10 min to allow the instrument to equilibrate at the starting temperature. Then the sample is heated to 450 °C at the rate of 2 °C/min. A final 10 min isothermal process is taken to ensure the crucibles equilibrate at the upper temperature of interest. A measuring temperature range of 250–450 °C is selected because it brackets the 290–390 °C operating range of most parabolic trough concentrating solar power plants. Additionally, this thermal profile avoids the nitrate melting and decomposition temperatures. The single thermal profile is repeated three times for each run in order to decrease experimental uncertainty. After three repeats, the sample is finally cooled to room temperature.

3.3. Stability test

After the samples were used for the first round test, they were cooled down into the solid phase and stored in an argon glove box at room temperature. One and two months later, they were tested again with the same thermal profile in MDSC.

4. Results and discussion

We used the two-step method to synthesize nanofluids with nominal Al_2O_3 nanoparticle mass fractions of 0.125%, 0.25%, 0.5%, 0.75%, 1%, 1.5% and 2%. We measured the actual Al_2O_3 nanoparticle mass fraction from NAA and specific heat from MDSC.

4.1. NAA

We measured the actual mass fraction values of aluminum in the nanofluid using NAA. By using Eq. (1), we calculated the actual mass fraction of alumina. For each nanofluid with a nominal mass fraction of alumina, we did three separate NAA tests. As shown in Table 1, nominal mass fraction of alumina,

Table 1
Actual mass fraction of alumina nanoparticle from NAA.

$\varphi_{Al_2O_3}$ (%)	φ'_{Al} (%)	$\varphi'_{Al_2O_3}$ (%)	STDEV	Difference between $\varphi_{Al_2O_3}$ (%) and $\varphi'_{Al_2O_3}$ (%)
0	0	0	0	0
0.125	0.05	0.09	0.011	−28.0
0.25	0.09	0.17	0.004	−36.0
0.50	0.16	0.30	0.032	−40.0
0.75	0.28	0.53	0.039	−29.3
1	0.41	0.78	0.059	−23.0
1.5	0.51	0.96	0.171	−36.0
2	0.63	1.19	0.120	−40.5