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Synthesis and thermal stability of Field's alloy nanoparticles and nanofluid

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ABSTRACT

This paper describes a facile one-step method for synthesizing Field's alloy nanoparticles based on nanoemulsification technique. As-prepared Field's alloy nanoparticles were characterized by X-ray fluorescence spectrometry (XRF), and transmission electron microscopy (TEM). Reaction time influence on particle shape and size were also investigated. The thermal stability of nanoparticles and nanofluid (with ethyl carbamate modified Field's alloy nanoparticles dispersed in PAO) were evaluated by differential scanning calorimetry (DSC). Results show that the nanofluid exhibit good thermal stability, which may have potential applications in wide area.

1. Introduction

Phase change materials (PCMs) are a kind of substance that will absorb or release heat energy during the melting and freezing process. This property of PCMs can be used in a number of ways, such as thermal energy storage [1,2], solar heating systems [3], thermal insulation [4], and bio-detection [5]. More significantly, single liquid phase with the dispersion of solid nanoscale phase change materials (nano-PCMs), also called nanofluid, have aroused widespread concern by the research community as alternate coolants for heat transfer applications, such as thermal protection of electronic device [6], cooling of engines [7], and other systems requiring high heat transfer rates [8].

Basing on their applications, the type of PCMs is chosen according to their melting temperature. Currently, most of the developed PCMs focus on low temperature applications, so synthesis and improvement of properties and functionality of low melting point PCMs is critical to their adoption. Although we have some choices for those low melting point PCMs, such as paraffin, fatty acids, esters, polyethylene, and salt hydrates, those low melting point PCMs suffer from their low thermal conductivity and limit their wide applications. For many low melting point metals, such as In, Bi, Sn, Pb and their eutectics, their conductivity is at least two orders higher than that of inorganic PCMs, as well as comparable latent heat density and other thermal properties, making low melting point metals or eutectic alloys highly attractive PCMs. Besides, because of the disadvantages of liquid suspensions of large particles, such as easy to settle out and block the pipeline, the method of enhancing the heat capacity by adding PCMs is more preferred in nanoscale. The fast development of nanotechnologies provides an alternative way to avoid those disadvantages. A large number of nano-PCMs have been synthesized through different synthetic methods [9–11]. The outstanding features of nano-PCMs, such as small size, large surface area to volume ratio, and high mobility, make nanoparticles feasibly be well dispersed into heat transfer fluids, such as water, poly-alpha-olefin (PAO), glycols, hydrocarbons, and fluorocarbons, with surfactant to stabilize the nanoparticles suspension.

Herein, we describe a facile one-step method for producing Field's alloy nanoparticles by using nanoemulsification technique. Field's alloy is a eutectic alloy that becomes liquid at approximately 62 °C (144 °F) and with the weight percentage of 32.5% bismuth (Bi), 51% indium (In), and 16.5% tin (Sn). The composition, size and morphologies of the Field's alloy nanoparticles are characterized by X-ray fluorescence spectroscopy (XRF) and transmission electron microscopy (TEM), respectively. The thermal stability of nanoparticles and nanofluid (ethyl carbamate modified Field's alloy nanoparticles dispersed in PAO) are investigated by differential scanning calorimetry (DSC).

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2. Experimental section

2.1. Preparation of Field's alloy nanoparticles and nanofluid

The Field's alloy nanoparticles are synthesized by using nanoemulsification method. The illustrated nanoemulsion formation process in our experiment is shown in Fig. 1. The Field's alloy nanoparticles are harvested by centrifuge and re-dispersed into the organic solvent to make nanofluid with different concentration. Typically, 0.5g Field's alloy small pellet (RotoMetal, San Leandro, CA) and excess ethyl carbamate (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) as surfactant was added to 50 ml PAO oil (eCompressedair, Westfield, MA) in a three neck glass vessel, and then the mixture was heated up to certain temperature (50, 70, 100, 150, and 180 °C) assisted with as silicone oil thermal bath. The mixture was stirring with a magnet stirrer bar at 800r/min for 2-20hrs under 50-180 °C to make micro or nanoscale Field's alloy droplets. Once the reaction completes, the as-prepared particles are collected by centrifuge, and then washed thoroughly with acetone at least three times to remove excess surfactant and then dried or dispersed in PAO to make the nanofluid for ready to use.

2.2. XRF measurement

The compositions of bulk Field's alloy or as-prepared Field's alloy nanoparticles are derived with XRF spectrum, which is collected from a Mini-X system that using a Mini X-ray tube (Amptek, 40 kV, 100μA) and a solid state X-ray spectrometer detector (Amptek 123, reflection mode). The whole setup is enclosed in a lead containing acrylic chamber with 1 mm of lead equivalent thickness. Background spectra are obtained using an aluminum plate without nanoparticles.

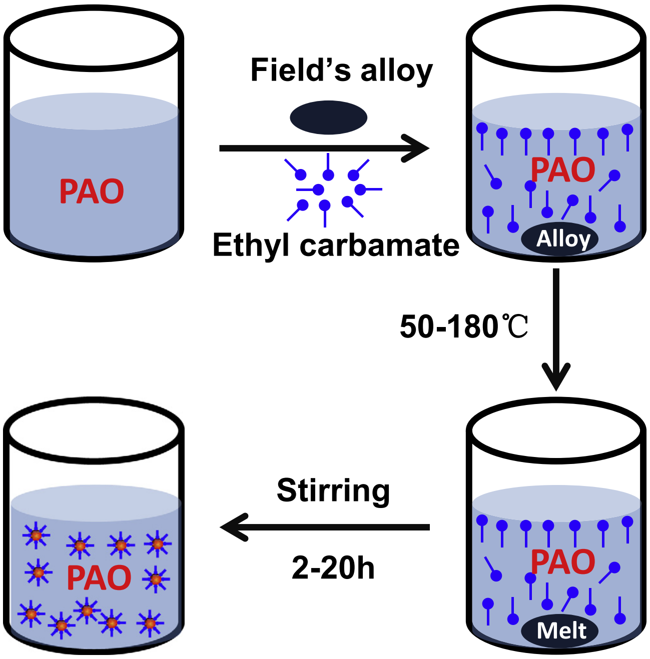

Fig. 1. Schematic illustrating the production of molten Field's alloy nanoparticles in PAO oil nanoemulsion. (a) PAO and molten Field's alloys are in the reaction vessel. These two liquids are immiscible and phase separate; (b) Polymer surfactant (ethyl carbamate) is soluble in PAO; (c) The mixture is heated up to certain temperature and the bulk molten alloy formed; (d) The microscale emulsion is stirred and breaks into microscale droplets until nanoemulsion is formed.

2.3. Characterization

The size and morphologies of the as-prepared Field's alloy nanoparticles are characterized by Transmission electron microscopy (TEM, JEOL 1011, accelerating voltage, 100 kV). For preparing the TEM samples, a droplet of nanoparticles dispersed in ethanol is dropped onto a carbon film coated copper grid. A differential scanning calorimeter (DSC3+, METTLER TOLEDO) is used to measure the thermal stability of Field's alloy nanoparticles and nanofluid, where a sample of 5 mg nanoparticles or 20 μL nanofluid is hermetically sealed in an aluminum pan and placed in DSC chamber with continuously purged nitrogen gas at heating rate of 5 °C/min scanning from 25 °C to 100 °C.

2.4. Results and discussion

The size and morphologies of as-prepared Field's alloy particles are characterized by TEM. Fig. 2A, B shows the TEM images of synthesized Field's alloy particles after boiling the Field's alloy pellets in PAO with excess surfactant of ethyl carbamate at 180 °C for 10 min (Fig. 2A) and 2 h (Fig. 2B), respectively. As the reaction time increases, the size of particles will decrease and become more spherical. After 10 min, the particles have irregular shapes with the size of 200 to 500 nm. 2 h later, they show spherical shapes with the size of about 20 nm. Fig. 2C shows the plot of reaction time with reaction temperature at 180 °C versus the size of particles. After 2 h, even though the reaction time increase (such as 5hrs, 10hrs, or even 20hrs), the particles size didn't change too much, which is also close to 20 nm. It is noted that the data for particles size (as shown in Fig. 2C) are extracted from those TEM images using Image Pro Plus software.

The composition of as-prepared Field's alloy nanoparticles is derived by XRF. As shown in Fig. 3A, no obvious difference is observed between the composition of the bulk Field's alloy materials and synthesized nanoparticles, which suggests that no phase separation happens during synthesis process. It also shows that $L_{\alpha1}$, $K_{\alpha1}$ and $K_{\alpha2}$ of indium at 3.29, 24.21, and 27.27 keV, $L_{\alpha1}$, $L_{\beta1}$ of bismuth at 10.84, 13.02KeV, $K_{\alpha1}$ of tin at 25.27 keV can be seen clearly. DSC was used to measure the thermal properties of as-prepared nanoparticles. Fig. 3B shows the DSC curves of bulk Field's alloy pellets and corresponding nanoparticles synthesized at different temperatures (50 °C, 70 °C, 100 °C, 150 °C, and 180 °C) with other experimental conditions unchanged. For melting peaks of those samples, the peak position and shape is close and similar to the bulk Field's alloy, where all of the samples are melt at about 62.5 °C. However, for freezing peaks, it shows different characteristics for those particles synthesized at different temperature. As the temperature increases, the freezing peak position will decrease and become more and more broaden. For example, the bulk Field's alloy is freezing at 55.2 °C, the nanoparticles synthesized at 50 °C for 2 h, 70 °C for 2 h, 100 °C for 2 h, 150 °C for 2 h, 180 °C for 2 h, and 180 °C for 20 h is at 55.2 °C, 53.9 °C, 52.5 °C, 43.4 °C, 32.6 °C, 32.6 °C, respectively. Comparing DSC curves of those samples under different temperature, the temperature-dependent freezing depressing is observed.

The thermal stability of ethyl carbamate modified Field's alloy nanoparticles and PAO nanofluids (Field's alloy nanoparticles dispersed in PAO) had been investigated using a DSC. Fig. 4A shows the cyclic DSC heating and cooling curves of Field's alloy nanoparticles in ambient and N_2 atmosphere with the ramp rate of 5 °C/min. The two DSC curves are almost the same, suggesting the synthesized nanoparticles are stable in ambient condition. Fig. 4B illustrates the DSC curves (including melting and freezing processes) of Field's alloy nanoparticles after running for 1st, 5th, 10th, 15th, 20th times, where shows all of the DSC curves are overlapped together. It is suggesting that the nanoparticles are stable in