Applied Thermal Engineering 124 (2017) 533–538

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research Paper

Investigation of specific heat and latent heat enhancement in hydrate salt based TiO_2 nanofluid phase change material

Yushi Liu, Yingzi Yang *

Key Lab of Structures Dynamic Behavior and Control (Harbin Institute of Technology), Ministry of Education, Harbin 150090, Heilongjiang, China
School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, Heilongjiang, China

HIGHLIGHTS

- Hydrate salt based TiO_2-P25 nanofluid PCM (EHS/TiO_2-P25) was prepared.
- EHS/TiO_2-P25 is an efficient approach to improve the specific heat and latent heat.
- Explanation on increase of solid specific heat is aided by the optical microscopy.
- The interaction between EHS and TiO_2-P25 is revealed by Raman spectra.
- Chemical thermodynamics offers a theoretical analysis for latent heat enhancement.

ARTICLE INFO

Article history:
Received 12 December 2016
Revised 30 April 2017
Accepted 27 May 2017
Available online 29 May 2017

Keywords:
Hydrate salt
Nanofluid
TiO_2 nanoparticles
Specific heat
Latent heat

ABSTRACT

In this study, the enhancements of specific heat and latent heat of inorganic hydrate salt based nanofluid phase change material were reported. The samples were prepared by incorporating TiO_2 nanoparticles with different mass fractions (0.1, 0.3, and 0.5 wt%) into the eutectic hydrate salt (EHS). The phase change enthalpy and specific heat capacity were measured by differential scanning calorimeter (DSC). The results showed that the loading of 0.3 wt% TiO_2 nanoparticles can increase specific heat by up to 83.5% and latent heat up to 6.4%. Moreover, the optical microscopy on crystal configuration confirmed the increase of solid specific heat and the corresponding mechanism. The interaction between EHS and TiO_2 nanoparticles, which was responsible for elevation of phase change temperature, was revealed by Raman spectra. The chemical thermodynamics gave an explanation for latent heat improvement. These findings suggested that hydrate salt based TiO_2 nanofluid offered a promising route for the achievement of high heat energy storage targets of hydrate salt phase change materials.

1. Introduction

The solid-liquid phase change material (PCMs), which can be used for thermal energy storage by absorbing and releasing heat energy during the phase transition process, have attracted much attention over the past few decades. PCMs are used in a variety of applications including building thermal comfort, solar energy conversion and industrial waste heat recovery [1–3].

Remarkably, among the large number of PCMs, inorganic hydrate salts PCMs have recently gained considerable importance in the utilization of energy because of the advantages of nontoxicity, non-flammability, low cost, etc. [4,5]. Also, hydrate salts exhibit relatively higher heat storage capacity compared with organic PCMs [5]. However, one of the primary limitations of traditional PCMs including hydrate salts is still the unsatisfactory heat storage capacity [4]. Heat energy storage of PCMs can be divided into two parts, sensible heat and latent heat [6]. The sensible heat is determined by specific heat of PCMs, and the latent heat corresponds to the fusion enthalpy. Almost all of hydrate salts have very low specific heat capacity, and the volume and cost of energy storage system will increase when the PCMs with low specific heat are applied [7]. Some efforts have been done to compensate for the low specific heat of PCMs. One method is to incorporate small quantities of nanoparticles into PCMs to enhance the specific heat. The stable colloidal suspensions by suspending minute concentrations of nanoparticles into liquid matrix are termed as "nanofluids" [8]. Pan et al. [9] found a considerable enhancement of 19.9% of the specific heat capacity by dispersing 0.063 wt% of alumina nanopar-

* Corresponding author at: Key Lab of Structures Dynamic Behavior and Control (Harbin Institute of Technology), Ministry of Education, Harbin 150090, Heilongjiang, China; School of Civil Engineering, Harbin Institute of Technology, Harbin 150090, Heilongjiang, China.

E-mail address: yzyang@hit.edu.cn (Y. Yang).

http://dx.doi.org/10.1016/j.applthermaleng.2017.05.150
1359-4311/© 2017 Published by Elsevier Ltd.

Nomenclature

T_m	phase change temperature	n_w	amount of substance of third component W
μ_w	chemical potential of third component W	G_1	Gibbs free energy of multicomponent system
G_0	Gibbs free energy of single system	S_1	entropy of multicomponent system
S_0	entropy of single system	T_1	temperature of multicomponent system
T_0	temperature of single system	V_1	volume of multicomponent system
V_0	volume of single system	P_1	pressure of multicomponent system
P_0	pressure of single system	H_1	enthalpy of multicomponent system
H_0	enthalpy of single system		
d	differential law		
ΔH_m	latent heat		

ticles into molten Hitec salt; Shin and Banerjee [10] observed that the dispersion of silica nanoparticles of 1.0 wt% in alkali metal chloride salt eutectics increased its specific heat capacity by 14.5%; Chieruzzi et al. [11] reported specific heat capacity in the $NaNO_3$-KNO_3 binary salt doped with 1.0 wt% of a mix of silica-alumina, which was 57% above that of the base salt; Also, in view of the specific heat capacity enhancement in molten salts based nanofluids, the phenomenological models were put forward [12]. However, to date, the specific heat enhancements in nanofluids have been attempted mostly for the molten salts as high-temperature PCMs. Thus, it is urged to perform a study on the specific heat of inorganic hydrate salt based nanofluid PCM. This work performs a specific heat enhancement of hydrate salt nanofluid, and the corresponding mechanism is explained.

Note that the latent heat of hydrate salts also plays a vital role in thermal energy storage. Nevertheless, apart from a few paper concerning the increase of latent heat of organic PCM based nanofluid, e.g., the carbon nanoadditives to enhance latent heat of paraffin wax PCM and its mechanism [13,14]; the latent heat of paraffin was increased when mixed with exfoliated graphite nanoplatelets (xGnP) at 1.0% by weight [15], there are little reports on the latent heat improvement of inorganic hydrate salt based nanofluids. Therefore, it's quite necessary to investigate the influence of nanoparticles on latent heat of hydrate salt.

The main purpose of the present work is to demonstrate the increment of specific heat and latent heat in the hydrate salt based nanofluid and disclose the specific effects of the nanoparticles with different mass loadings on thermal properties of hydrate salt PCM. In this study, Titania nanoparticles (TiO_2-P25) with an average size of about 21 nm were chosen as the nanoparticle fillers; $Na_2CO_3\cdot10H_2O$-$Na_2HPO_4\cdot12H_2O$ eutectic hydrate salt (EHS) with melting temperature of 27.3 °C/no phase separation (which was developed in our previous work [16]) was adopted as the control hydrate salt PCM. The hydrate salt based TiO_2 nanofluid PCM was prepared by doping EHS with minute amount of TiO_2-P25 nanoparticles (0.1, 0.3, and 0.5 wt%). The DSC method was used to investigate the specific heat and latent heat of TiO_2 nanofluid PCM. The mechanism analysis was presented to explain the change of specific heat capacity by referring to the crystal configuration characterized by optical microscopy (OM). Moreover, the theory of chemical thermodynamics was applied in this paper to interpret the latent heat improvement of TiO_2 nanofluid PCM.

2. Materials and methods

2.1. Materials

Disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4\cdot12H_2O$, purity > 99%) and sodium carbonate decahydrate ($Na_2CO_3\cdot10H_2O$, AR) were adopted as inorganic hydrated salts PCMs; Titania nanoparticles (TiO_2-P25) containing 80% anatase and 20% rutile with an average size of about 21 nm were provided by Degussa Co. (Germany). All reagents were used as received.

2.2. Synthesis of hydrate salt based TiO_2-P25 nanofluid PCM (EHS/TiO_2-P25)

The $Na_2CO_3\cdot10H_2O$-$Na_2HPO_4\cdot12H_2O$ eutectic hydrate salt (EHS) was prepared according to the method provided by Ref. [16]. The mass ratio of $Na_2CO_3\cdot10H_2O$ and $Na_2HPO_4\cdot12H_2O$ is 40:60. The EHS solution was placed into the beaker and kept at 55 °C in thermostated water bath. Then a certain amount of TiO_2-P25 nanoparticles (0.1 wt%, 0.3 wt% and 0.5 wt%) were added to the solution and stirred at 1500 rpm for 2 h. Subsequently, all the suspensions were ultrasonicated for 30 min at 120 W to obtain the final products.

2.3. Characterization

Differential Scanning Calorimetry (DSC, NETZSCH, 200F3) was used to evaluate the specific heat and latent heat of samples. The scanning rate was 5 °C/min. According to ASTM E1269-11 [17], the sapphire was chosen as a heat flow calibration standard for the measurement of specific heat capacity due to its excellent thermal stability and available specific heat capacity literature values as a function of temperature. The X-ray diffraction (XRD) patterns of the samples were recorded on an X-ray diffractometer (PANalytical B.V., Empyrean, Cu Ka radiation). Raman spectra were collected on a Renishaw inVia Raman microscope (Renishaw Corporation, Britain) with an argon-ion laser (532.0 nm) as the source. The crystallography features of samples were observed using the optical microscopy (OM, OLYMPUS, DSX 500). The apparent viscosities of nanofluids were measured using a Brookfield DV-II + Pro Viscometer. The viscosity determinations were performed in triplicate at 40 °C for each nanofluid, and the data were presented as the mean ± standard deviation (SD).

3. Results and discussion

Fig. 1A shows the morphology of TiO_2-P25, indicating that raw TiO_2-P25 nanoparticles are basically granular and their sizes range from 15 nm to 35 nm. The FTIR spectrum of TiO_2-P25 shown in Fig. 1B suggests the presence of hydroxyl groups (ν O—H at approximately 3390 cm^{-1}, δ O—H at 1609 cm^{-1}), that should belong to Ti—OH bonds. The peak at 665 cm^{-1} is attributed to the vibration of Ti—O [18]. Since the melted EHS is an aqueous electrolyte solution, and that the hydrophilicity of TiO_2-P25 nanoparticles is given by its abundant surface hydroxyl, the EHS/TiO_2-P25 nanofluid suspensions, with 0.1, 0.3 and 0.5 wt% TiO_2-P25, exhibit good stability after 12 h of standing and 100 thermal cycles by visual observation, as shown in Fig. 1C. However, in order to further demonstrate the stability of EHS/TiO_2-P25 nanofluid suspensions, the rheological