Heat transfer during melting of graphene-based composite phase change materials heated from below

CrossMark

Li-Wu Fan [a,b,*], Zi-Qin Zhu [a], Yi Zeng [c], Qian Lu [d], Zi-Tao Yu [a,b]

[a] Institute of Thermal Science and Power Systems, Department of Energy Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China
[b] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, People's Republic of China
[c] Department of Mechanical Engineering, Auburn University, Auburn, AL 36849, United States
[d] Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

ARTICLE INFO

ABSTRACT

Transient heat transfer during melting of graphene-based composite PCMs heated from below was investigated experimentally. Composite PCMs filled with graphene nanoplatelets (GNPs) were prepared at various loadings up to 3% by weight. The thermal conductivity, dynamic viscosity and latent heat of fusion of the composite PCMs were measured. A variety of boundary temperatures were also adopted to vary the intensity of natural convection. It was shown that when the boundary temperature is 55 °C, melting is accelerated by 8% at the highest loading of 3 wt.% GNPs due to the doubled thermal conductivity of the composite PCM as compared to that of the base PCM. Increasing the boundary temperature leads to more intensive natural convection that in turn slows down melting because the contribution by natural convection is significantly suppressed by the dramatically grown dynamic viscosity, e.g., 10-fold increase at the loading of 3 wt.%. The melting rate is determined by competition between the enhanced heat conduction and deteriorated natural convection. In addition, both the melt fraction and heat transfer were correlated to dimensionless groupings that govern this problem. Universal correlations that are valid for the entire ranges of the parameters investigated were proposed with an uncertainty below 20%.

1. Introduction

Heat transfer during solid–liquid phase change, i.e., melting and solidification, has long been studied with applications to thermal energy storage (TES) by means of phase change materials (PCMs) [1]. Heat transfer enhancement, often realized by increase of the effective thermal conductivity of PCMs [2], is of theoretical interest as well as of practical significance toward performance promotion of TES systems. The use of composite PCMs filled with highly-conductive nanostructured materials has been proposed as a novel alternative for thermal conductivity enhancement of PCMs [3]. The performance of TES systems employing composite PCMs with increased thermal conductivity has been tested on various combinations of the base PCMs and nanofillers [4–9], with an emphasis on the melting/solidification heat transfer characteristics at system level.

In the presence of composite PCMs, revisit of melting/solidification problems with classical geometric and thermal boundary conditions has attracted increased attention. By neglecting thermal convection effect, solidification of composite PCMs has been modeled analytically and numerically within a pure heat conduction framework [10–15]. Experimental results have revealed that unidirectional solidification of composite PCMs is accelerated in proportional to the increased thermal conductivity [12,13], suggesting that the homogenous assumption with effective thermophysical properties, predicted by simple mixture theory or empirical correlations, may be valid for modeling heat transfer of composite PCMs disregarding the instability issue in practice. Nevertheless, the dynamics of nanoparticles during solidification and their interactions with the moving solid–liquid interface have been studied analytically by considering transport of nanoparticles by an extended Stefan problem formulation [14,15].

Accompanied by the presence of strong thermal convection effect, melting is usually not pertinent to be considered a pure heat conduction problem. Indeed, convection often occurs and dominates melting with the implication that the increased viscosity of composite PCMs may play an important role in addition to the

---

* Corresponding author at: Institute of Thermal Science and Power Systems, Department of Energy Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China. Tel./fax: +86 571 87952378.
E-mail address: liwufan@zju.edu.cn (L.-W. Fan).

Nomenclature

a, b, c	constants in correlations
A	area (m^2)
C_p	specific heat capacity (kJ/kg K)
d	distance (mm)
f	mass fraction of molten PCM
Fo	Fourier number
g	gravitational acceleration (m/s^2)
H	height (m)
k	thermal conductivity (W/m K)
L	latent heat of fusion (kJ/kg)
m	mass of molten PCM
M	total mass of PCM
Nu	Nusselt number
Nu^*	modified Nusselt number
Q	total heat (J)
q''	heat flux (W/m^2)
Ra	Rayleigh number
Ste	Stefan number
t	time (s)
T	temperature (°C)

Greek symbols

β	thermal expansion coefficient (1/K)
δ	measurement error
ϕ	loading of the GNPs (wt.% or vol.%)
μ	dynamic viscosity (mPa s)
ρ	density (kg/m^3)
τ	elapsed time period (s)

Subscripts

1–5	notation of different thermocouple locations
b	bottom
GNP	graphene nanoplatelets
i	initial condition
L	liquid phase
m	melting
PCM	phase change materials
S	solid phase
vol	volume fraction
wt	mass (weight) fraction

thermal conductivity enhancement. Under the homogeneous assumption, melting of composite PCMs, reflecting charging process of TES systems, has been studied numerically [16–18]. Unlike the solidification problem, larger disagreement has been demonstrated between the experimental and numerically predicted results of melting of composite PCMs [19–22]. The primary reason for such discrepancy has been identified to be the adoption of unreliable effective thermophysical property data of composite PCMs, especially the viscosity, in the modeling that depart greatly from the measured values [23]. It is, however, suggested that the homogeneous assumption may still be used for modeling melting of composite PCMs as long as the actual effective thermophysical properties are adopted [23].

In the above-mentioned few recent experimental studies of melting of composite PCMs, metal oxide nanoparticles and carbon nanotubes (CNTs) have been employed as the nanofillers. It is understood that carbon-based nanomaterials, such as CNTs, are sound filler materials due to their inherently high thermal conductivity and low density. The filler-induced alignment of the PCM molecules, paraffin for example, has been identified to contribute to the pronounced thermal conductivity increase of CNTs [24]. The dramatic increase of viscosity associated with CNT-based composite PCMs, however, has been realized to be undesirable because the weakened convection effect may compensate or even offset the enhanced heat conduction due to thermal conductivity enhancement. The emerging family of two-dimensional planar carbon nanomaterials, i.e., graphene and its derivatives outperforms significantly CNTs in enhancing the thermal conductivity of composite PCMs due to their geometry-induced low filler-matrix thermal interface resistance [25,26] as well as more significant filler clustering effect that has been identified as the main heat conduction mechanisms [27,28]. In contrast to the superior thermal conductivity enhancement, however, graphene materials lead to much lower viscosity increase than that of CNTs as a result of their particular planar structure enabling inter-particle sliding and alignment [25]. Due to these advantages, the family of graphene materials, from monolayer graphene, few-layer graphene nanosheets, to exfoliated graphite/graphene nanoplatelets (GNPs), have recently been the subject of a number of investigations toward preparation and application of high-performance composite PCMs for TES [29–38]. There is, however, so far a lack of examination on melting

heat transfer of such emerging graphene-based composite PCMs, although their thermophysical properties have been extensively characterized and documented.

In this study, a classical configuration for melting heat transfer will be considered where the PCM is heated from the bottom [39]. Graphene-based composite PCMs will be prepared and tested at various loadings. A detailed heat transfer analysis will be performed by correlating to pertinent dimensionless groupings governing this problem.

2. Experimental

2.1. Preparation and characterization of graphene-based composite PCMs

A straight-chain saturated fatty alcohol, i.e., 1-tetradecanol ($C_{14}H_{30}O$), with a nominal melting point (T_m) of 37 °C was adopted as the base PCM, while commercially-available GNPs, the same as those adopted by Fang et al. [37], with a specified in-plane diameter of 5–10 μm and a thickness of 4–20 nm were used as the nanofillers. The two-step protocol employed by Fang et al. [37] was also followed for preparing the graphene-based composite PCM samples. During the preparation process, an outstanding difference in the present study lies in the utilization of a commercial dispersant, from the same supplier of the GNPs, that was used at equal amounts by weight to the GNPs. This polymeric dispersant helped improve dispersion and long-term stability of the composite PCMs.

Composite PCM samples with three different loadings (by weight) of the GNPs, i.e., 0.5 wt.%, 1 wt.% and 3 wt.%, were prepared and then subjected to melting heat transfer tests as well as a variety of microscopic characterizations. Higher loadings were not attempted due to stability concern. As described by Fang et al. [37], the size and thickness of the pristine GNPs and their distribution after being dispersed into the base PCM were examined by various microscopes. As similar results were obtained, the observations in this study are not presented and one may refer to the literature for details [37]. In addition, rigorous long-term stability tests of the composite PCM samples were performed by visually inspecting the precipitation of the GNPs subjected to consecutive