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Microencapsulation of eutectic and hyper-eutectic Al-Si alloy as phase change materials for high-temperature thermal energy storage

Takahiro Nomura[a,*], Julalak Yoolerd[b], Nan Sheng[a], Hiroki Sakai[b], Yuta Hasegawa[b], Miki Haga[b], Genki Saito[a], Tomohiro Akiyama[a]

[a] Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan
[b] Graduate school of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan

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ABSTRACT

Thermal energy storage using phase change materials (PCMs) has been world-widely accepted as an effective technology for energy saving. In this study, Micro-Encapsulated PCMs (MEPCMs) were developed from Al-Si alloys, in which four kinds of Al-Si microspheres with different Al-Si compositions: Al-12%Si, Al-17%Si, Al-20% Si, and Al-30%Si (mass%) were encapsulated by two facile steps for controlling heat storage property. First, boehmite film was formed over the Al-Si microspheres as a precursor shell during boiling in distilled water. Subsequently, the boehmite-coated particles were oxidized by pure oxygen at the high temperatures to ensure the formation of a stable Al_2O_3 shell. Three different temperatures, 1100 °C, 1150 °C, and 1200 °C, were chosen to study the effect of temperature on the product; the shell morphology, structure, and latent heat storage capacity. Interestingly, the results revealed an increase in MEPCM thermal storage capacity with decreasing Si content and lowering the temperature. The MEPCM melting point was almost identical to its eutectic temperature at ~577 °C, in contrast the larger supercooling was observed for samples with the higher Si content. The cyclic durability of MEPCM was also evaluated through repeated heating and cooling processes in air. The obtained results showed no significant change in both MEPCM structure and thermal storage capacity. It indicated a good repetition durability of MEPCMs oxidized at high temperatures. In conclusion, the Al-Si microencapsulated PCMs appealed great potential as MEPCMs for use in high-temperature thermal energy applications.

1. Introduction

In recent years, latent heat storage systems using phase change materials (PCMs) have been extensively investigated for their potential in advanced thermal energy storage technology. As a result, they have received great attention as an alternative to sensible heat storage (SHS) [1–3], which is the most common way to retain energy. In latent heat storage systems, heat is stored when the material undergoes melting, and is released when the material undergoes solidification. For the same heat storage capacity, heat storage and the release of PCMs occur within a narrow temperature range, whereas SHS operates in a comparatively wider temperature range. Moreover, PCMs exhibit other advantages such as high-energy storage density, compactness, and reusability. Thus, PCMs are prominent for use in various areas such as space heating [4–8], concentrated solar power [7–13], textile materials [14,15], and waste heat recovery [16–19].

Extensive research has demonstrated that compared to conventional PCMs such as paraffin, metal-based PCMs exhibit better performance and are more suitable for application to thermal energy storage. This was attributed to their high melting temperature, high heat storage density, and high thermal conductivity. There have been several reports on the great capabilities of metallic PCMs used for thermal energy storage application. For example, P. Blanco-Rodríguez et al. [20] reported the high suitability of Mg-51%Zn alloy PCM for direct steam generation in concentrated solar power application because of its thermal diffusivity, heat capacity, and energy density. E. Risueñoa et al. [21] studied the thermophysical properties of Al-70%Mg-24.9%Zn and Al-6%Mg-85.8%Zn and confirmed their good thermal stability, suitable for long-term usage G. Nardin et al. [17] proposed highly efficient energy recovery using Al as a PCM in the electric arc furnace process employed in the steel industry. X. Wang et al. [22] reported that an Al-12%Si phase change storage heater provides far superior thermal performance than a Fe_3O_4 sensible heat storage heater. Moreover, the high heat storage ratio and small size of the developed phase change heater

* Corresponding author.
E-mail address: nms-tropy@eng.hokudai.ac.jp (T. Nomura).

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make it more economically feasible for space heating applications.

Although metallic PCMs display an outstanding heat storage performance, especially in high-temperature applications, the leakage of melted PCMs during heat storage and the high corrosive nature of the metal are of major concern. The microencapsulation of PCMs is a promising solution to overcome these problems since PCMs can be perfectly isolated in suitable containers. This technique makes PCMs easier to handle, improves their thermal properties by increasing the heat transfer area, avoids interaction with the surrounding environment, and allows the combination of PCMs with other materials to create a composite material.

Many literatures comprehensively review preparation methods, capsule shell properties and applications of microencapsulated PCMs (MEPCMs) [23–30]. Moreover, melting temperature and latent heat storage capacity of MEPCMs developed in recent year have been surveyed in our previous study [35]. The survey clearly demonstrated that most of studies deal with low temperature MEPCM, especially lower than 100 °C, but few reports on the synthesis of high-temperature MEPCMs are available to date. The need for the development of high-temperature MPCMs has been raised to support high-temperature applications [31–33] such as solar power and industrial exhaust heat utilization.

The successful preparation of an Al-25mass%Si-based MEPCM (melting temperature T_m = 577 °C) with high thermal durability to achieve the microencapsulation of high-temperature PCMs has been reported in our previous studies [34,35]. PCM core-ceramic shell microspheres containing internal small voids were developed by boehmite coating followed by heat oxidation treatment at high temperatures. Latent heat storage capacity of the developed MEPCM, 233–247 J g^{-1}, is quite large in comparison with the value reported in previous literatures. These studies strongly indicate the great possibility of Al-Si MEPCM for high-temperature applications.

Considering a phase diagram of Al–Si system, Al-25mass%Si, which is a hyper eutectic composition, would not be the most suitable composition from viewpoint of latent heat storage capacity at eutectic temperature. Remarkable improvement of heat storage ability of Al-Si based MEPCM is expected by using a sample with the composition being close to eutectic. On the other hand, it would be difficult to achieve microencapsulation using lower Si concentration of Al-Si alloy as a raw material because lower Si concentration brings higher volume expansion ratio of a Al-Si alloy during solid to liquid phase changing. Therefore, this work investigated Al-Si alloys with various Si contents (%) for use in MEPCM development. The main objectives of this study were to reveal the effect of the Si content in the PCM core on thermal storage ability of MEPCM to suggest the optimum composition of Al-Si PCM and to reveal the effect of heat oxidation treatment temperature on cyclic performance of the developed MEPCM.

2. Materials and methods

2.1. Preparation of MEPCMs

The four compositions of commercial Al-Si microspheres (Hikari Material Industry Co. Ltd.), Al-12mass%Si (mean particle size, D_m: 44 μm), Al-17mass%Si (D_m: 29 μm), Al- 20mass%Si (D_m: 29 μm), and Al-30mass%Si (D_m: 37 μm) were chosen as raw materials for MEPCM synthesis in this study. The encapsulation of Al-Si microspheres was prepared in two steps consisting of boehmite coating and heat oxidation treatment as purposed in a previous study [34,35]. Initially, the Al-Si micro-particles were boiled in distilled water at 100 °C for 3 h and a boehmite film formed over the particle surface as the hydrolysis reaction proceeded. Next, the sample was filtrated and dried at 100 °C overnight. Subsequently, the boehmite-coated microspheres were introduced to the heat oxidation treatment step. A 100 mg sample was placed into an Al_2O_3 crucible and heated from room temperature to different constant temperatures (1100 °C, 1150 °C, and 1200 °C) at a heating rate of 10 °C min^{-1}. The temperature was maintained at the set temperature for 3 h before cooling down to room temperature at a cooling rate of 50 °C min^{-1}. The heat oxidation treatment was performed on a thermobalance-apparatus (METTLER TOLEDO TG-DSC-1) under an O_2 (99.5% purity) flow of 200 mL min^{-1}. For simplicity, hereafter, the synthesized MEPCMs are labeled as MEPCM-AlxSi where "x" is the mass% Si content in the raw material. Additionally, to indicate the temperature employed in the heat oxidation treatment, the temperature follows the labeled name. For example, MEPCM prepared from Al-12mass%Si oxidized at 1100 °C will be referred to as MEPCM-Al12Si-1100.

2.2. Characterization

The morphology and surface structure of the synthesized MEPCMs were characterized by scanning electron microscopy (SEM, JEOL, JSM-7001FA). The element distribution after heat-oxidation treatment was observed from the cross-section of the particles. Prior to observation by energy dispersive spectroscopy (EDS, JEOL, JSM-7001FA), the particles were mounted in resin, polished with abrasive paper, and subsequently sputter-coated with Au to create a conductive specimen. Phase compositions were determined by powder X-ray diffraction (XRD) with a 1D silicon strip detector (Rigaku Miniflex600, D/teX Ultra2, Cu Kα). Furthermore, the phase transition temperature and thermal storage ability of the MEPCMs were measured using a differential scanning calorimetry (DSC) analyzer (METTLER TOLEDO DSC-823). The sample (10 mg) was placed in an Al_2O_3 crucible and measured under an Ar stream with flow rate 50 mL min^{-1} and a heating/cooling rate of 2 °C min^{-1}.

MEPCM durability was evaluated via cyclic testing performed on a METTLER TOLEDO TG-DSC-1. The sample (30 mg) was loaded into an Al_2O_3 crucible, then repeatedly heated and cooled from 500° to 650°C at a heating/cooling rate of 50 K min^{-1} for 10 cycles under a 200 mL min^{-1} air flow. Furthermore, 100 cycles were performed on the Al-12mass%Si MEPCMs; these exhibited the largest thermal expansion during phase transition.

3. Results and discussion

3.1. Morphology and phase composition

The microencapsulation of Al-Si microspheres was carried out via a boehmite coating process followed by heat oxidation treatment at high temperatures to thermally decompose the boehmite precursor shell to the stable phase of Al_2O_3 [36].

Fig. 1 presents SEM images of Al-12mass%Si (a) raw material (b) after boehmite coating, and (c)–(e) after heat oxidation treatment at various temperatures. The raw materials possess spherical shape with a smooth surface. On the other hand, interconnected nano-fibrillar crystals with a flower-like structure formed on the boehmite-coated samples. After heat oxidation treatment the original spherical shapes and the growth of the fibrillar crystals were still observed. Moreover, a band of crystals was revealed, which produced a relatively rough surface on the synthesized MEPCM. The observed shell morphology was similar to those of the Al-25mass%Si MEPCMs reported in previous studies [34,35]. The surface morphologies of MEPCM-Al12Si samples oxidized at various temperatures are compared in Fig. 1(c)–(e). The SEM images confirm the growth of continuous bands of crystals, especially in the higher temperature heat oxidation samples. Fig. 2 displays the SEM images of MEPCM species prepared from Al-Si microspheres with various Si concentrations: a) Al12Si, b) Al17Si, c) Al20Si, and d) Al30Si-1100. There is no significant difference in the surface morphology of the MEPCM prepared from the other raw materials as illustrated in Fig. 2(a)–(d). Similar to MEPCM-Al12Si samples, MEPCM-Al17Si, -Al20Si, and -Al30Si retained their original shape and the MEPCM surface consisted of fibrillary crystals and continuous bands of crystals.