# Inorganic microencapsulated core/shell structure of Al–Si alloy micro-particles with silane coupling agent

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## Abstract

Al–Si eutectic alloy is a kind of ideal high temperature phase change materials (PCMs) because of its high latent heat and good heat transfer performance. However, it is difficult for Al–Si alloy to be safely applied because of its causticity and incompatibility. In this paper, an inorganic Al–Si/$Al_2O_3$ micro-particles core/shell structure was prepared by the sol–gel process with the modification of silane coupling agent. The direct evidence for the forming of the dense and stable $\alpha$-$Al_2O_3$ shell layer, whose thickness is about 3–5 μm, is presented by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD). In terms of the analyses of Fourier transform infrared (FT-IR) and thermogravimetry (TG), it is apparent that the silane coupling agent is successfully grafted on the surface of Al–Si alloy micro-particles, which promotes the condensation between boehmite sols and silanol groups. The latent heat of the encapsulated Al–Si alloy was 307.21 kJ/kg and decreased during the process of microencapsulation. The reasons for the reduction of the latent heat are the excess alumina sols and the depletion of Al–Si alloy.
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*Keywords:* Al–Si alloy particles; Core–shell structure; Sol–gel; Silane coupling agent

## 1. Introduction

Al–Si alloy, especially for Al–Si eutectic alloy (88Al–12Si), is an ideal material used as high temperature (500–600 °C) phase change materials (PCMs). Based on its high heat of fusion (or latent heat density) [1,2], good heat transfer performance [3,4] and thermal reliability [5], low manufacturing cost [6], low energy consumption and $CO_2$ production [3], Al–Si alloy has been applied widely in the fields of high temperature solar energy storage [3,7,8]. However, its high causticity and incompatibility [7] are primary problems limiting its applications, when Al–Si alloy changes from solid phase to liquid phase. Traditionally, the methods of impeding the flow of liquid phase are applied to store Al–Si alloy in a clay and ceramic container [1] or a thick metallic container

whose inner surface is coated by the corrosion layers [5,9]. These methods, however, generally result in a large and heavy package structure which has to be replaced periodically because of the serious corrosion induced by liquid Al–Si alloy.

Compared with traditional applications, it is worth considering to prepare certain thick ceramic layers on the surface of Al–Si alloy particles in order to compose core/shell structures. As examples of known, many kinds of core/shell structures and quotable methods have been mentioned by many researchers. Jong Min Kim [10] prepared uniform core/shell particles of $SiO_2$/$ZrO_2$ by adjusting the reaction conditions of the hydrolysis and condensation in the sol–gel process to carefully control the generation rate of $ZrO_2$ nano-particles. Tyagi [11] presented a review on microencapsulation technology for better utilization of PCMs with building parts. A new micro-PCM based on n-octadecane core and silica shell was synthesized through interfacial polycondensation by Zhang [12] and the thermal conductivity was evaluated to be in the range from 0.20 W/(m K) of traditional polymer shell to 1.3123 W/(m K) of the silica microcapsules. Barmatova [13]

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built a simple geometrical model to realize the prediction of the thickness of mesoporous shells over monodisperse spherical particles based on the example of mesoporous Ti-silicate particles with the core–shell structure. Tang [14,15] prepared the composite coating particles ($\alpha$-Al(OH)$_3$ cores with silica shell) by heterogeneous nucleation-and-growth process and these particles were provided with mullite stoichiometric ratio. Hong Lei [16] described a series of novel alumina/silica core/shell abrasives in slurries and concluded that the specimens exhibited better surface planarization and less scratch.

The most often used microencapsulation chemical methods are interfacial polymerization, in situ polymerization and matrix polymerization [11]. In some different methods, the sol–gel process is an effective technology to synthesize core–shell particles owing to its simplicity, maneuverability and controllability for the parameters. According to no correlative results for Al–Si/Al$_2$O$_3$ core/shell structure after investigating abundant references, the exploitation of Al–Si eutectic alloy micro-particles packed by ceramic layer is therefore dependent on a good understanding of hydrolysis and condensation on the surface of Al–Si alloy in the sol–gel process.

At present, based on the results of references, most of researches on inorganic core/shell structure mainly focus on nanometer or submicron particles and rarely on micro-particles. Furthermore, there are hardly any references on encapsulating Al–Si alloy micro-particles. In view of the application of Al–Si alloy in the field of PCMs, it is a significant work to realize inorganic microencapsulated core/shell structure of Al–Si eutectic alloy micro-particles. In this paper, the purpose is to search for a method of obtaining Al–Si/Al$_2$O$_3$ core/shell micro-particles by the sol–gel process with the help of silane coupling agent. The dense shell is desired in order to prevent the flow of liquid during the solid–liquid phase change. The connections of chemical groups between the surface of Al–Si alloy and alumina sol are investigated, and the direct microencapsulated evidences are shown by means of SEM.

## 2. Experimental

### 2.1. Synthesis of Al–Si/Al$_2$O$_3$ core/shell particles

Commercial Al–Si eutectic alloy particles (Al 87.48 wt%, Si 12.06 wt%, others elements 0.46 wt%) were selected as the PCMs. Firstly, after sieved, the Al–Si alloy particles were washed by using absolute alcohol in order to remove the greasy dirt on their surfaces and then dried at 110 °C in a drying oven for 24 h. Then, silane coupling agent KH-560 (named $\gamma$-(2,3-epoxypropoxy)propyl trimethoxysilane, Nanjing, China) was chosen to modify the surfaces of Al–Si particles. In this process, 0.5 g KH-560 was added into 100 g alcohol solution (absolute alcohol and deionized water were 95 g and 5 g respectively). The pH value was adjusted to 4–5 by adding glacial acetic acid. The mixed solution was stirred at 120 °C for 24 h. After mixing equably, some excess coupling agent was rinsed by absolute alcohol and then particles were dried again at 120 °C for 3 h. Aluminum sec-butoxide (ASB, analytical reagent, Shanghai,

China) was selected as an aluminum precursor to prepare alumina sols. The modified Al–Si alloy particles (4 g) were dispersed in the 50 ml ASB solution (the molar ratio of ASB and deionized water = 1: 80) and 0.2 mol/L nitric acid (analytical reagent, deionized water as solvent) was used to adjust pH value to 4–5. The mixture solution was stirred at 50 °C till the gel emerged. Finally, these particles were dried at 30 °C for 24 h and then heated at 1200 °C for 4 h. Fig. 1 shows the experimental procedures for preparing Al–Si/Al$_2$O$_3$ core/shell particles. For simplicity, the prefix AS is used to denote the original Al–Si alloy particles. The particles modified by KH-560 and the Al–Si/Al$_2$O$_3$ core/shell particles prepared subsequently are coded as AS-M and AS-EnM, respectively.

### 2.2. Characterization

Fourier transform infrared (FT-IR) spectra were recorded in an EQuINox-55 FT-IR instrument. Three powder samples were diluted in dry KBr and pressed into pellets. The Microscopic morphology of Al–Si/Al$_2$O$_3$ particles was observed by scanning electron microscopy (SEM, Quanta 200, FEI, USA) at a 20 kV acceleration voltage. The samples were sputter-coated with a thin layer of Au. Phase analysis was performed by X-ray diffraction (XRD, D/Max2200, Rigaku, Japan) using Cu-K$_\alpha$ radiation at 40 kV and 25 mA. The weight-loss behaviors and thermal properties of Al–Si alloys and Al–Si/Al$_2$O$_3$ core/shell particles were studied contrastively by thermo gravimetric and differential scanning calorimeter (TG-DSC, TGA/SDTA851e, Mettler-Toledo Co., Switzerland) performed in an air atmosphere in the temperature range of 25–650 °C.

## 3. Results and discussion

### 3.1. FT-IR investigation

FT-IR spectrums of AS and AS-M are shown in Fig. 2(a) and (b) in the range 4000–400 cm$^{-1}$ in order to understand the synthesis course by investigating the changes of functional groups. FT-IR spectrum of AS-EnM is also simultaneously shown in Fig. 2(c).

The presence of broad bands around 3300–3600 cm$^{-1}$ is an evidence for the existence of some hydroxyl groups (–OH). These –OH groups mainly originate from AlO–H vibration of the alumina networks [17], which is one of the reasons to achieve the modification of Al–Si alloy by coupling agent [18]. Compared with the curves of AS, –OH band of AS-M is shifted from 3435 cm$^{-1}$ to 3417 cm$^{-1}$. The shift suggests that Si–OH groups progressively replace Al–OH groups due to silanization of KH-560 [19]. Hydroxyl groups almost disappear as shown in Fig. 2(c) after heat-treatment at 1200 °C. The bands between 3000 cm$^{-1}$ and 2800 cm$^{-1}$ are the cross-linked organic groups adsorbed onto the surfaces of Al–Si alloy belonging to alcohol and KH-560. The bands at 2972 cm$^{-1}$ and 2917 cm$^{-1}$ in Fig. 2(b) are related to –CH$_2$– and –CH$_2$–O– groups of newly added KH-560 respectively and stronger than the bands originating from alcohol at 2972 cm$^{-1}$ and 2924 cm$^{-1}$ in Fig. 2(a) [20,21]. The bands