Nano Energy 25 (2016) 218–224

Contents lists available at ScienceDirect

Nano Energy

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

Tunable endothermic plateau for enhancing thermal energy storage obtained using binary metal alloy particles

Chih-Chung Lai [a,1], Shih-Ming Lin [a,1], Yuan-Da Chu [b], Chun-Che Chang [a], Yu-Lun Chueh [a,*], Ming-Chang Lu [b,*]

[a] Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan
[b] Department of Mechanical Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan

ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form
5 February 2016
Accepted 28 February 2016
Available online 14 April 2016

Keywords:
Thermal energy storage
Latent heat
Tunable endothermic plateau
Sn_xZn_{1-x}/SiO_x core–shell alloy particles

ABSTRACT

Thermal energy storage is crucial for various industrial systems. Enhancements in energy storage induced by latent heat have been demonstrated by using phase-change materials. However, these enhancements occur only at the melting points of the materials. In this study, we demonstrated the controllability of latent heat absorption/release in a certain temperature range. A wide endothermic plateau from 370 to 407 °C for the Hitec salt was obtained by releasing the latent heat of alloy particles embedded in the salt. The alloy particle-doped salt was applied to a Stirling engine to demonstrate its effectiveness in enhancing the energy and power outputs of the engine. Compared to pure salt, the alloy particle-doped salt can enhance the engine's energy output by 21%. With the advantages of scalable synthesis and superior thermal properties, the alloy particles have potential applications in energy storage enhancement in various thermal energy systems.

1. Introduction

Global warming has had a severe impact on Earth. The average global temperature has risen by 0.8 °C since 1880, and the global sea level has increased by 17 cm in the past century [1,2]. Because 80% of the global total energy consumption is related to thermal energy and 45% of energy is eventually dumped into waste heat [2,3], global warming could be feasibly reduced by improving energy efficiency (e.g., reusing waste heat) [4,5]. Waste heat generated from power plants and other manufacturing facilities can be stored through a proper heat-capturing process and can be recycled to improve the overall energy efficiency of power plants [6,7]. In addition, increasing the contribution of solar energy to global energy consumption is an effective approach for alleviating global warming. Materials with a high thermal energy storage capacity are required for efficient heat recovery processes and solar-thermal power generation. Latent heat storage is superior to sensible heat storage because the latent heat of materials is generally substantially higher than their sensible heat. The enhancement of thermal energy storage through phase-change materials (PCMs) has recently been demonstrated [8,9]. However, latent-heat-based improvements of energy storage occur at the melting points of the PCMs [10,11]. Moreover, the organic compounds employed in the current literature generally have a low thermal conductivity and are targeted at low temperature applications [12,13].

In this study, we propose a concept to create enhanced latent heat absorption in a temperature range, rather than at a specific temperature, using the metal-based PCMs. The metal-based PCMs also possess a large thermal conductivity and a high heat of fusion as opposed to organic compounds. Besides, they are applicable to a wide range of temperature from medium temperature (120–650 °C) to high temperature (> 650 °C). Specifically, a heat absorption plateau was achieved by releasing the latent heat of metal alloy particles. Furthermore, latent heat-enhanced energy absorption could be designed in a particular temperature range because of its dependence on the composition of the alloy particles. The Hitec salt (a common working fluid in solar-thermal power plants [14,15]) doped with the synthesized Sn_xZn_{1-x}/SiO_x core–shell alloy particles exhibited an endothermic plateau from 370 °C to 407 °C. To the best of our knowledge, this is the first study to show the ability to control latent heat absorption/release in a certain temperature range. Consequently, the adjustable endothermic plateaus can be applied to enhance energy storage for various industrial systems under different working temperature conditions. The Hitec salt doped with the alloy particle mixture was applied to a Stirling engine to demonstrate its ability in enhancing energy output and power output for the Stirling engine. It was showed that the energy output of the engine was enhanced by

* Corresponding authors.
E-mail addresses: ylchueh@mx.nthu.edu.tw (Y.-L. Chueh), mclu@mail.nctu.edu.tw (M.-C. Lu).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.nanoen.2016.02.058
2211-2855/

21% using the alloy particles doped salt as compared to the engine using a pure salt as the working fluid.

2. Materials and methods

2.1. Synthesis of Sn_xZn_{1-x}/SiO_x core–shell alloy particles

Fig. 1a illustrates the procedure for synthesizing Sn_xZn_{1-x}/SiO_x core–shell alloy particles (i.e., Sn_xZn_{1-x} core and SiO_x shell particles). First, Zn particles (99.9%, 325 mesh, Strem Chemicals) acting as a reducing agent were dispersed in absolute ethanol ($\geq$99.7%) forming a 0.06 M solution. Second, the shell metal precursor, 10 mL of a 0.125 M $SnCl_4$ $5H_2O$ (98%, Showa chemicals), was added to the solution. Third, a redox chemical reaction as shown in Eq. (1) occurred through the vigorous stirring of the chemical bath at 1150 rpm from 3 to 240 min at room temperature [16]:

$$Sn_4^{+} + 2\,Zn \rightarrow Sn + 2\,Zn_2^{+} \quad (1)$$

Forth, the sol–gel polymerization method was then applied to encapsulate the Sn_xZn_{1-x} alloy particles with SiO_x shells [17]. The synthesized particles were dispersed into 40 mL of ethanol (95 vol%, Sigma-Aldrich). 100 μL of 3-Aminopropyl trimethoxysilane (APTMS, 97%, Alfa Acsar) was carefully dropped into the solution and stirred for 5 min. Fifth, the formation of the SiO_x shell layer was initiated by stirring the mixed solution at pH=4–5. These pre-products were thermally annealed for 1.5–2 h. As-synthesized core–shell particles were filtered out, washed, and dried at 60 °C in an oven. Finally, the dried particles were annealed at 500 °C for 10 min in a tube furnace to form the alloy core. Fig. 1b shows the scanning electron microscope (SEM) image of the Sn_xZn_{1-x}/SiO_x core–shell alloy particles. The inset of it shows the optical image of powder-like product. Fig. 1c highlights an individual synthesized particle. The composition of the core–shell alloy particle was confirmed by examining the energy-dispersive X-ray spectroscopy (EDX) linescan profiles shown in the figure. The average size of the synthesized core–shell Sn_xZn_{1-x} alloy particles was 56.7 ± 15.2 μm (see Fig. S1). The thickness of Sn shells on the Sn_xZn_{1-x} alloy particle (i.e., the Zn/Sn ratio) can be controlled by adjusting either the atomic ratio between Sn and Zn or the reaction time. To demonstrate the controllability of the composition, we conducted the processes by using different reaction times while maintaining the same molar ratio for the reactants (i.e., [Zn]/[$SnCl_4$]=1). A longer reaction time resulted in a thicker Sn layer on the Sn_xZn_{1-x} alloy particle. As-synthesized Sn_xZn_{1-x}/SiO_x core–shall alloy particles were examined at different reaction times by using X-ray diffraction (XRD) techniques (Fig. 1d). The diffraction peaks matched Sn [JCPDS# 04-0673] and Zn [JCPDS# 04-0831] signals. The content of Sn/Zn in alloy particles can be obtained quantitatively by conducting reference intensity ratio (RIR) analysis by using XRD spectra [18,19]. Table 1 lists the compositional information of the alloy particles synthesized using different reaction durations, which were varied from 0 to 240 min (denoted as Sample A–Sample E in Table 1). As shown in the table, the Sn weight percentage in the samples increased with the reaction time. Sample A in Table 1 with zero reaction time is the pure Zn element.

2.2. Characterization

The phase and crystallinity of the Sn_xZn_{1-x} alloy particles were characterized using an X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu Kα (λ=0.154 nm) serving as the radiation source. The morphologies were examined through field-emission scanning electron microscopy (S-8010, Hitachi). The heat capacity profile of the Sn_xZn_{1-x} alloy particles, three particle mixtures (EP-01, EP-02, EP-03 in Table 2), and Hitec salt doped with EP-01 were examined at a heating rate of 20 °C/min by using a differential scanning calorimeter (DSC, DSC 1, METTLER TOLEDO).

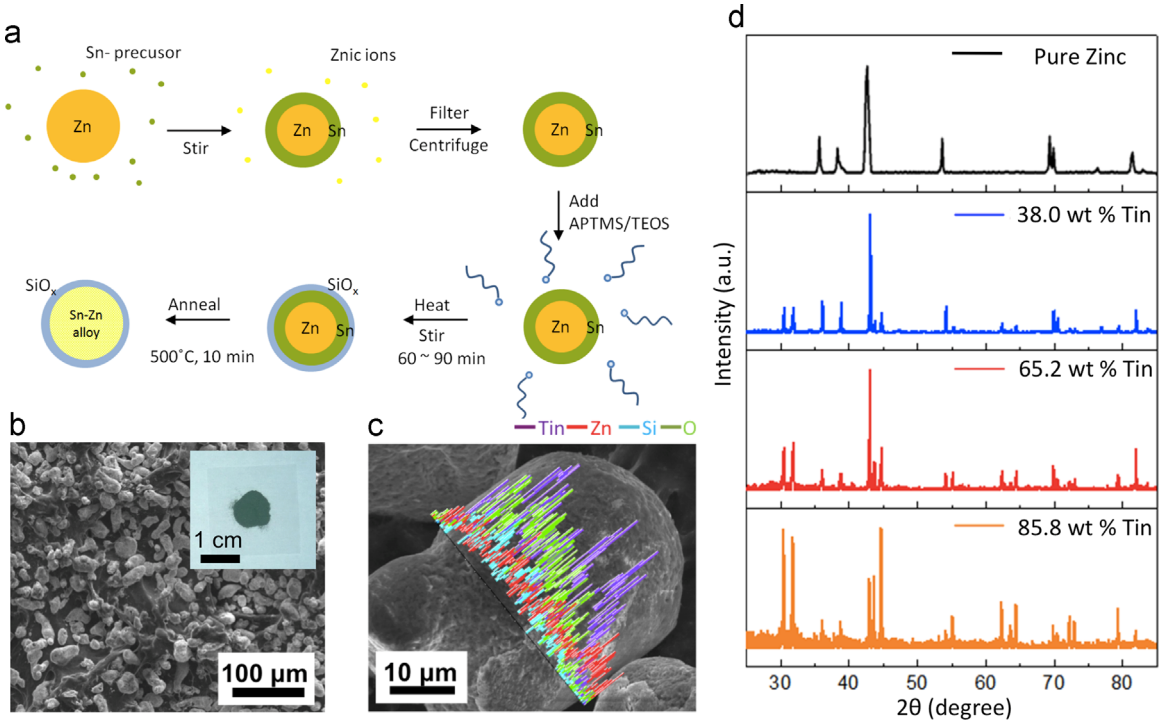

Fig. 1. Synthesis of Sn_xZn_{1-x} alloy particles by electroless plating. (a) Procedure for synthesizing the Sn_xZn_{1-x}/SiO_x core–shell alloy particles. (b) Low-magnification SEM image revealing the morphology of the Sn_xZn_{1-x} alloy particles. Inset of (b) is the optical image of powder-like product. (c) SEM image highlighted individual synthesized particle. The composition of the core–shell alloy particle was confirmed by EDX linescan profiles. (d) XRD spectra of the synthesized Sn_xZn_{1-x} alloy particles whose compositions were analyzed using XRD-RIR method.