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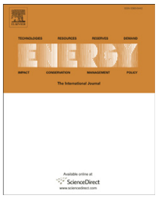

Cyclic thermal storage/discharge performances of a hypereutectic Cu-Si alloy under vacuum for solar thermochemical process

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ABSTRACT

A copper-silicon alloy (Cu-Si alloy) was examined and evaluated as a phase-change material (PCM) for thermal energy storage applications such as load shaving and peak load shifting when coupled to a solar thermochemical reactor, reformer, or gasifier for the production of solar fuel. The Cu-Si alloy was selected as a high-temperature PCM thermal storage medium alternative to molten carbonate salts, and the compatibility of this alloy with a graphite-carbon encapsulation material was experimentally examined. The cyclic thermal storage/discharge properties of the Cu-Si alloy as a latent-heat energy storage material were studied with respect to thermal cycles. A thermal stability test was performed on Cu-20 wt% Si, Cu-25 wt% Si, and Cu-30 wt% Si alloys placed in a graphite container under vacuum. The performances of the Cu-Si alloys with increasing and decreasing temperature were measured during the thermal storage (heat-charge) and cooling (heat-discharge) modes, respectively. The elemental distribution of each Cu-Si alloy after the cyclic reaction was evaluated using an electron probe microanalyzer (EPMA). The heat storage capacities before and after the cyclic reaction were evaluated using differential scanning calorimetry (DSC) and were compared to the thermal storage properties of the molten carbonate salt.

1. Introduction

Because of the increasing importance of efficient use of energy, development of highly effective energy saving solutions is paramount in the context of the current energy demand. Utilization of renewable energy sources such as solar radiation is a potential approach to reduce the carbon dioxide emissions caused by power generation [1]. In concentrating solar power (CSP) systems, which can be used for cost-competitive power generation, especially in the sun-belt region where direct solar light is abundant [2], solar energy is concentrated by a solar collector and transported by a heat transfer fluid (HTF) into a thermal energy storage (TES) system [3]. However, the intrinsic low density and intermittent nature of solar radiation are major barriers to achieving economic viability [4]. To compensate for the intermittency of this resource, CSP plants must support their generation using auxiliary sources or backup fossil fuels to continue supplying electricity when solar radiation is below a threshold [5]. Similarly, a solar chemical reactor, where concentrated solar radiation is used as an energy source to drive a thermochemical reaction for hydrogen production, must also effectively receive concentrated solar radiation and convert the high-temperature solar heat into chemical fuels by means of endothermic thermochemical processes [6,7]. It is well known that the incorporation of TES systems into CSP plants and solar chemical reactors can increase the operational periods of both systems [8].

A TES system enables the storage of excess solar energy in the daytime for utilization during the night or for balancing load levels in electrical grids during the times of peak demand. TES systems can utilize sensible heat, latent heat, chemical energy (the heat of a reaction), or a combination of these methods [9,10]. Sensible TES materials undergo no phase change within the temperature range required for the storage application [10,11]. Latent TES is based on the heat absorption or release that occurs when a storage material undergoes a phase change (a solid-liquid phase transformation in most cases for use at high temperatures). Chemical TES involves

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Abbreviations: CSP, concentrating solar power; DSC, differential scanning calorimeter; EPMA, electron probe microanalyzer; HTF, heat transfer fluid; PCM, phase-change material; SEM, scanning electron microscopy; TES, thermal energy storage.

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reversible chemical reactions of both endothermic and exothermic processes. In the field of solid sensible TES, concrete and cast ceramics have been extensively studied because of their low cost, good thermal conductivities, and moderate specific heats [12,13]. With regard to liquid sensible TES, molten salts are widely used in current CSP plants [13,14] because they are in the liquid phase at ambient pressures, provide efficient and low-cost media, and are nonflammable and nontoxic.

Molten salts have been considered for liquid sensible TES for CSP applications since the mid-1970s [15–17]. These salts are still being researched [18–21], and one of the most important goals is extending the working temperature range by either increasing the decomposition temperature or decreasing the melting point. In order to further increase the energy storage capacity and energy density, the focus has been directed to latent TES using the solid-liquid phase transitions of molten salts. Latent heat TES, as a technique for matching the energy supply and demand, plays an important role with regard to thermal efficiency and economic feasibility. In comparison with sensible TES systems, the use of latent TES systems presents advantages such as working within a narrow temperature range and allowing the design of a smaller storage capacity for CSP. Moreover, latent heat TES systems can function coupled to a solar chemical reactor, where the endothermic chemical reaction occurs using high-temperature solar heat as an energy source. If the functioning temperature of the solar chemical reactor is compatible with the melting point of the TES material, a large amount of the latent heat released at this temperature can be used as an energy source to drive an endothermic chemical reaction in a solar chemical reactor.

Molten salts such as nitrate, fluoride, chloride, and carbonate, as well as mixed molten salts, can be selected as thermal storage media, and have been studied in relation to solar power generation and solar thermochemical processes for upgrading fossil fuels through endothermic chemical reactions. Because of their suitable phase-change temperature, high latent heat density, good thermal reliability, and low corrosive properties at high temperatures for metallic PCM containers such as low-carbon steel and stainless steel, the present authors have focused their studies on a molten carbonate salt as a latent heat TES material for solar thermochemical reformers [22–25]. This particular molten salt was selected for the following reasons: 1) it is mildly corrosive in comparison with the fluoride and chloride molten salts; and 2) it has a relatively large heat capacity (C_p) and a large latent heat when solidifying or melting at the phase-change temperature [22–25]. In order to improve the very low thermal conductivity of Na_2CO_3 as a high-temperature latent heat TES material and suppress the convective flow inside the container of the solar reactor/receiver thereby delaying corrosion of the PCM container, a Na_2CO_3/MgO composite material (MgO ceramic particles mixed with Na_2CO_3) was tested as a thermal storage medium for the double-walled reactor tubes of a solar reformer/receiver [22–25].

The advantages and disadvantages of using a molten carbonate salt in the reactor tubes are summarized in Fig. 1. The Na_2CO_3/MgO composite has a high phase-change temperature of about 850 °C and a large latent heat of about 300 kJ/kg. Therefore, reactor tubes filled with this thermal storage material can discharge latent heat from molten Na_2CO_3 at the phase change temperature (850 °C), and supply the endothermic heat of the reforming reaction occurring with methane conversion at a level of >90% [22–25]. However, the drawbacks of the Na_2CO_3/MgO composite, as well as the molten Na_2CO_3 salt, include limited thermal conductivity and a corrosive nature; the addition of MgO to Na_2CO_3 produces a trade-off between the thermal storage capacity and thermal conductivity.

In this study, the authors focused on a metal alloy as a new latent heat TES material and as an alternative to molten carbonate salts. The cyclic thermal storage/discharge properties of the Cu-Si alloy were examined under vacuum to evaluate it as a potential PCM thermal storage material. The temperature performances of the Cu-Si alloy were measured during the thermal storage (heat-charge) and cooling (heat-discharge) modes. The elemental distribution of the Cu-Si alloy after the cyclic reaction was evaluated using an electron probe microanalyzer (EPMA).

2. Potential of metallic PCM as a latent thermal storage medium at high temperatures

Metallic PCMs were first proposed for CSPs and considered as TES materials more than three decades ago [26]. Since then, they have been experimentally studied to some extent for TES applications [27–29]. Recently, most investigations have concentrated on eutectic alloys as PCMs in high-temperature TES systems because of their suitable phase-change temperature, high latent heat density, and good thermal reliability [29–34]. The largest latent heat values, based on mass or volume, were obtained with binary and ternary eutectic alloys of the relatively plentiful elements Al, Cu, Mg, Si, and Zn.

For CSP applications, temperatures >650 °C (above the decomposition temperature of molten nitrate salts) are desirable for enhancing power generation efficiency. Moreover, for solar thermochemical reforming processes, this temperature should be above 650 °C to ensure methane conversion levels of >90% at ambient pressure [24]. The melting temperature of the selected material is therefore a key parameter to consider for a PCM material combined with the CSP application or solar thermochemical reforming processes. Concerning the cost and availability of the materials, Mg, Cu, Si, Al, and some others are found to be the most appropriate candidates for metal alloy PCMs [29–34]. In a previous study, the present authors have examined and evaluated a hypereutectic aluminum-silicon alloy (Al-Si alloy) with a higher Si content than needed for a eutectic process (chemical composition: Al-12.2 wt% Si; melting point: 577 °C) as a metallic PCM [30]. In comparison with the molten Na_2CO_3 salt, this Al-Si alloy has a larger thermal conductivity (190 W/m K), larger latent heat, and smaller thermal expansion.

In this study, a hypereutectic copper-silicon alloy (Cu-Si alloy) with a higher Si content than needed for a eutectic process was selected to ensure both a eutectic temperature higher than 700 °C and a high thermal storage capacity because of the excess Si content and thermal conductivity of copper. Addition of silicon was also expected to alleviate the thermal expansion of the eutectic mixture above 802 °C because of the nature of the abnormal liquid. Therefore, this study focused on the potential of the Cu-Si alloy as a PCM thermal storage material.

Some advantages and drawbacks of the Cu-Si alloy in comparison with the molten Na_2CO_3 salt for solar thermochemical process are listed in Fig. 1. The noteworthy characteristics of the Cu-Si alloy are as follows: first, the temperature range for latent heat can vary depending on the Cu-Si chemical composition. The melting of eutectic mixture at 802 °C and the melting of the primary Si crystal above 802 °C can both be used for latent heat thermal storage in a hypereutectic Cu-Si alloy. This means there is a large latent heat capacity over a wide range between 802 °C and the liquidus temperature. Namely, there is a large latent heat during the eutectic process at a constant temperature of 802 °C, and both a latent heat arising from the melting of the primary Si crystal and sensible heat arising from the melted eutectic mixture over a wide range between 802 °C and the liquidus temperature that can be used. If the latent heat released/stored at a constant temperature of 802 °C is required as a PCM thermal storage for CSP plants and solar chemical reactors, the eutectic mixture should be selected. If the maximum