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Macro-encapsulation and characterization of chloride based inorganic Phase change materials for high temperature thermal energy storage systems

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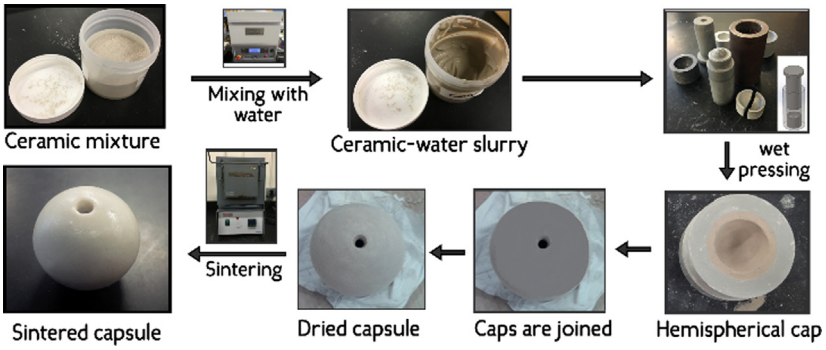
HIGHLIGHTS

- A novel approach to encapsulate high temperature chloride based PCM is presented.
- Low-cost ceramics with excellent thermal and chemical stability were used.
- Ceramics sintered at 1190 °C did not show any reactivity with molten sodium chloride.
- Capsules survived more than 150 thermal cycles.
- No degradation in thermophysical properties of the capsules and PCM on cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach involving the use of ceramic materials was investigated for encapsulating chloride based PCMs with melting points higher than 650 °C. Low-cost ceramics with excellent thermal and chemical stability under molten-salt conditions were identified as the encapsulants. The processing procedure for these materials was discerned by systematic porosity distribution and materials compatibility studies. The influence of sintering temperature on the reactivity of feldspar, ball clay, kaolin and the mixture thereof with molten sodium chloride was investigated by IR spectroscopy. The porosity of the sintered ceramic samples was analyzed through water and dye absorption tests, as well as SEM analysis. The results were used for developing an optimum ceramic capsule fabrication procedure, which involved the use of a green ceramic body followed by sintering at 1190 °C. Sodium chloride and its eutectic with potassium chloride were used as the PCMs. The selected PCM was poured into and filled the fabricated ceramic capsule through a hole which was sealed at a temperature close to or higher than the melting temperature of the PCM. The fabricated capsules have been tested and have survived more than 150 thermal cycles without showing degradation in their thermo-physical properties.

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Nomenclature

LHS	latent heat storage
PCMs	phase change materials
FTIR	Fourier transform infrared spectroscopy
DSC	differential scanning calorimeter
EDS	energy dispersive spectroscopy
IR	infrared spectroscopy
U_c	combined standard uncertainty
σ_{random}	random error
$\sigma_{systematic}$	systematic error
T	temperature (°C)
L	latent heat of fusion (J/kg)
h	hours

1. Introduction

Operation of Concentrated Solar Power (CSP) Plants at high temperatures (> 600 °C) offers greater plant efficiency and larger throughput [1]. Integration of thermal energy storage systems with CSP plants is necessary to fully exploit these benefits and successfully compete with conventional and other renewable power generation technologies. Latent heat (LH) thermal energy storage has been recently looked into as a viable high temperature storage system for CSP plants [2,3]. A major part of research in this field is focused on identifying and characterizing new Phase Change Materials (PCMs)[4–7]; however, the low thermal conductivity of PCMs is a concern [8,9]. Much research has been conducted to improve the heat transfer properties of the bulk PCM—e.g., through the inclusion of heat dissipating fins [10] or higher conductivity nanoparticles [11]. A detailed summary of such methods can be found in the review by Ibrihim et al. [12].

Macroencapsulation of PCMs [13–15] has been shown as a very effective method to overcome low thermal conductivity of PCMs. We have recently reported a very effective method to encapsulate nitrate based inorganic PCMs that comprised a PCM core surrounded by a polymer-metal shell [16–18]. The key innovative steps in that encapsulation method are: (1) the coating of a flexible and selectively porous high temperature polymer, which allows the air trapped in the shell to diffuse out as the capsule is heated while at the same time expanding with the PCM as it melts; and (2) coating of a metal over the polymer. These capsules are effective (survived > 2500 thermal cycles) at temperatures of about 450 °C or lower as most of the polymeric materials degrade above this temperature. In light of this limitation, we have investigated macro-encapsulation of relatively high-temperature (600–830 °C) inorganic chloride based PCMs, such as NaCl and NaCl-KCl eutectic, using low-cost ceramic materials. Chloride based inorganic PCMs were chosen as these salts have high energy storage density and are much cheaper than metallic PCMs. However, these salts have high volumetric expansion [19] and are highly corrosive [20,21], especially in their molten state, rendering their encapsulation a challenging task. The present endeavor is to identify materials and a procedure to encapsulate chloride based PCMs.

Ceramics are very effective in high temperature applications as they are less prone to corrosion under high temperature molten-salt conditions (hot corrosion) than metals and metal-alloys [22]. However, they are inherently porous in nature, which could be detrimental for our application as molten salts normally seep through pores. Porosity also influences chemical and mechanical properties such as compressive strength, thermal diffusivity and hardness of the ceramic materials [23]. For example, thermal diffusivity, which is important for the present application, decreases with an increase in porosity [24]. We have analyzed the influence of sintering temperature on the porosity and reactivity of the selected ceramic mixture comprising feldspar, kaolin, ball clay and silica. This was done to find the right ceramic composition and sintering temperature for the fabrication of ceramic capsules. The present paper reports an innovative approach to encapsulate high temperature (> 650 °C) chloride based PCMs using low-cost ceramic materials with excellent thermal and chemical stability. These capsules will be used for thermal energy storage in the next generation CSP plants, especially those based on supercritical CO_2 Brayton cycle operating at temperatures of 650 °C and above.

2. Materials and methods

2.1. Materials

Sodium chloride (ACS reagent, ≥99.0%) and potassium chloride (ACS reagent, ≥99%) were obtained from Sigma-Aldrich, USA. Selected ceramic components were mixed in a requisite proportion by using a speed mixture machine (FlackTek). The DSC analysis was carried out using the SDT-Q 600 by TA instruments which can simultaneously perform differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Based on metal melting standards, the heat flow, temperature and weight accuracy of this device are ± 2%, ± 1°C and ± 1%, respectively. All the DSC analyses were performed at a ramp rate of 20 °C/min under an inert (argon) atmosphere. The Fourier transform infrared spectroscopy (FTIR) spectra of ceramic samples were measured by using a JASCO 6300 FTIR instrument. Dye absorption by ceramic samples was analyzed with a Leitz Optical Microscope (5× to 100×). SEM analysis of the fabricated ceramic samples was performed by using a Hitachi S-800 field emission scanning electron microscope (FE-SEM).

2.2. Fabrication procedure for the flat circular ceramic discs

A 1″ diameter circular metal mold was used (Fig. 1) to optimize the capsule fabrication procedure, using a wet pressing technique. A ceramic slurry in water was poured onto a wood sheet for drying purposes. After drying it for 2 h, a workable ceramic dough was obtained. The workable ceramic dough was shaped into ceramic balls weighing approximately 9 g each. These clay balls were then shaped using a metallic mold and a 5 lb metal block was placed on it. After 2 h, the metal block was taken off and the molded flat circular green ceramic discs were dried in air for 24 h. A total of 24 samples were made, and eight samples were sintered at 800 °C for 6 h. Another eight samples were sintered at 1000 °C and the rest were sintered at 1190 °C.

2.3. Dye absorption test

A Patent Blue VF dye (10% v/v) solution in water was used. Fabricated ceramic samples were initially submerged in the Patent Blue VF/aqueous solution for 20 min. These were then placed in a vacuumed

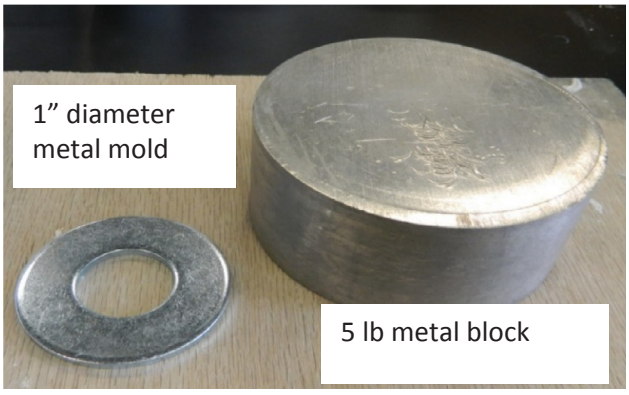

Fig. 1. Ceramic molding apparatus.