Impregnation of porous mullite with Na_2SO_4 phase change material for thermal energy storage

Ruiping Liu [a], Fang Zhang [a], Weiming Su [a], Huiyou Zhao [a], Chang-an Wang [b],*

[a] Department of Materials Science and Engineering, China University of Mining & Technology (Beijing), Beijing 100083, China
[b] School of Materials Science and Engineering, State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

ABSTRACT

The porous mullite/Na_2SO_4 composites with both novel structure and improved heat storage properties were successfully prepared by infiltration of the molten Na_2SO_4 into the porous mullite matrix, which was fabricated by TBA-based freezing casting method. The effects of fabrication parameters on pore structure of the porous mullite matrix, the infiltration ratio of molten Na_2SO_4 and heat storage properties of the composites were investigated extensively. The results show that the infiltration ratio of the molten Na_2SO_4 decreases with decreasing the porosity and increasing the infiltration temperature and the average pore size of the porous mullite matrix. While it increases initially with increases of the infiltration time, and tends to remain constant thereafter. The optimal infiltration temperature and infiltration time are 950 °C and 1 h, respectively. The unidirectionally aligned open pores in the porous mullite matrix benefit the infiltration process, and the higher infiltration ratio of the molten Na_2SO_4 and the relatively larger specific heat capacity of the mullite powders both contribute to the higher heat storage density of the composites.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Recently, the increasing energy consumption and shortage of fossil fuels have been a big challenge for the development of human society. Hence the investigation of new energy resources as well as efficient ways of energy storage and recovery have attracted much attention [1,2]. Phase change materials (PCMs) are widely employed as thermal energy storage materials in many applications because of their capacity of storing and releasing a large amount of thermal energy during melting and solidifying at phase change temperature. Lots of inorganic and organic PCMs and their mixtures have been investigated as latent heat storage materials [3–5]. Among them, Na_2SO_4 has been widely used for latent heat storage applications in the fields of solar heating systems, engineering thermal physics, recovery and utilization of industrial waste heat, and so on, due to its low cost, relative large latent heat, high temperature chemical stability, and proper phase change temperature [6–8]. In spite of these desirable properties of Na_2SO_4, the leakage of phase change materials, low thermal conductivity and the complicated energy storage systems of latent heat materials limit its application to a large extent [9,10].

In order to resolve these problems, newly emerged phase change materials/ceramic composite materials including the porous ceramics matrix and phase change materials distributed in the pores have attracted much attention in recent years [11,12]. It not only combines the advantages of conventional phase change material and the sensible heat of the ceramics, but also is expected to solve some of the problems in the application of the phase change materials, especially its encapsulation, phase separation, low thermal conductivity and the corrosive to the matrix. Most of the previous research have been focused on the impregnation of organic PCMs into the porous silica matrix prepared by either adding pore forming agent [13–15] or sol–gel method [16,17]. However, both the lower specific heat capacity and open porosity of porous silica and the lower phase transition temperature limit their subsequent infiltration process of PCMs and applications as high temperature thermal energy storage materials. Moreover, the effects of porosity and pore size on the properties of the PCMs/ceramic composite thermal energy storage materials were rarely investigated [18,19].

Compared to silica, as promising structural materials, mullite ($3Al_2O_3 \cdot 2SiO_2$) and mullite-based ceramics have been studied extensively in the last decades for their interesting properties, such as relatively low thermal expansion coefficient, low density, high creep resistance, and relatively higher thermal conductivity than silica [20,21]. Due to the low thermal expansion coefficient,

mullite-based ceramics with good thermal shock resistance are widely applied in high-temperature thermal cycling environments. On the other hand, the freeze-casting process has emerged as a candidate method for the preparation of the porous ceramics, as it can produce interconnected pore channels in a tailored manner, e.g. aligned pore channels on a scale of several microns, which will offer superior mechanical properties and higher open porosity [22–24].

Herein, we intend to report a porous mullite/Na_2SO_4 composite with novel structure used for the thermal energy storage. The porous mullite matrix with unidirectionally aligned gradient pores and high open porosity were fabricated by *tert*-butyl alcohol (TBA)-based freezing casting method. The porous mullite/Na_2SO_4 composite was prepared by the impregnation of the molten Na_2SO_4 into the porous mullite matrix. The effects of porosity, pore size distribution of the porous mullite matrix and the infiltration process on the properties of the composites were investigated systematically. The obtained novel composites with unique structure can improve the heat storage properties effectively, and are expected to exhibit comparable high performance as other thermal storage materials.

2. Experimental procedure

2.1. Sample preparations

Commercially available mullite powder (Songyan furnace powders Co. Ltd., Henan, China) and sodium sulfate (Na_2SO_4, Sinopharm Chemical Reagent Beijing Co., Ltd, China) were used as starting material. The mullite powder has a median size (d_{50}) of 14.7 μm and a specific surface area of 1.24 m^2/g. The porous mullite with gradient unidirectional aligned pores used in this work was prepared by TBA-based freezing casting method [22–24]. Typically, mullite powder (15–40 vol%) was mixed with the premixed solution (60–85 vol%) containing TBA, 0.5 wt% PVB and 5 wt% BYK-163. The as-obtained mixture was ball-milled for 4 h to generate a homogeneous suspension. The slurry was de-aired by stirring under vacuum and then poured into the mold to be frozen unidirectionally ($-20--100$ °C). After freezing, the frozen bodies were freeze-dried for 12 h in vacuum at -50 °C using a freeze-dryer (Type FD-1A-50, Boyikang Corp., Beijing, China) and carefully removed from the molds. Subsequently, the porous mullite matrix with the diameter of 30 mm and height of 60 mm were prepared after sintering at 1550 °C for 2 h in air. In order to eliminate the effects of temperature gradient in the freezing direction of the samples on the pore structure, as well as the subsequent characterization and infiltration test of the samples, each porous mullite ceramic cylinder was sliced into several sections, and the section with the diameter of 30 mm and height of 15 mm from the same location which near the middle was chosen for the subsequent characterization and infiltration test. The porous mullite/Na_2SO_4 phase change thermal storage materials were prepared by spontaneous melt infiltration of molten Na_2SO_4 phase change materials into the porous mullite matrix at different infiltration temperatures (900–1050 °C) for different infiltration time (0.5–2 h).

2.2. Characterization

The thermal stability of the Na_2SO_4 and the latent heat of the samples were measured by using TG-DSC analysis. The porosity of the samples was evaluated by Archimedes method, and a theoretical density of 3.16 g/cm^3 for dense mullite was used. The average pore size and pore size distribution were measured by a mercury intrusion porosimetry (AutoPore IV 9510). To evaluate the compatibility of the mullite and Na_2SO_4, wide-angle X-ray diffraction (XRD) analysis of the samples was conducted using a Bruker D8 advance instrument (Karlsruhe, Germany). The microstructures of the sintered porous mullite and porous mullite/Na_2SO_4 composites were observed using scanning electron microscopy (SEM, JEOL JSM-7001F, Japan) after sputtering gold coating on the surfaces. The specific heat capacity of the composites was measured by laser thermal constant instrument (Model TC-7000H, Japan).

3. Results and discussion

3.1. Characterization of Na_2SO_4 and porous mullite matrix

Fig. 1 shows the TG and DSC curves of the Na_2SO_4 powder. It can be seen that the Na_2SO_4 powder is stable from ambient temperature to high temperature up to 1000 °C. The phase transition temperature of Na_2SO_4 is around 888.85 °C, which corresponds to the melt temperature of Na_2SO_4, and the phase change heat latent is 182.8 J/g. It can be seen that no reaction occurs between Na_2SO_4 and mullite powders below 1000 °C, as illustrated by the XRD analysis results (Fig. 2), and after sintered at 1000 °C for 2 h, the phase compositions of the sample are still Na_2SO_4 (JCPDS: 37-1465) and mullite (JCPDS: 15-0776).

In order to obtain the porous mullite matrix with different pore structures, the freezing temperature and solids loading were changed from -20 °C to -100 °C and 15–40 vol%, respectively, with the fixed freezing time of 1 h, and a series of porous mullite matrix were fabricated by adjusting the corresponding parameters. Fig. 3 shows
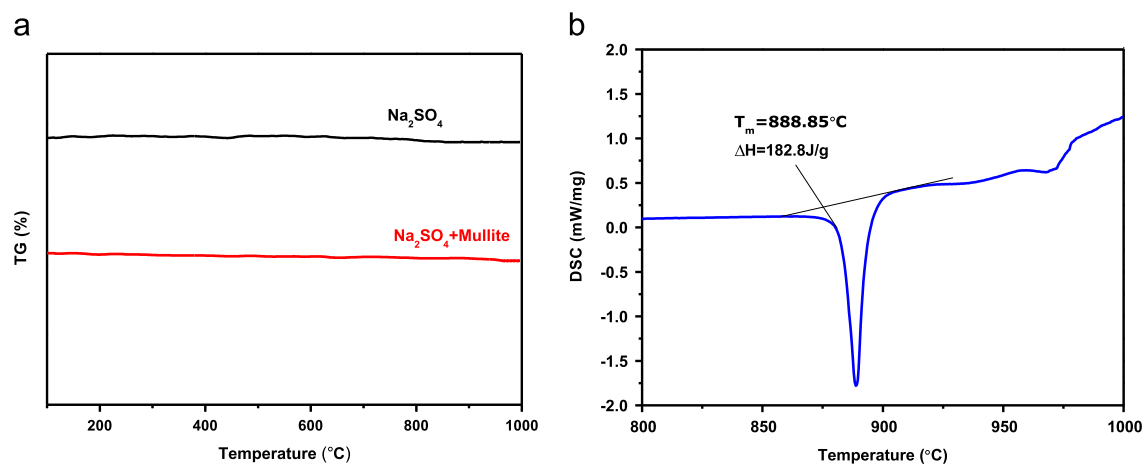

Fig. 1. TG (a) and DSC (b) curve of the Na_2SO_4.