Construction and Building Materials 177 (2018) 184–191

Contents lists available at ScienceDirect

Construction and Building Materials

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

Utilizing blast furnace slags (BFS) to prepare high-temperature composite phase change materials (C-PCMs)

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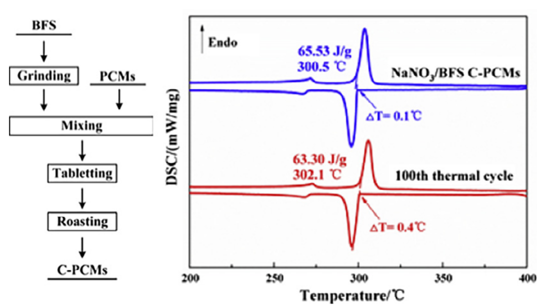
HIGHLIGHTS

- Utilization of BFS to prepare high-temperature C-PCMs was proposed.
- Porous structure and thermostability of BFS were characterized.
- Excellent chemical compatibility between $NaNO_3$ and BFS was demonstrated.
- $NaNO_3$/BFS C-PCMs have good thermal stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 September 2017
Received in revised form 20 March 2018
Accepted 12 May 2018

Keywords:
Blast furnace slag
Composite phase change materials
Thermal energy storage
$NaNO_3$

ABSTRACT

Blast furnace slag (BFS) is a typical solid waste generated in the steel production. Most of previous investigations have reported that the BFS has been used as traditional construction materials (cement, roadbed filling, concrete). In this study, a novel use route for BFS was proposed to prepare high-temperature composite phase change materials (C-PCMs) for thermal energy storage. Three typical inorganic PCMs ($NaNO_3$, Al and Na_2SO_4 with different operating temperature) were blended with the pre-ground BFS to fabricate BFS-based C-PCMs by means of a mixing and sintering process. The results showed that $NaNO_3$ had excellent chemical compatibility with BFS and the prepared C-PCMs had perfect phase change performance. The enthalpies of $NaNO_3$/BFS C-PCMs was 65.53 J/g with melting point 300.5 °C and the super-cooling was only 0.1 °C. Furthermore, the $NaNO_3$/BFS C-PCMs could retain good thermal reliability after 100 thermal cycles, which presented a potential application in the thermal energy storage system. In addition, the morphological structure, thermal reliability and heat transfer property of the $NaNO_3$/BFS C-PCMs were characterised by using SEM, TGA and TG-DSC.

1. Introduction

The energy crisis has aroused a lot of attention with the enormous consumption of fossil fuels. Therefore, many energy utilization systems such as wind power generation [1], solar heating [2] and bootstrap [3] have been developed quickly in the past few decades. However, these systems encounter a severe problem of discordance between energy supply and consumption. Phase change materials (PCMs) can absorb and release a large amount of thermal energy by changing their phases. Applying such PCMs to heat storage system can not only solve above problems, but also improve efficiency of energy utilization. Depending on the type of PCMs, energy storage process could be described as solid-solid, solid-liquid, liquid-gas or solid-gas [4]. Recently, solid-liquid PCMs have

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https://doi.org/10.1016/j.conbuildmat.2018.05.110
0950-0618/

gained much more attention for the high thermal storage density, small temperature variation and volume change during energy storage process. Compared with other PCMs, high temperature molten salts or metals usually exhibit high heat capacity and have the potential for being used as storage media in solar power plants or industrial waste heat recovery system [5].

Nevertheless, the PCMs may leak into their surroundings during heat storage process if they are applied directly without being encapsulated. These disadvantages, as reported, can be overcome by employing porous materials with good thermal stability and thermal conducting property to manufacture composite phase change materials (C-PCMs) [6]. The C-PCMs have much better shape stabilization, and the operating temperature of PCMs could be improved to a higher value than its melting temperature. Metals, ceramics and clay minerals are usually used as structural materials for preparing the C-PCMs. Especially, nickel, copper, kaolin, diatomite, expanded graphite, expanded vermiculite and expanded perlite are common structural materials [7–14]. However, these materials usually need to be pretreated and it will consume much extra energy. Especially for the high-temperature C-PCMs, good oxidation resistance and corrosion resistance were crucial, while the metals and natural clay minerals can't meet the requirement [15]. Therefore, the simplicity and affordability of technologies for production of C-PCMs were very important.

Blast furnace slag (BFS) is a nonmetallic by-product generated in the steel industry, mainly composed of SiO_2, Al_2O_3, CaO and MgO. According to the world mineral production report by the British Geological Survey, the output of pig iron in China was approximately 700 million tonnes (Mts) and the BFS was more than 200 Mts in 2015 [16]. The BFS and other metallurgical slag not only occupied precious lands but also brought great risks for environmental pollution [17,18]. In the past few decades, the BFS was widely used as construction materials, such as Portland cement [19], ceramic wall tiling [20] and lightweight concrete [21]. The usage of BFS contributes to a better abrasion resistance, the long term compression, rheological properties and lower comprehensive environmental impact as well as lower concrete resistance against carbonation [22–24]. In addition, the BFS was also used to fabricate sorbents to remove phosphate, sulphate or heavy metals from aqueous solutions by taking advantage of its porous surface structure [25–27]. S.A. Memon et al. [28] have successfully incorporated paraffin into BFS through vacuum impregnation which showed that BFS can be used to prepare low temperature C-PCMs although the maximum percentage of paraffin retained by BFS was only 9%. Previous study showed that the BFS had a porous structure and adsorption capability [29]. In addition, the BFS has many characters including good corrosion resistance, oxidative resistance, thermal stability under certain condition [30].

Therefore, the BFS was first proposed to used as structural materials for high-temperature C-PCMs by mixing and sintering method in this study. $NaNO_3$, Al and Na_2SO_4 with different operating temperature were selected as the PCMs. Different kinds of BFS-based C-PCMs were characterized by using TG-DSC, XRD, FTIR, SEM, etc. The difference of our work from the previous publications was that we have studied the feasibility of utilizing BFS to prepare high-temperature C-PCMs. The prepared C-PCMs can be used in solar energy storage system, industrial waste heat recovery system and other high temperature fields.

2. Materials and method

2.1. Materials

$NaNO_3$, Al, and Na_2SO_4 powders with 99.9 wt% purity were purchased from Beijing Chemical Reagents Company. The BFS used in this study was supplied by a steel company in Hunan, China, which was cooled and solidified by rapid water quenching. The chemical constituents of the BFS shown in Table 1 included 35.18 wt% CaO, 30.28 wt% SiO_2, 14.17 wt% Al_2O_3 and 13.21 wt% MgO. Fig. 1 shows the XRD pattern of the BFS, indicating that the BFS was a glassy state and the main phases were gehlenite ($Ca_2Al_2SiO_7$), akermanite ($Ca_2MgSi_2O_7$) and forsterite (Mg_2SiO_4).

Table 1
Main constituents of the BFS (wt%).

Component	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	TiO_2
Content	35.18	30.28	14.17	13.21	1.10	0.24

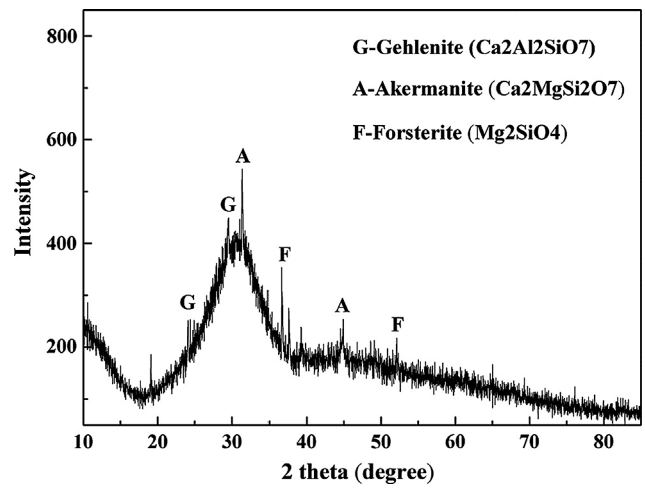

Fig. 1. XRD pattern of the BFS.

The TG-DSC curves of the BFS are plotted in Fig. 2. The TG curve showed that the mass of the BFS almost kept unchanged as the temperature rose from 25 °C to 1000 °C. The DSC curve presented that there was no chemical reaction occurred when temperature was less than 800 °C. However, an obvious exothermic peak was found at 800–950 °C, which was caused by the crystallization reaction of the glassy phase [31].

The raw BFS, generally, had a large grain size, hence, a pre-grinding process was conducted in a ball grinding mill for the BFS until the BFS was ground to 100 wt% less than 74 μm. Then, two samples of raw BFS (Sample #1) and the ground BFS (Sample #2) were characterized. The SEM images showed in Fig. 3 indicated Sample #2 had a more coarse surface with a honeycomb structure consisting of a large number of irregular micropores below 1 micrometer. Fig. 4 presented the adsorption-desorption isotherm curves of the two samples. The results showed that the total pore volume was 0.008 cm^3/g for Sample #1 and 0.025 cm^3/g for Sample #2, respectively, and BET was 3.90 m^2/g for Sample #1 and 10.60 m^2/g for Sample #2.

2.2. C-PCMs preparation and design of thermal cycle test

In this study, the C-PCMs were prepared by a mixed and sintering process. Three typical high-temperature PCMs ($NaNO_3$, Al and Na_2SO_4) with different operating temperature were employed as a thermal storage medium. The experimental

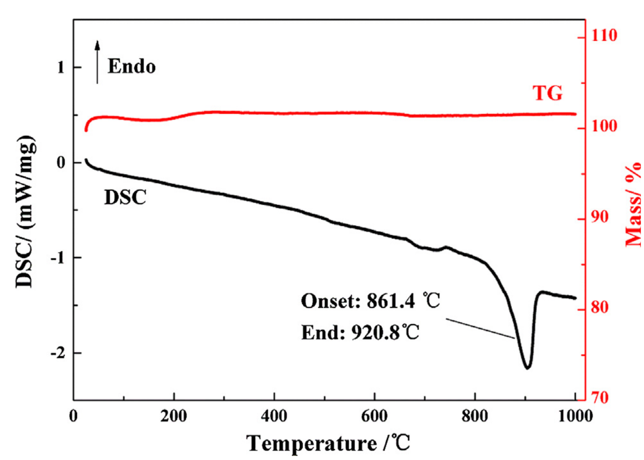

Fig. 2. TG-DSC curves of the BFS.