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Study on preparation of thermal storage ceramic by using clay shale

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ABSTRACT

Shale was used as main raw material for developing thermal storage ceramics. The samples were fabricated via semi-dry pressing followed by pressureless sintering. The result showed that the sample (75% shale, 10% kaolin, 10% potash feldspar and 5% soda feldspar) fired at 1080 °C exhibited the best comprehensive performance. Ocular examination reveals that no cracks were observed after 30 cycle times thermal shock tests (wind cooling from 600 °C to room temperature). The results presented that the high bending strength remained after 20 cycle times thermal shock tests but plummeted at the thirtieth time. Other properties were given as follows: bulk density: 2.60 g/cm^3; thermal conductivity: 2.33 W/(m °C); and heat storage density: 578.50 mJ/m^3. XRD analysis indicated that the quartz and hematite were the main solid phases in the sample. Some isolated pores, quartz crystals, granular hematite crystals and needle-like mullite crystals were observed in the matrix according to the SEM (Scanning Electron Microscope) analysis. More pores were found with temperature rizing according to SEM analysis. The relatively high content of Fe_2O_3 contributed to the formation of the vitreous phase and favored the densification. Overall, the introduction of shale effectively reduced the firing temperature and performed the better thermal storage properties.

1. Introduction

Environment protection and sustainable development are the main trends nowadays. Solar energy, as a renewable and clean energy resource, is increasingly being encouraged and supported by the government as an electricity generating resource. Particularly, with the high performance in energy storage density and energy conversion efficiency, concerns are growing about thermal applications in the solar energy research field [1]. Since the intermittency is one of the main disadvantages in all solar thermal power generations, thermal energy storage becomes kernel in solar thermal application. At present, concrete, rock, molten salt and metal are the common thermal storage materials. However, these materials have their own drawbacks, and such drawbacks either lower the energy conversion efficiency of the power-station or shorten the serving life of the thermal storage device [2].

Ceramic, as an excellent corrosion resistance and high temperature resistance material, is considered as an optimal candidate for solar thermal storage materials. Many efforts [2–7] have been made on the preparation of thermal storage ceramic. The most common ceramic materials applied in solar thermal storage materials are based on alumina, silicon nitride and silicon carbide, because they have high thermal conductivity and heat storage density [8–13]. Many arguments focus on the thermal shock resistance and oxidation resistance of these materials, but these limitations should be addressed as the technology matures [3–6]. However, the chief objection to synthesis those ceramics is their high cost. Some initial attempts [2,7] have been made to lower the cost by using natural clay and minerals as main raw materials. The attempts delivered some significant results. For example, an in-situ synthesized cordierite-andalusite composite was obtained with high performance in thermal shock resistance, but low thermal conductivity and thermal storage. Moreover, the synthesis temperature of such material was very high. [2] However, the high sintering temperature is an obvious cost.

Shale is a type of sedimentary rock and also a fine-grained rock mainly composed of clay mineral flakes. The main chemical compositions are SiO_2 and Al_2O_3. Most shale also contain Fe_2O_3, which makes the products low value-added. Currently, shales are widely applied in shale bricks, shale ceramsites and porous ceramics [14–16]. On the other hand, the high content of Fe_2O_3 promotes the liquid phase formation and the specimen becomes dense. The high bulk density corresponds to high thermal storage density which provides an opportunity to use shale to prepare solar thermal storage materials.

In this study, shale is used as main raw material to prepare the low-cost thermal storage ceramics for the comprehensive utilization. Some other raw materials (kaolin clay, quartz and feldspar)

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are added in order to enhance the bending strength and to improve the bulk density of the samples. The firing properties, phase compositions, microstructure, and thermophysical properties of the ceramics are also examined in this study.

2. Materials and methods

2.1. Materials and sample preparation

The shale, collected from the east of China, was characterized with respect to its chemical, microstructural and mineralogical analysis. The chemical compositions of all the raw materials were analyzed by X-ray fluorescence (XRF) analyzer. The results are listed in Table 1. The data revealed that this shale has a high content of Fe_2O_3 (10.39 wt%). Table 2 lists the batch formulas of the samples. The phase compositions of the shale used in this study were confirmed by X-ray diffraction (XRD). The XRD patterns in Fig. 1 reveal that the main phases of the shale are muscovite, quartz and nacrite (polymorphous with kaolinite). The shale was analyzed by Scanning Electron Microscope (SEM) after Au-Pd coating. Fig. 2 shows the morphology of the shale. Lots of small flakes can be observed and these flakes were stacked together to form agglomerates. The producers and the models of the machines, which were mentioned above, will be given in the next section.

All the raw materials were pre-crushed by different suppliers. The small particles of each material were sifted through a 250 mesh (63 μm) sieve. After that, the raw materials were thoroughly dry-mixed in a ball mill for 30 min according to the batch formula, pelleted by adding 10 wt% water and aged for 24 h. The pre-treated mixtures were pressed into disks (Φ30 mm × 5 mm) and rectangular bars (37 mm × 6.5 mm × 6.5 mm) under a pressure of 60 MPa and 40 MPa respectively by a uniaxial pressing machine (Model NYL-500, Wuxi machine factory, China). All the green bodies were dried at 110 °C for 24 h before experiment and then placed close to a B-type thermocouple in a box-type furnace. The furnace has SiC heating elements, which enabled a maximum temperature of 1300 °C. In order to figure out the firing temperature range and the best comprehensive performance of different samples, the pressure-less firing of compacts (series sample A1–A3) were conducted from 1020 °C to 1200 °C with an interval of 20 °C. The heating rate was with 5 °C/min when the temperature of the furnace was lower than 1000 °C and with 3 °C/min if the temperature of the furnace was past 1000 °C. The samples were soaked for 30 min at every 100 °C and heated up to the maximum temperature with a holding period of 2 h. Because of the good thermal insulating properties of refractory in the furnace, the temperature inside the furnace decreased slowly (less than 5 °C/min). Thus, after that, the program of the furnace was terminated and the samples cooled down with the temperature decreased in the furnace.

2.2. Characterization

The chemical compositions of all the raw materials were determined by X-ray fluorescence (XRF) analyzer (Axios-Advanced, PANalytical B.V., Netherlands). A thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) of different mixtures were performed from ambient temperatures to 1300 °C with a heating rate of 10 °C/min by using a TG/DSC simultaneous thermal analyzer (Netzsch STA 449 F3, German). The phase compositions of raw materials and samples after experiment were identified by X-ray diffraction (XRD). D/MAX-IIIA diffractometer (Rigaku Corporation, Japan) equipped with Cu Kα (λ=1.54 Å) radiation was employed. The scanning angle was from 5° to 80° (2θ). The microstructures and morphologies of the shale and the samples were observed by the JSM-5610LV Scanning Electron Microscope (SEM, Model JSM-5610LV, Jeol., Japan). To reveal the morphology of the crystalline structure, the sample was etched with 5 wt% HF (hydrofluoric acid) solution for 60 s to remove the glassy phase in the samples. Element mapping in the area of the sample were given by Field Emission Scanning Electrons Microscope (QUANTA FEG 450, US).

To evaluate the firing behavior of the samples, three parameters, water absorption rate (Wa), open porosity (Pa) and bulk density (Db) were tested by using a digital display ceramic water absorption apparatus (Model TXY, Xiangyi Machine Co., Ltd., Xiangtan, China) and an electronic analytical balance (Model AUY120, Japan). The tests of thermal shock resistance of the samples were carried out in a box furnace. A cycle of thermal

Table 2
The batch formula of samples (wt%).

Sample no.	Shale	Kaolin	Potash feldspar	Soda feldspar	Quartz
A1	65	10	10	5	10
A2	75	10	10	5	0
A3	80	5	10	5	0

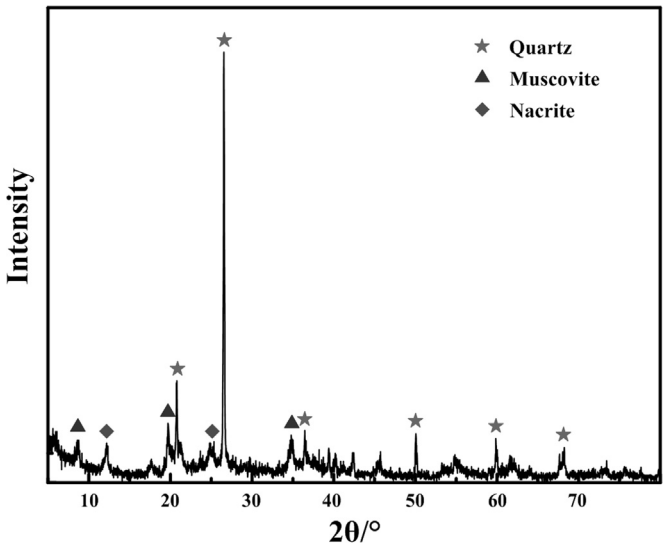

Fig. 1. The XRD pattern of the shale.

Table 1
Chemical composition of the raw materials (wt%).

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Others	I.L.	Total
Shale	51.96	22.15	10.39	0.78	1.07	1.45	2.37	0.08	0.55	9.21	100.00
Kaolin	54.60	41.30	1.46	0.00	0.15	0.22	2.01	0.19	0.07	0.00	100.00
Potash feldspar	66.36	17.64	0.12	0.00	0.54	0.00	10.31	3.89	0.76	0.38	100.00
Soda feldspar	66.52	18.06	0.06	0.02	0.94	0.21	0.33	12.48	0.37	0.41	100.00
Quartz	98.35	0.89	0.08	0.05	0.04	0.00	0.17	0.00	0.13	0.30	100.00

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