Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Rapid preparation of CaB_6 powders via induction heating from low-cost colemanite and petroleum coke

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ARTICLE INFO

Keywords:
Induction heating
Petroleum coke
Colemanite
CaB_6
Morphology

ABSTRACT

Calcium hexaboride (CaB_6) powders were successfully prepared at 1650 °C for 20 min by induction heating technology using low-cost natural colemanite and petroleum coke as starting materials. The effects of synthesis temperature, holding time, raw material ratio and milling duration on the formation of CaB_6 were investigated. The synthesis temperature and time for CaB_6 were reduced versus traditional carbothermal reduction methods. The final products obtained after repeated HCl pickling, washing, and drying have good crystallization with a uniform particle size distribution. This rapid preparation of CaB_6 can be ascribed to the rapid formation of the B_2O_3-CaO molten liquid phase that is conducive to the synthesis reaction under induced electromagnetic field. Thus, induction heating technology is a time-saving and energy efficient way to prepare CaB_6.

1. Introduction

Calcium hexaboride (CaB_6) is a typical alkaline-earth hexaboride that has received considerable attention for its superior properties, such as high melting point (2235 °C), high hardness (27 GPa), high chemical stability, high electrical/thermal conductivity, low expansion coefficient, and stable specific resistance [1,2]. These excellent properties of CaB_6 enable its utilization as a neutron-absorbing material in nuclear reactors, a deoxidation agent in the production of oxygen-free copper, an additive for refractory materials, and others [3,4].

Current synthesis methods prepare CaB_6 powders via direct reaction of elemental powders, borothermal reduction, metallothermic reduction, carbothermal reductions, mechanical alloying and low-temperature solid phase reaction [5–9]. Of these, carbothermic reduction is the most extensively used in industry. According to Yildiz [10], CaB_6 powders were synthesized via carbothermal reduction in a traditional tube furnace using colemanite and petroleum coke as raw materials. The CaB_6 initially formed at 1700 °C after a holding time of 180 min and the synthetic reaction will not be completed until the synthesis temperature reaches 2000 °C. In addition, B_4C reduction is believed to be another popular method for synthesis of CaB_6 because it involves relatively low reaction temperatures and high product purity [11]. Zheng [12] reported that CaB_6 was synthesized under vacuum at temperatures over 1400 °C using $CaCO_3$, B_4C, and carbon powders as starting materials. However, the B_4C reductant is often commercially synthesized by the carbothermal reduction of boron oxide at ~2000 °C. Therefore, the ultra-high synthesis temperatures and expensive boron sources are major obstacles to the large-scale industrial production and application of CaB_6.

Natural colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$) is a cost-effective calcium-containing borate mineral and a promising candidate material for synthesizing CaB_6. It is not only a boron source but also a calcium source. Recently, many noval methods such as microwave heating [13–15], spark plasma sintering (SPS) [16–18], combustion synthesis [19], and induction heating [20–22] have been applied to prepare ceramic powders. Among them, induction heating technology (IHT) has drawn particular attention because of its outstanding advantages such as fast heating and cooling rates, facile control, high thermal efficiency, safety, cleanliness, and so on. A series of ceramic materials and non-oxide powders including $MoSi_2$ [23], WC-TiC [24], 2Ti-ZrO_2 [25], $MoSi_2$-SiC [26], Al_2O_3-Al_2SiO_5 [27], HfB_2 [28], and TiC [29] have been successfully prepared by IHT. However, similar detailed studies of CaB_6 powder synthesis using IHT are rarely reported.

Here, CaB_6 powders were prepared via a carbothermal reduction route in an induction furnace using colemanite and petroleum coke as raw materials. The effects of the induction heating temperature, holding time, initial raw materials composition, and milling duration on the phase composition and morphology evolution of the products were investigated.

2. Experimental procedures

Turkish colemanite (Hainuosen Industry & Trade Co. Ltd., Tsingtao, China) and petroleum coke (Double Yisheng Industry & Trade Co. Ltd.,

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https://doi.org/10.1016/j.ceramint.2018.05.004
Received 6 December 2017; Received in revised form 16 April 2018; Accepted 1 May 2018
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Table 1
Chemical analysis of the colemanite and petroleum coke.

Raw material	Element (wt%)								
Colemanite	B_2O_3	CaO	SiO_2	MgO	SrO	Na_2O	Al_2O_3	Fe_2O_3	IL
	37.32	29.58	4.86	1.9	0.58	0.09	0.1	0.13	24.82
Petroleum coke	C	Ad	Vd	H_2O	S	K_2O	Na_2O	CaO	
	88.98	0.064	10.96	4.44	0.56	0.004	0.012	0.07	

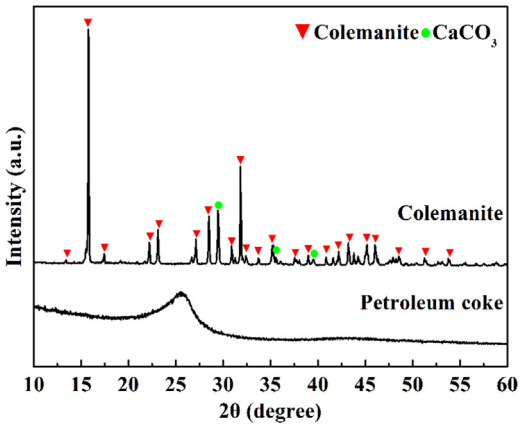

Fig. 1. The XRD patterns of the colemanite and petroleum coke.

Fusun, China) were used as the starting materials. The chemical analysis and XRD patterns of the Turkish colemanite and petroleum coke are presented in Table 1 and Fig. 1, respectively. The major crystalline phase in colemanite is $2CaO{\cdot}3B_2O_3{\cdot}5H_2O$ containing traces of $CaCO_3$ as an additional crystalline component (Fig. 1). The broad peak in the XRD pattern of petroleum coke indicates the amorphous nature of the carbon.

The CaB_6 powders were prepared in accordance with Eq. (1) [11]. The colemanite and petroleum coke starting materials with a particle size smaller than 0.074 μm were first dried at 110 °C for 24 h in a drying oven. In order to study the influence of raw material ratio on the products, a series of powder mixtures were prepared from colemanite and petroleum coke with different n_p:n_c molar ratios, and the batch compositions are given in detail in Table 2.

$$2(2CaO{\cdot}3B_2O_3{\cdot}5H_2O) + 12C \rightarrow 2CaB_6 + 2CaO + 9CO_2 + 3CO + 10H_2O \quad (1)$$

To evaluate the effect of milling time, the powder mixtures were thoroughly mixed in alcohol in a high energy ball mill for 1, 3, and 6 h, respectively, using tungsten carbide balls as the ball mill medium. The mixed powders were uniaxially pressed into cylinders 20 mm in diameter and 10 mm in height under a pressure of 100 MPa. After drying at 110 °C for 24 h, the samples were loaded into a graphite crucible, and the crucible was subsequently introduced into an induction furnace (ZGIL0.01-50-4B, Jinzhou Electric Furnace Co. Ltd., China). The synthesis reaction proceeded at 1200–1700 °C with an interval of 100 °C before 1600 °C and 50 °C after 1600 °C and held for 10–30 min in an Ar atmosphere (purity 99.9%). After cooling to room temperature, the products were removed and ground into powders. The synthesized powders were black/gray and were purified with 4 mol L^{-1} hot HCl, and then washed several times with hot distilled water until no Cl^- remained. The final products were dried at 110 °C for 24 h and then characterized.

Table 2
Batch composition (wt%).

Sample No.	Colemanite	Petroleum coke	n_p:n_c
P0	90.2	16	6:1
P1	90.2	18.7	6.5:1
P2	90.2	21.3	7:1
P3	90.2	24	7.5:1

p: petroleum coke, c: colemanite.

Thermogravimetric (TG) and differential scanning colorimetry (DSC) analysis of the powder mixture of colemanite and petroleum coke were performed with a simultaneous thermal analyzer (Netzsch-STA 449C) by heating to 1100 °C at a heating rate of 10 °C/min in Ar. The crystalline phases of the synthesized products were identified by X-ray diffraction (XRD) analysis using a Philips X'Pert PRO diffractometer (PANalytical, NETHER-LAND, 40 kV, 40 mA). Spectra between 10° and 70° (2θ) were recorded at 40 mA and 40 kV using Cu Kα radiation (λ = 0.1542 nm). The scan rate was 2 °/min with a step of 0.05. ICDD cards No. 31-0254, 32-0155, 18-0279, 48-1885, and 35-0798 were used to identify CaB_6, CaB_2O_4, $Ca_2B_2O_5$, $Ca_3B_2O_6$, and B_4C, respectively. MDI Jade 6.0 software was used to calculate the lattice constant. The Rietveld refinement method was used to calculate the relative contents of the crystalline phases in the samples. The morphologies were observed with a field emission scanning electron microscope (FE-SEM, Nova400NanoSEM, PHILIPS, NETHERLANDS, 15 kV) and a transmission electron microscope (TEM, JEM-2100UHRSTEM, JEOL, Japan, 200 kV). For each sample, at least 300 particles from the SEM images were selected to evaluate the mean particle size and particle size distribution via Image Pro Plus (IPP) software.

3. Results and discussion

3.1. Phase evolution processes

The TG-DSC analysis curves of the mixed powders of colemanite and petroleum coke in argon are presented in Fig. 2. Two obvious endothermic peaks at 389.6 °C and 405 °C are seen in the DSC curve—these can be interpreted as the loss of crystal water in colemanite. The dehydration of colemanite was previously reported to occur at 398 °C and 402 °C [30], which is basically consistent with our findings. A gentle exothermic peak is seen from 500° to 700°C. This indicates that petroleum coke experiences a thermal decomposition-condensation

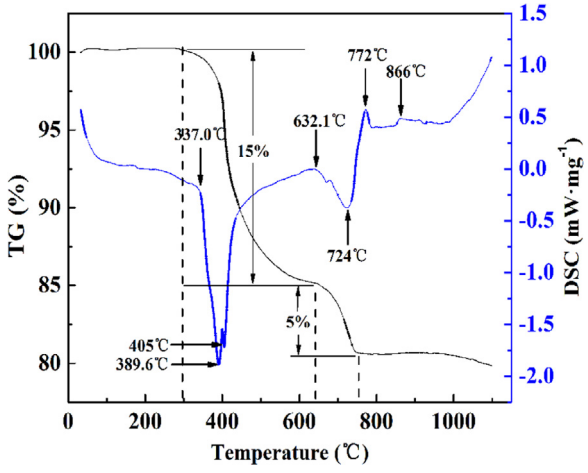

Fig. 2. TG-DSC curves of the mixture of colemanite and petroleum coke.

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