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Short communication

Reaction mechanism and size control of CaB_6 micron powder synthesized by the boroncarbide method

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Abstract

Reaction synthesis mechanism of Calcium hexaboride (CaB_6) powder was investigated by using $CaCO_3$-B_4C-C system. Micron-scale $CaCO_3$ and B_4C powders were used as main raw materials. The synthesized powder was determined by X-ray diffraction, showing no left reactants if enough $CaCO_3$ was added to compensate the evaporation of calcium atoms at high temperature. The powder morphology was observed through SEM. The synthesized CaB_6 powder formed hard agglomerates which consisted of cubic CaB_6 crystallites when the reaction completely finished. Reaction process was illustrated indicating it was a solid-state reaction occurred from B_4C surface to the centre. The dry high-energy ball milling was used to investigate the influence of ball-milling time on the shape and size of powder particles. The particle granularity was measured by laser size analysis method. It is obvious that the particles were refined greatly after ball milling for 8 h. However, the CaB_6 powder could not been refined markedly after 16 h. Finally, optimized parameters for size controlling were given in this paper.

Keywords: Calcium hexaboride; Boroncarbide method; Solid-state reaction mechanism; High-energy ball milling

1. Introduction

Calcium hexaboride (CaB_6), one of the 2A group alkaline earth borides, is a good candidate for abrasive, tool and structural ceramics with excellent properties such as high melting point (2373 K), high hardness (27 GPa) and high chemical stability [1–3]. CaB_6 also showed its usage as a good deoxidant in copper metallurgy and an additive stuff in the high temperature antioxidant materials [4,5]. In recent years, the study about CaB_6 focused on its physical properties including thermoelectricity and ferromagnetism [6–9]. Ott et al. [10] have found that $La_{0.01}Ca_{0.99}B_6$ has a very high Curie temperature, a value close to 900 K has been reported, which pave the way for its use in the spin electronics. All of these theoretical investigations have expanded the application of CaB_6.

The preparation of CaB_6 micron and submicron powder by several methods has been studied, such as direct combination of the elements [11], boronthermal reduction of CaO [12], boroncarbide method [13], and by reaction of $CaCl_2$ with $NaBH_4$ in an autoclave [14], and so forth [15]. Up till now, the research about this material synthesis has been focused on the optimum for technological parameters as well as phase composition and element content. However, there was no clear description about the morphology and the formation process. In this paper, boroncarbide method was adopted to synthesize the CaB_6 powder. Micron-scale $CaCO_3$ and B_4C were used as main raw materials. The formation mechanism of CaB_6 powder was provided through analyzing and comparing the morphologies of the above CaB_6 powder and that prepared by different size $CaCO_3$. The influence of ball milling on the shape and size of CaB_6 powder was also investigated, which provided a foundation for size controlling to obtain fine and high dispersive CaB_6 powder.

2. Experimental

Boroncarbide method [13] was employed to prepare CaB_6 powder according to the following equation:

$$3B_4C + 2CaCO_3 + C = 2CaB_6 + 6CO\uparrow$$

The microstructures of main raw materials $CaCO_3$ and B_4C were provided in Fig. 1, which average particle sizes are

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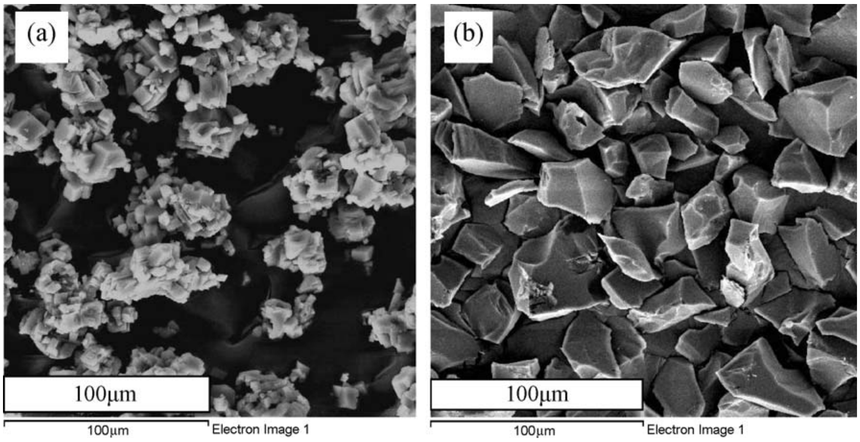

Fig. 1. Microstructures of the main raw materials to synthesize CaB_6 (a) $CaCO_3$ and (b) B_4C.

28.3 μm and 29.2 μm, respectively. Noticeably, most $CaCO_3$ particles existed as aggregates composed by small spheral particles which size varied from 1 μm to 10 μm. The edges of B_4C particles were sharp and surfaces were smooth as shown in Fig. 1(b).

The reaction was carried out using a vacuum resistance furnace (model: SL-63-78, Shanghai Electric Machinery Group, P.R. China) at 1400 °C for 3 h which working vacuum degree is 6.73×10^{-2} Pa. The mixed raw materials were put into a high pure graphic crucible and then placed in the batch which size is Φ140 mm × 160 mm. The reactants were heated at a rate of 30 °C min^{-1} using high pure graphite as heater material and furnace cooling. Then the production was purified by hydrochloric acid pickling and distilled water to remove superfluous transitional phases. After drying in vacuum at 60 °C for 4 h, the final gray powder product was obtained.

X-ray diffractometer (XRD, model: D/max-rB, Rigaku, Japan) was employed to analyse the obtained powders with Ni filtered Cu Ka radiation ($V = 40$ kV, $I = 100$ mA, $\lambda = 0.154056$ nm) at a scanning rate of 4 deg/min. Scanning Electron Microscope (SEM, model: S-2500, Hitachi, Japan) was employed to observe the morphology. The obtained powder was put in a planet type high-energy ball milling machine (model: QM-1SP, Nanjing University Instrument Plant, P.R. China) with working rotational speed of 380 rpm and a rubbing medium of carnelian ball. The ratio of balls to materials is 3:1, and the ball-milling time was 2.5 h, 5 h, 8 h and 16 h and 24 h, respectively. The particle granularity was measured using Laser size analyzer (model: LS13320, Beckman Coulter Inc., USA).

3. Results and discussion

3.1. XRD analysis of the synthesized powder

In consideration to the molar ratio of the synthesis formula and the volatility of $CaCO_3$ at high temperature, two times of stoichiometric content $CaCO_3$ was added to modify the reactant ratio in order to compensate the evaporation of $CaCO_3$ during reaction process. The XRD patterns of the result powder before and after purification were shown in Fig. 2. It is found that $Ca_3B_2O_6$ as the superfluous transitional phase which formed due to extra $CaCO_3$ added existed in the production before acid treatment. However, this phase was easy to be removed by hydrochloric acid and only CaB_6 left in the ultimate obtained powder.

3.2. Morphology of the obtained powder

The SEM photographs of the obtained powder were given in Fig. 3. It can been seen from Fig. 3(a) that the size distribution and the general shape of CaB_6 particles were similar to that of B_4C as shown in Fig. 1(b), except that the shape of CaB_6 was ball-like and different from B_4C with sharp edges. The average particle CaB_6 size was 16.92 μm measured by Laser size analyzer. Higher magnification observation revealed that every CaB_6 particle contained small crystallites of cubic shape, as shown in Fig. 3(b). The average crystallite size was about 3 μm.

Such morphology shown in Fig. 3(b) was very similar to that of CaB_6 powder synthesized by nanoscale $CaCO_3$ and 29.2 μm B_4C [16], in which most CaB_6 big particles were also composed by small particles (about 2–3 μm). It is concluded that under the condition of employing the same size B_4C, the morphologies of production were nearly the same, proving CaB_6 morphology was mainly predominated by B_4C.

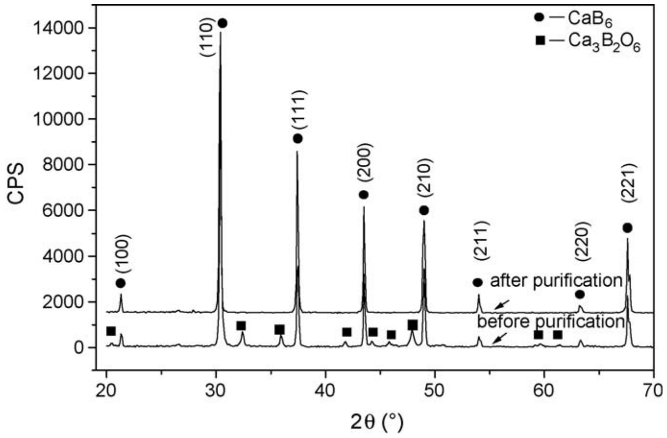

Fig. 2. XRD pattern of the synthesized powder by boroncarbide method.

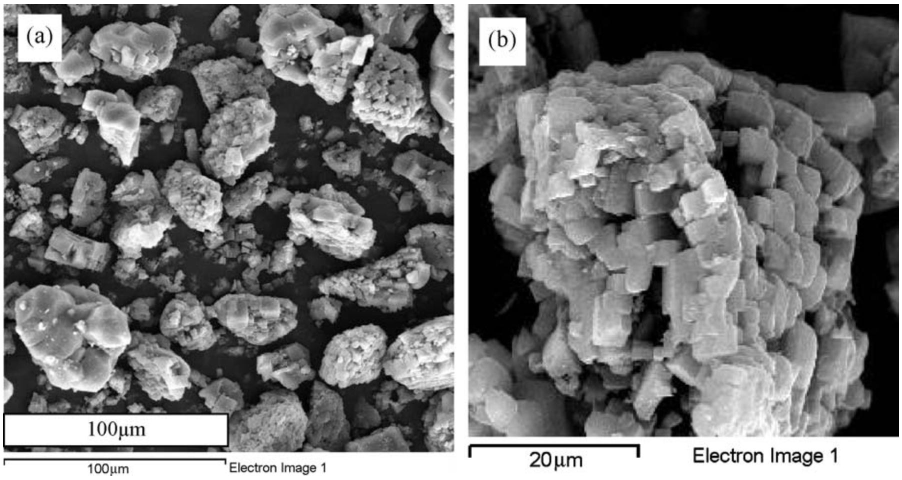

Fig. 3. SEM photographs of synthesized CaB_6 (a) and the higher magnification (b).

The schematic illustration for the structure evolution of CaB_6 increasing with temperature was given in Fig. 4, corresponding to the morphology formation in Fig. 3(b). It can be supposed that the $CaCO_3$ particles adhered on the large B_4C particles. First $CaCO_3$ was decomposed to CaO and CO_2 gas above 800 °C. Then the transitional phases $Ca_3B_2O_6$ and CaB_2C_2 first formed [13] at the joint of CaO with B_4C. Accompanied with temperature increased, the reaction occurred from the surface to the centre continuously. Then the forming transitional phases turned to CaB_6 and CO gas. This reaction mainly happened at about 1200 °C. The ultimate agglomerates were strongly bonded with solid bridges and when the reaction was completed finished at 1400 °C, these solid bridge were all CaB_6, as shown in Fig. 3.

According to the analysis above, the size of raw material B_4C was an important factor to predominate the ultimate CaB_6 size. That is, when smaller B_4C was employed, the prepared CaB_6 would be also fined. This has been proved by other experimental results [16].

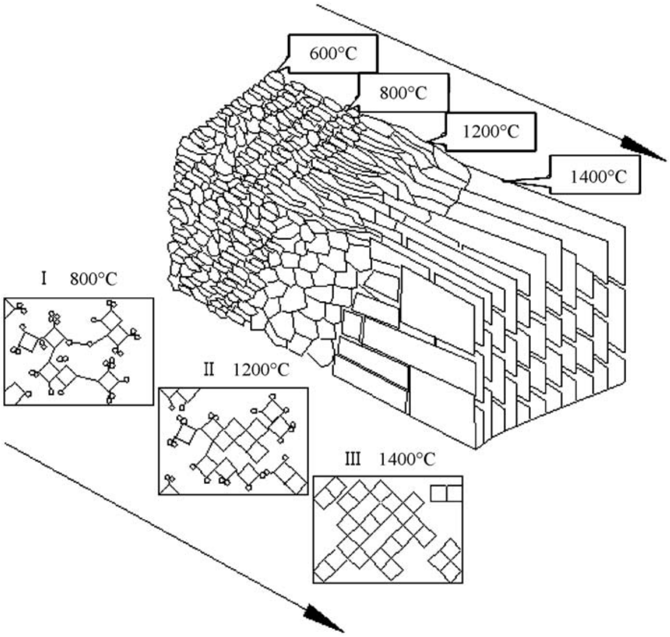

Fig. 4. Schematic illustration for structure evolution of reaction synthesized CaB_6 powder.

3.3. *Influence of ball-milling time on the powder morphology*

Besides selecting the raw materials size, the high-energy ball milling is also an effective means to control particle granularity. Fig. 5 gave the particle size of CaB_6 powder with average original size 10.28 μm after high-energy ball milling for different time 2.5 h, 5 h, 8 h, 16 h and 24 h. The powder particles were refined continuously accompanied with milling time, especially below 8 h, which average size was 4.97 μm, decreased about 52% compared with original size. However, the milling effect was not so obvious after 8 h. The average size was 4.61 μm for 16 h while 4.36 μm for 24 h as seen in Fig. 5.

Fig. 6 gave the size distribution curves of CaB_6 after ball milling for different time. When the ball-milling time was less than 8 h, the drastic bounces and frictions between carnelian balls and mill pot made CaB_6 aggregates turn to small particles or rip big particle. But when balling for 8 h, 16 h and 24 h, the position of peaks signed by dashed line 1 in Fig. 6 was the same,

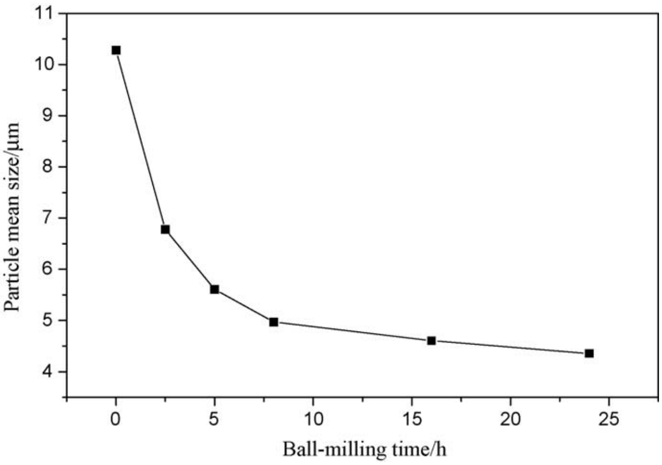

Fig. 5. Average particle sizes of CaB_6 powders curves vs. the time of high-energy ball milling.

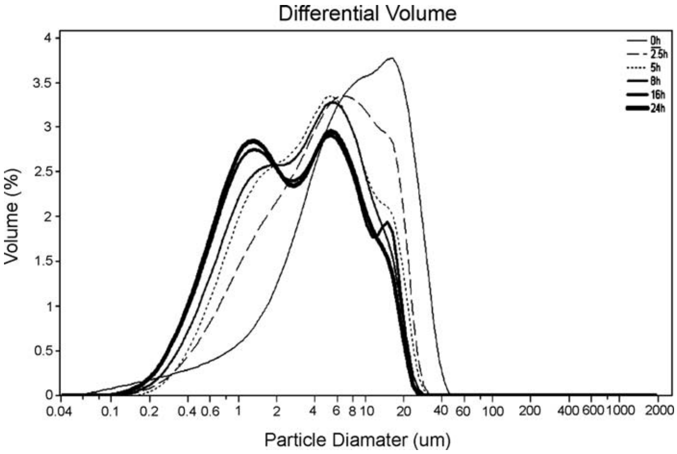

Fig. 6. Particle size distribution curves of CaB_6 powder after high-energy ball milling for different time.

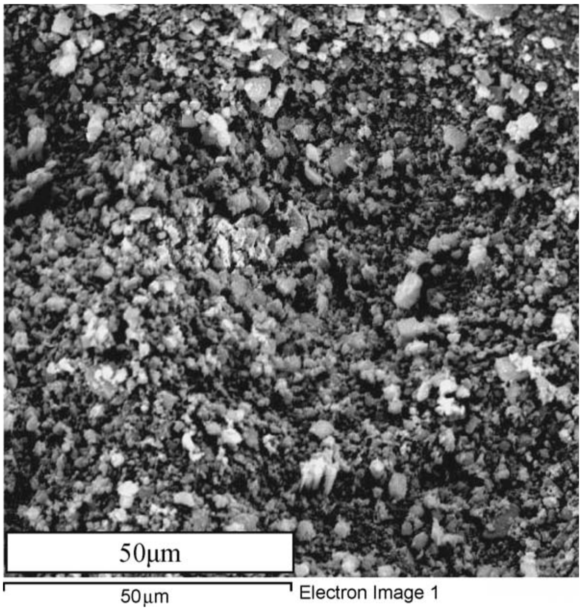

Fig. 7. SEM photograph of CaB_6 powder after ball milled for16 h.

proving 8 h is enough to break up aggregates. The peaks signed by dashed line 2 in the curves of 16 h and 24 h showed that the main work was to further refine small particles during this period. The two curves of 16 h and 24 h were very similar except for the peaks signed by dashed line 3, illuminating the refining process was very difficult after 16 h. According to the measurement, about 50 vol% of the powder particles were less than 2.60 μm in the CaB_6 powder milled for 16 h and 24 h. Fig. 7 shows the microstructure photograph of CaB_6 powder after ball milled for 16 h, showing dispersive and fine powder could be prepared.

4. Conclusions

(1) CaB_6 powder without impurities could be synthesized by boroncarbide method under the condition that enough superfluous raw material $CaCO_3$ was added to compensate the evaporation of calcium atom at high temperature.

(2) The mechanism of the CaB_6 formation was put forward to illustrate the reaction process. The characteristics of raw material B_4C played an important role in the synthesized CaB_6 powder.

(3) CaB_6 agglomerates could be deagglomerated and the size decreased due to the high-energy ball milling treatment. Ball milling for 16 h is an optimum parameter to achieve fine and dispersive CaB_6 particles.

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