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Original Research Paper

Effect of calcium carbonate particle size on formation and morphology of calcium hexaboride powder synthesized from condensed boric acid-poly(vinyl alcohol) product

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ABSTRACT

Calcium hexaboride (CaB_6) powder was synthesized by carbothermal reduction via the transient boron carbide (B_4C) formation starting from a condensed boric acid (H_3BO_3)-poly(vinyl alcohol) (PVA) product. The effect of the size of calcium carbonate ($CaCO_3$) particles on the formation behavior of CaB_6 and the obtained particle morphology was investigated in this study. CaB_6 powder was prepared using $CaCO_3$ powders with microsize or nanosize particles. The CaB_6 formation reaction was accelerated at lower temperature and shorter heat treatment time when using nanosize $CaCO_3$ particles. The complete formation of CaB_6 was achieved at 1400 °C for 3 h in an Ar flow. Furthermore, CaB_6 powder with nanosize particles was obtained. The precursor powder obtained using nanosize $CaCO_3$ particles transiently formed fine B_4C and calcium borate particles, which are reactive species of CaB_6, leading to the facile formation of fine CaB_6 particles.

1. Introduction

Calcium hexaboride (CaB_6), which is an alkaline-earth hexaboride, has attractive properties (high melting point, high hardness, and high chemical stability) and specific functions (good electrical properties and high neutron-absorbing capability). The boron carbide (B_4C) method, which is the reduction of a metal oxide using B_4C, is useful for the synthesis of CaB_6 powder [1–3]. In contrast, we reported a novel low-temperature synthesis method for CaB_6 powder without the use of B_4C as a raw material [4]. CaB_6 is formed by the carbothermal reduction of calcium oxide (CaO) and boron oxide (B_2O_3) (CaO–B_2O_3-C system; Eq. (1)) starting from a condensed boric acid (H_3BO_3)-poly(vinyl alcohol) (PVA) product via transient B_4C formation at a low temperature.

$$CaO + 3B_2O_3 + 10C \rightarrow CaB_6 + 10CO \quad (1)$$

This method is based on our low-temperature synthesis method for B_4C powder using a polyol [5–10]. The formation of a borate ester (B—O—C) bond by a dehydration condensation reaction between H_3BO_3 and polyol leads to the homogeneous dispersion of the boron source and carbon source at the molecular level. B_4C precursor consisting of B_2O_3 and carbon components is prepared from a condensed H_3BO_3-polyol product by thermal decomposition in air. The carbon content in the B_4C precursor (C/B_2O_3 ratio) is controllable by varying the thermal decomposition conditions in air. Within the obtained B_4C precursor powder, a B_2O_3/carbon structure with a homogeneous arrangement at the nanometer scale is spontaneously formed. The B_4C precursor prepared from a condensed H_3BO_3-PVA product consists of homogeneously dispersed nanosize B_2O_3 particles and a carbon matrix [4,6,8,9]. The diffusion of reacting species becomes facile with increased contact area of the B_2O_3 and carbon components, enabling synthesis of B_4C powder at a low temperature (1200–1250 °C). The B_4C precursor is mixed with calcium carbonate ($CaCO_3$) powder, followed by heat treatment in an Ar flow. Thereby, CaB_6 powder was synthesized at 1400 °C for 10 h [4]. The formation of CaB_6 by the previous carbothermal reduction without the use of B_4C as a raw material requires the high synthesis temperature (above 1700 °C) owing to the high transient formation temperature of B_4C (above 1500 °C) [11]. In contrast, the transient formation of B_4C occurs at a low temperature of 1200 °C for our approach, and thus the synthesis temperature of CaB_6 powder becomes low (1400 °C) [4]. This demonstrates that our low-temperature synthesis method for B_4C powder is a key for the low-temperature synthesis of CaB_6 powder without the use of B_4C as a raw material.

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The morphology of particles is important for ceramic engineering. For the synthesis of CaB_6 powder by the B_4C method, the relative sizes of B_4C and $CaCO_3$ particles have a dominant effect on the size of CaB_6 particles [2]. When B_4C particles are much coarser than $CaCO_3$, the formed CaB_6 exists as aggregates. In contrast, when the size of B_4C particles is near to $CaCO_3$, the formed CaB_6 is dispersive. In this study, we focused on the size of $CaCO_3$ particles in order to control the morphology of obtained CaB_6 particles in our low-temperature synthesis method without the use of B_4C as a raw material. CaB_6 powder was synthesized using the condensed H_3BO_3-PVA product and $CaCO_3$ powders with microsize or nanosize particles. The effect of the $CaCO_3$ particle size on the CaB_6 formation behavior and the obtained particle morphology synthesized using the CaO–B_2O_3-C system via the transient B_4C formation starting from the condensed H_3BO_3-PVA product was investigated.

2. Experimental procedure

2.1. Materials

PVA was supplied by Kuraray Co., Ltd., Japan, for which the degrees of polymerization and hydrolysis were 310 and 98.3 mol %, respectively. H_3BO_3 (99.5%) and $CaCO_3$ (99.5%) powders were purchased from Wako Pure Chemical Industries, Ltd., Japan, and were used as received. The commercial $CaCO_3$ powder has microsize particles, and is called micro-$CaCO_3$. $CaCO_3$ powder with nanosize particles (nano-$CaCO_3$) was synthesized by a reaction in the calcium hydrate ($Ca(OH)_2$)-carbon dioxide (CO_2)-water system using ultrasonic irradiation [12]. $Ca(OH)_2$ (Wako, 96.0%) was dissolved in deionized water to prepare a 2.5 wt% $Ca(OH)_2$ suspension. CO_2 gas (500 ml/min) was bubbled into the $Ca(OH)_2$ suspension using a glass filter (pore size: 40–50 μm) under ultrasonic irradiation using a Hielscher UP100H ultrasonic processor (100 W, 30 kHz) for 8 min. The precipitate was filtered and dried into powder form. The obtained powder was a mixture of $CaCO_3$ and $Ca(OH)_2$. Nano-$CaCO_3$ was obtained by washing this mixture in deionized water under ultrasonic irradiation for 30 min to remove $Ca(OH)_2$, followed by filtering and drying.

2.2. Synthesis of CaB_6 powder

A condensed product was prepared by the dehydration condensation of H_3BO_3 and PVA with a H_3BO_3:PVA (hydroxyl group of PVA) molar ratio of 1:4. PVA was dissolved in deionized water (ca. 5 wt%) by stirring and heating in a water bath at 80 °C for 1 h. Then, H_3BO_3 was dissolved in deionized water (ca. 1.5 wt%) and added dropwise to the PVA solution. The blended solution was heated until the water evaporated, followed by drying at 120 °C in air. The resulting product was a white solid. The condensed product was placed in an alumina crucible after grinding and thermally decomposed at 600 °C for 3 h in air. The thermal decomposition time was determined with the aim of achieving a C/B_2O_3 ratio of 3.3 [4], which is the stoichiometric C/B_2O_3 ratio for Eq. (1). The thermally decomposed product was mixed with $CaCO_3$ powder and ground with an agate mortar and pestle. The amount of $CaCO_3$ added was chosen to satisfy the ratio $CaCO_3$:B_2O_3 = 1:3 on the basis of the stoichiometric ratio ($CaCO_3$ (CaO):B_2O_3 = 1:3) for Eq. (1). Two types of precursor powder (a mixture of the thermally decomposed product and micro-$CaCO_3$ (P-micro) or nano-$CaCO_3$ (P-nano)) was placed in a graphite boat and heated at 600–1400 °C for 0–10 h in an Ar flow (200 ml/min) at a heating rate of 10 °C/min.

2.3. Characterization

X-ray diffraction (XRD) measurements of the $CaCO_3$ powders and the products were performed using a powder X-ray diffractometer (Rigaku RINT-Ultima III) operated at 40 kV and 30 mA with monochromatized CuKα radiation. Scanning electron microscopy (SEM) observations of the morphologies of the $CaCO_3$ powders and the products were conducted with a Hitachi S-4100 field-emission scanning electron microscope operated at 15.0 kV. The samples were coated with Pt-Pd before the observation. The specific surface area of $CaCO_3$ powders was evaluated by the BET method (Quantachrome NOVA-TOUCH). Thermogravimetric (TG) measurements of $CaCO_3$ powders were carried out using a Rigaku Thermo Plus TG8120. Heating scans were performed up to 900 °C at a rate of 10 °C/min under an Ar flow (100 ml/min).

3. Results and discussion

The XRD patterns and SEM images of commercial micro-$CaCO_3$ and synthesized nano-$CaCO_3$ are shown in Figs. 1 and 2, respectively. Both samples were single-phase $CaCO_3$ (calcite). Aggregates of microsize primary particles (D_{50} = 5.5 μm) were observed for micro-$CaCO_3$ (Fig. 2(a)). On the other hand, the aggregates of nanosize primary particles (D_{50} = 44 nm) were observed for nano-$CaCO_3$ (Fig. 2(b)). The specific surface areas of micro-$CaCO_3$ and nano-$CaCO_3$ were 0.70 and 38.85 m^2/g, respectively. This indicates the formation of nanosize $CaCO_3$ particles with high specific surface area. Thus, these $CaCO_3$ powders were used for the synthesis of CaB_6 powder to investigate the size effect of $CaCO_3$ particles.

Fig. 3 shows the XRD patterns of products obtained by heat treatment of the precursor powders at 600–1200 °C for 5 h in an Ar flow. The formation of B_4C is closely related to the morphology of the precursor powder [6,7,9,10]. Thus, the morphology of the intermediate products was identified by SEM observation. Fig. 4 shows the SEM images of products obtained by heat treatment of the precursor powders at 600–1200 °C for 5 h in an Ar flow. Peaks attributed to $CaCO_3$ were observed in the XRD patterns of the products prepared at 600 °C (Fig. 3). $CaCO_3$ particles were dispersed on the surface of the B_4C precursor (B_2O_3/carbon structure) in the pro-

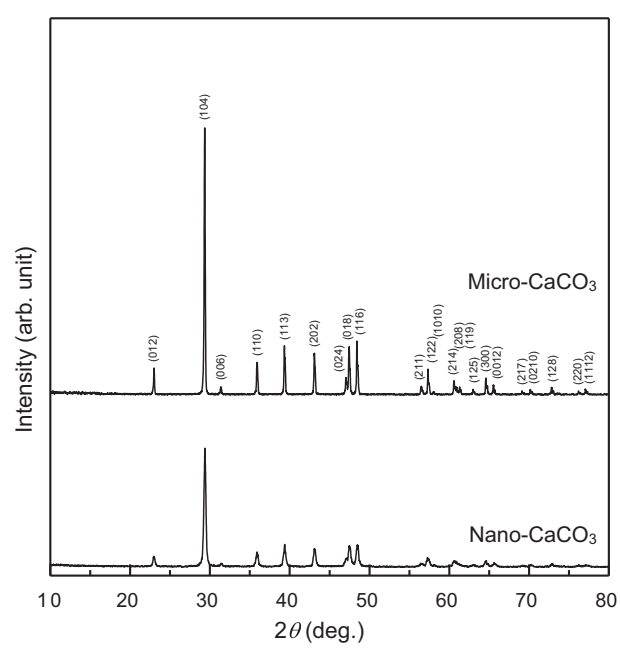

Fig. 1. XRD patterns of micro-$CaCO_3$ and nano-$CaCO_3$.