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Effects of addition of seed grains on morphology and yield of boron carbide powder synthesized by carbothermal reduction

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Abstract

B_4C powders were synthesized by carbothermal reduction using mixtures of B_2O_3, carbon black, and B_4C seed grains, and the effects of addition of B_4C seed grains on the morphologies and yields of the synthesized B_4C powders were investigated. The B_4C particles added to the starting mixture of B_2O_3 and C acted as seeds for crystal growth, resulting in an improvement in the B_4C yield. The B_4C yields of the products obtained by heat-treatment at 1450 °C increased with increasing amounts of B_4C seed grains. In the case of heat-treatment at 1550 and 1750 °C, the B_4C yields of the products increased with the amount of seed grains up to a certain B_4C-seed/B_2O_3 ratio, and then decreased slightly above that ratio. The B_4C yields improved significantly compared with those obtained under the same conditions without seeds in the case of heat-treatment at 1450 °C (B_4C-seed/B_2O_3 ratio > 0.05) and at 1550 °C. Truncated octahedral B_4C particles could be synthesized selectively by addition of small B_4C seeds and heat-treatment at 1450–1750 °C. The particle size of the synthesized B_4C decreased with increasing amounts of seed grains. In the case of addition of smaller amounts of seeds, the B_4C particles synthesized at 1450 and 1550 °C were polyhedral, and the morphologies of the B_4C particles synthesized at 1750 °C were dendrite-like and polyhedral. In the case of addition of larger amounts of seeds, the morphologies of the B_4C particles synthesized at 1450–1750 °C were mainly truncated octahedral.

Keywords: A. Grain growth; B. Crystal morphology; D. Carbides

1. Introduction

Boron carbide (B_4C) has excellent properties such as a light weight, superior hardness, high elastic modulus, high thermal stability, and large neutron absorption cross-section, therefore B_4C has been used for armor materials, wear-resistance parts, grinding media, and neutron absorbers of control rods for nuclear fission reactors [1]. In addition, its application in fast-moving parts of semiconductor manufacturing equipment has been studied in recent years because of its superior rigidity.

Microstructural control of sintered materials and powder, such as control of grain size and morphology, is required to improve the sinterability and properties of ceramics. In the synthesis of B_4C powder, changes in morphology and particle size have been reported by several researchers, for example, by carbothermal reduction [2–6] of mixtures of B_2O_3 and carbon, sol–gel methods [7–9], and borate precursor methods [10–12]. However, there have been very few studies giving details of the effects of synthesis conditions on the morphologies and particle sizes of the synthesized B_4C powders and their growth mechanisms, because these studies have mainly focused on reduction of residual carbon and lowering the heat-treatment temperature of B_4C synthesis. In our previous work, the effects of heat-treatment temperature and composition of the starting mixture of B_2O_3 and carbon black on the morphology of B_4C particles were studied, and it was clarified that the heat-treatment temperature and the composition affected the number of B_4C nuclei and the morphology of the B_4C grains, respectively [6]. The B_4C

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powder obtained in the previous work consisted of various kinds of polyhedra and had a large particle size.

In this study, carbothermal reduction using a mixture of B_2O_3 and carbon black with B_4C seed grains is used for the synthesis of B_4C powder, and the effects of seed grains on the yield and morphology of the synthesized B_4C powder are investigated. It was shown that the morphology of the synthesized B_4C particles was mostly truncated octahedral, and the particle size of the powder was controlled by the amount of seeds. Furthermore, the yield of B_4C improved significantly as a result of the addition of seed grains.

2. Materials and methods

B_2O_3 (boron trioxide, 97% purity, Kanto Chemical Co., Inc., Japan) and carbon black (Asahi Thermal, average particle size: 80 nm, Asahi Carbon Co., Ltd., Japan) were used as the starting materials. Commercial B_4C powders with different particle sizes were used as seed grains. B_4C powders with a particle size of 0.8 μm (#1200, Denka-Boron, Denki Kagaku Kogyo Kabushiki Kaisha, Japan) and with a particle size of 10 μm (Kojundo Chemical Laboratory Co., Ltd., Japan) are designated as small seed grains and large seed grains, respectively [shown in Fig. 1(a) and (b)]. The B/C ratio of the mixture was fixed to be $B_2O_3/C = 1.66$ by weight, which is the stoichiometric composition of the carbothermal reduction (reaction 1). The amount of seed grains in the mixture was changed from a weight ratio of $B_4C\text{-seed}/B_2O_3 = 0.01$ to $B_4C\text{-seed}/B_2O_3 = 0.20$. B_2O_3, carbon black, and B_4C powder were mixed in ethanol using a silicon carbide mortar for 1 h. The powder mixtures were put in graphite crucibles separately, and heat-treated at 1450–1750 °C for 3 h at a heating rate of 30 °C/min in an Ar flow (2 L/min) using a graphite heater furnace (Hi-Multi 5000, Fuji Dempa Kogyo Co., Ltd., Japan). The crystalline phases of the powders synthesized in this study were identified by X-ray diffractometry (XRD; PW-1700, Philips, The Netherlands) using monochromated CuKα radiation. The particle morphology was observed with a scanning electron microscope equipped with a field-emission gun (FE-SEM; S-4800, Hitachi High-Technologies Corp., Japan).

$$2B_2O_3 + 7C \rightarrow B_4C + 6CO \quad (1)$$

The B_4C product yield was estimated from the amount of synthesized B_4C using Eq. (2)

$$B_4C\ \text{yield} = \frac{F_f W_f - F_i W_i}{W_{B4C,th}} \quad (2)$$

where F and W are the B_4C content and the weight of the product, respectively. The subscripts i and f indicate the B_4C content and weight of the product before and after the heat-treatment. $W_{B4C,th}$ is the ideal weight of B_4C synthesized using the mixture. The amount of B_4C was estimated from the XRD peak intensity of the products using a standard calibration curve. The volatilization loss of B_2O_3 from the mixture during heat-treatment was estimated from the amount of synthesized B_4C and Eq. (3), which is a modification of reaction (1)

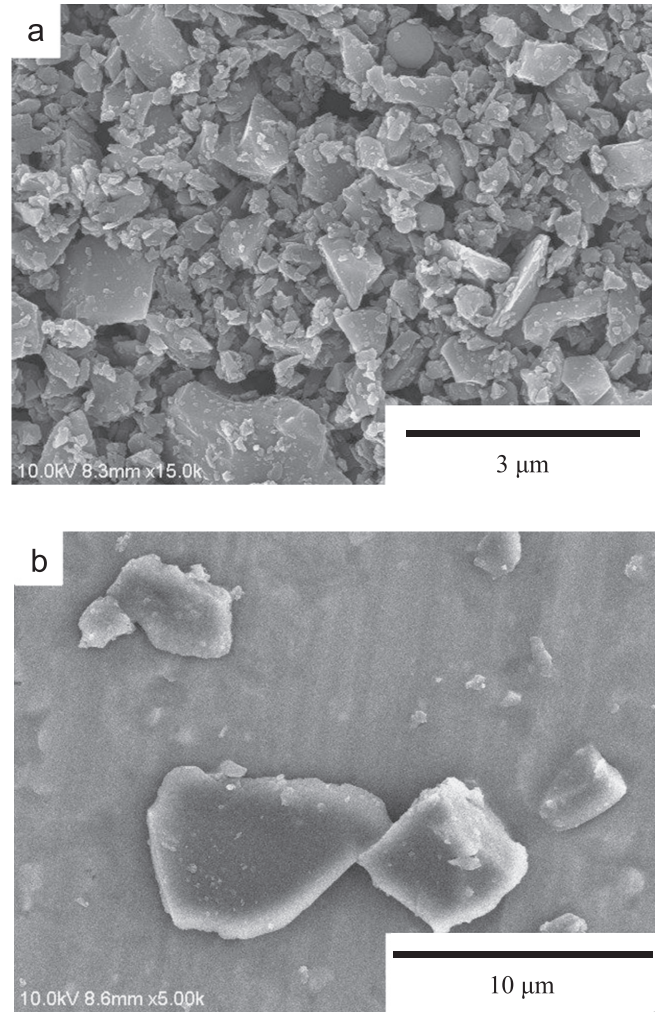

Fig. 1. B_4C seed grains used in this study: (a) small grains and (b) large grains.

$$2B_2O_3 + 7C \rightarrow xB_4C + 6xCO\uparrow + 2(1-x)B_2O_3\uparrow + 7(1-x)C \quad (3)$$

where x (B_4C yield) is less than 1.

3. Results and discussion

3.1. Crystalline phase and B_4C yield in reaction products

Fig. 2 shows XRD patterns of the powders heat-treated at 1550 °C with $B_4C\text{-seed}/B_2O_3 = 0.01–0.20$, using small B_4C seed grains. For comparison, the XRD pattern of a synthesized powder without seed addition is also shown in Fig. 2. The XRD analysis shows that the powder products obtained by heat-treatment at 1550 °C consisted of B_4C and C. The intensity of the strongest peak, at $2\theta = 26°$, derived from C in the products, decreased with increasing amounts of B_4C seed grains up to $B_4C\text{-seed}/B_2O_3 = 0.10$, and the intensity of the C peak for $B_4C\text{-seed}/B_2O_3 = 0.20$