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

Tomohiro Kobayashi[a,*], Katsumi Yoshida[b], Toyohiko Yano[b]

[a]Department of Nuclear Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan
[b]Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

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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

*Corresponding author. Tel.: +81 3 5734 3082.
E-mail address: kobayashi.t.bc@m.titech.ac.jp (T. Kobayashi).

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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)

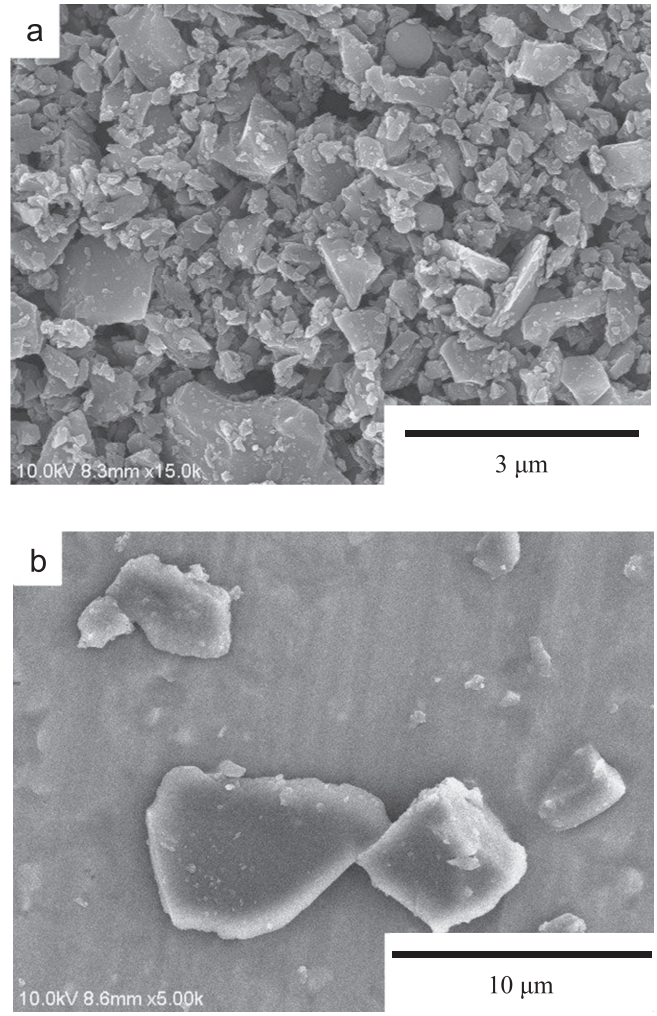

Fig. 1. B_4C seed grains used in this study: (a) small grains and (b) large grains.

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

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 $B_4C\text{-seed}/B_2O_3=0.20$

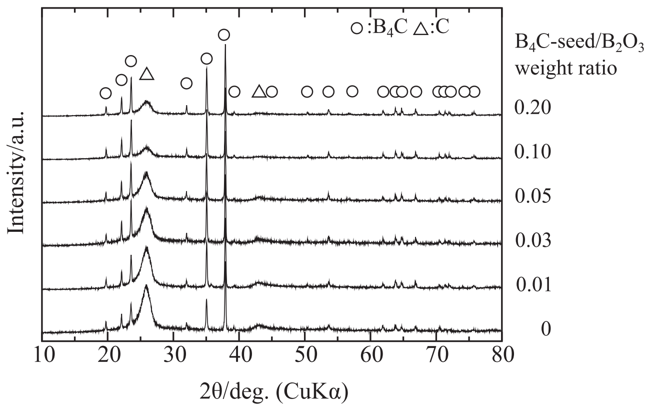

Fig. 2. X-ray diffraction patterns of products obtained by heat-treatment at 1550 °C using mixtures with B_4C-seed/B_2O_3=0–0.20 (small B_4C seed grains).

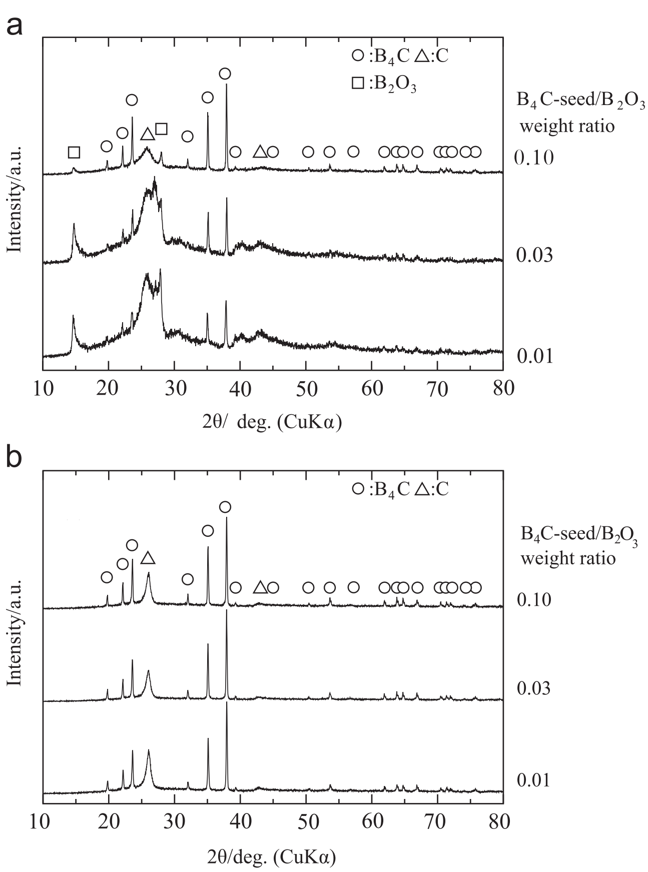

Fig. 3. X-ray diffraction patterns of products obtained by heat-treatment at (a) 1450 °C and (b) 1750 °C using mixtures with B_4C-seed/B_2O_3=0.01, 0.03, and 0.10 (small B_4C seed grains).

was almost the same as that for B_4C-seed/B_2O_3=0.10. Fig. 3(a) and (b) shows the XRD patterns of the powders heat-treated at 1450 and 1750 °C with B_4C-seed/B_2O_3=0.01, 0.03, and 0.10, using the small B_4C seed grains. Residual B_2O_3 existed in the product for all compositions after heat-treatment at 1450 °C, and the intensity of the peaks from B_2O_3 gradually decreased with increasing amounts of seed grains. The powder heat-treated at 1750 °C for mixtures of all compositions consisted of B_4C and C. Up to B_4C-seed/B_2O_3=0.03, the intensity of the C peak in the products decreased, and beyond 0.03, it was almost constant.

Fig. 4(a) shows the changes in B_4C yield for the powder heat-treated at 1450–1750 °C as a function of the amounts of small and large seed grains. These values did not include the amount of seed grains added to the raw mixture. The B_4C yield of the powder heat-treated at 1450 °C increased with increasing amounts of B_4C seed grains (small). The B_4C yields of the powders heat-treated at 1550 °C and 1750 °C increased with the amount of small seed grains up to a certain B_4C-seed/B_2O_3 ratio, and then decreased slightly above that ratio. The B_4C-seed/B_2O_3 ratio for the maximum B_4C yield moved to lower seed contents with increasing heat-treatment temperature, as shown in Fig. 4(a). Furthermore, at a heat-treatment temperature of 1450 °C, a certain amount of B_4C seeds was necessary to improve the B_4C yield compared to the yield of the powder obtained without seeds. The effect of seed addition on

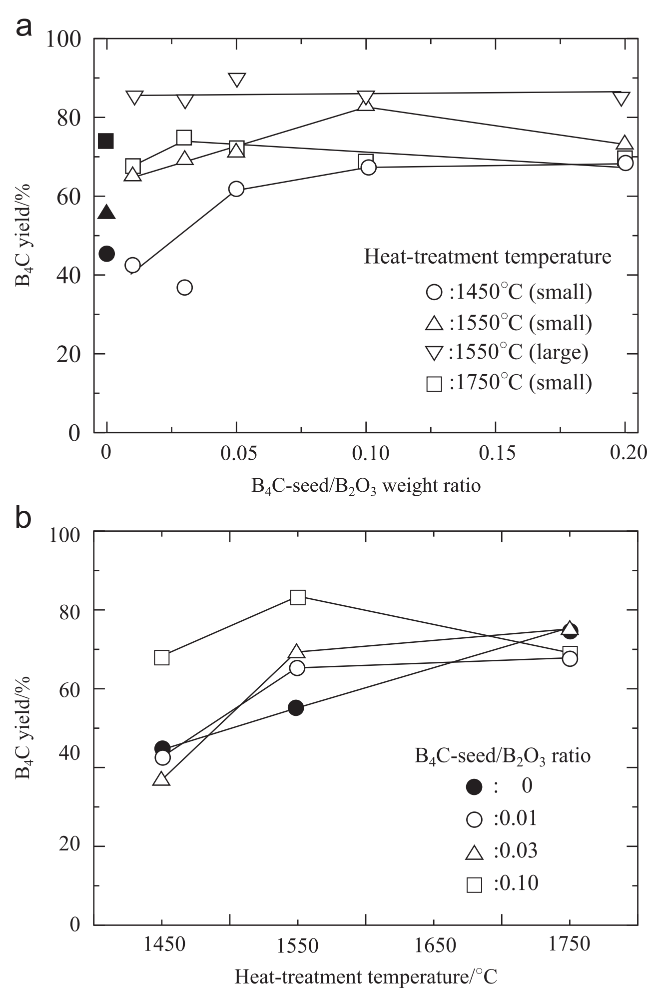

Fig. 4. (a) Changes in B_4C yields of products synthesized at 1450 (○), 1550 (△), and 1750 °C (□) (small seeds), and 1550 °C (▽) (large seeds) as a function of B_4C-seed/B_2O_3. Filled symbols indicate B_4C yields of the products without seeds synthesized at 1450 (●), 1550 (▲), and 1750 °C (■). (b) Changes in B_4C yields of the products synthesized using mixtures with B_4C-seed/B_2O_3=0 (●), 0.01 (○), 0.03 (△), and 0.10 (□) as a function of the heat-treatment temperature (small B_4C seed grains).

improvement of the B_4C yield disappeared for heat-treatment at 1750 °C. As shown in Fig. 4(a), the yields of products obtained by heat-treatment at 1550 °C using larger seeds varied from 83% to 89%, regardless of the amount of seeds added. These values were slightly higher than that of the product obtained using smaller seeds with B_4C-seed/B_2O_3 = 0.10, in spite of the low number density of the seeds. No effect of seed number density on the B_4C yield is seen in the case of large seeds. Fig. 4(b) shows changes in the B_4C yields of the powder heat-treated with various B_4C-seed/B_2O_3 ratios (small seed grains) as a function of the heat-treatment temperature. The amounts of B_4C in the products using mixtures with B_4C-seed/B_2O_3 = 0, 0.01, and 0.03 increased with increasing heat-treatment temperature. In the case of B_4C-seed/B_2O_3 = 0.10, the B_4C yield of the product heat-treated at 1750 °C was lower than that of the powder heat-treated at 1550 °C. The effect of seed addition on the B_4C yield was significant for heat-treatment at 1550 °C.

The calculated volatilization losses of B_2O_3 from the mixtures during heat-treatment (1550 °C and 1750 °C) are shown in Fig. 5. The calculated volatilization losses consist of B_2O_3 gas and B–O gas species generated by reactions of B_2O_3 and B_4C [13]. The calculated losses of the products obtained using large seeds are also shown in Fig. 5, and were almost constant, regardless of the amount of large seeds added. As shown in Figs. 4(a) and 5, the yields of the products obtained by heat-treatment at 1550 °C with B_4C-seed/B_2O_3 = 0.01 and 0.03, using small seeds, were lower than those of the products obtained by heat-treatment at 1750 °C using the same compositions, and the calculated losses from the mixtures during heat-treatment at 1550 °C were higher than those of the mixtures during heat-treatment at 1750 °C. Beyond B_4C-seed/B_2O_3 = 0.10, the changes in the yields and the calculated losses showed the opposite tendency. In contrast, in the case of synthesis from a B_2O_3–C mixture without seeds, the calculated volatilization losses of B_2O_3 decreased with increasing heat-treatment temperature [6]. These results suggest that the increase in the losses at higher B_4C-seed/B_2O_3 ratios and heat-treatment temperature may be caused by generation of B_2O_2 gas by a reaction between B_4C and B_2O_3 [13], and B_2O_2 gas does not contribute to the production of B_4C.

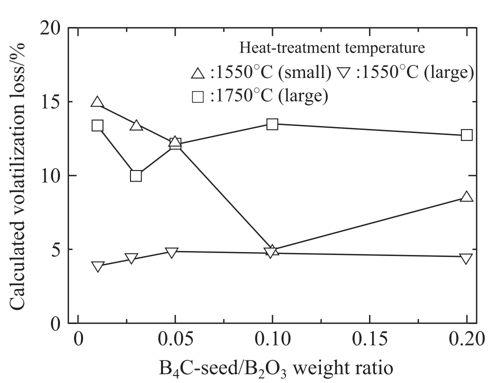

Fig. 5. Calculated volatilization losses of B_2O_3 from mixtures with various B_4C-seed/B_2O_3 ratios during heat-treatment at 1550 (△) and 1750 °C (□) (small seeds), and 1550 °C (▽) (large seeds).

3.2. *Effect of amount of seed grains on morphology of synthesized B_4C*

Fig. 6(a)–(e) is SEM images of B_4C powders synthesized at 1550 °C from mixtures with B_4C-seed/B_2O_3 ratios of 0.01–0.20, using small seeds. The primary B_4C particles aggregated with each other and formed large agglomerations (tens of micrometers) for B_4C-seed/B_2O_3 ratios of 0.01–0.20. In the case of B_4C-seed/B_2O_3 = 0.01, small B_4C particles, as well as larger B_4C particles, were observed in the product, and the B_4C powder consisted of polyhedral particles, such as truncated octahedra and twinned octahedra. Beyond a B_4C-seed/B_2O_3 ratio of 0.03, the morphology of the B_4C powder was mainly truncated octahedral, and rarely octahedral. The edges of several B_4C particles in the product of B_4C-seed/B_2O_3 = 0.20 were rounded. The particle size of the synthesized B_4C powder decreased slightly with increasing amounts of added seeds. In previous work, the morphology of B_4C powder synthesized at the same temperature, using a B_2O_3–carbon black mixture without B_4C seed grains, was a mixture of various kinds of polyhedra and the particle size was much larger (~44 μm) than that of the B_4C powder obtained in this study [6]. This is the first report of selective synthesis of truncated octahedral B_4C particles.

Fig. 6(f) shows a SEM image of the B_4C powder synthesized at 1550 °C, using large seed gains, with B_4C-seed/B_2O_3 = 0.10. The particle size of the synthesized B_4C powder was about 10 μm, and the morphology was mainly truncated octahedral. The morphology of the B_4C synthesized using large seed grains was same as that using small seed grains; however, the particle size of the powder using large seeds was much larger than that of the powder using small seeds, although the weight ratios of B_4C-seed/B_2O_3 were the same. The SEM observations show that the particle size of the synthesized B_4C powder decreased with increasing added amounts of B_4C seed grains. When the B_4C-seed/B_2O_3 weight ratios were the same, the particle size of the synthesized B_4C depended on the particle size of the B_4C seed grains. The number density of the B_4C seeds is very low in the case of large seeds, and a larger number of B_4C nuclei may deposit on each seed grain compared with the case of small seeds with large surface areas, so the particle size of the synthesized B_4C increases significantly.

Fig. 7 shows schematic illustrations of the B_4C particles observed in the product synthesized at 1550 °C with B_4C-seed/B_2O_3 = 0.10 (large seeds). The sketches in the upper row and the lower row are of the same B_4C crystals viewed from different directions. Fig. 7 shows that if two or four planes of the octahedron [Fig. 7(a)] become larger, and are located on the opposite sides of a crystal, the octahedron can be viewed as a plate-like [Fig. 7(b)] or rod-like particle

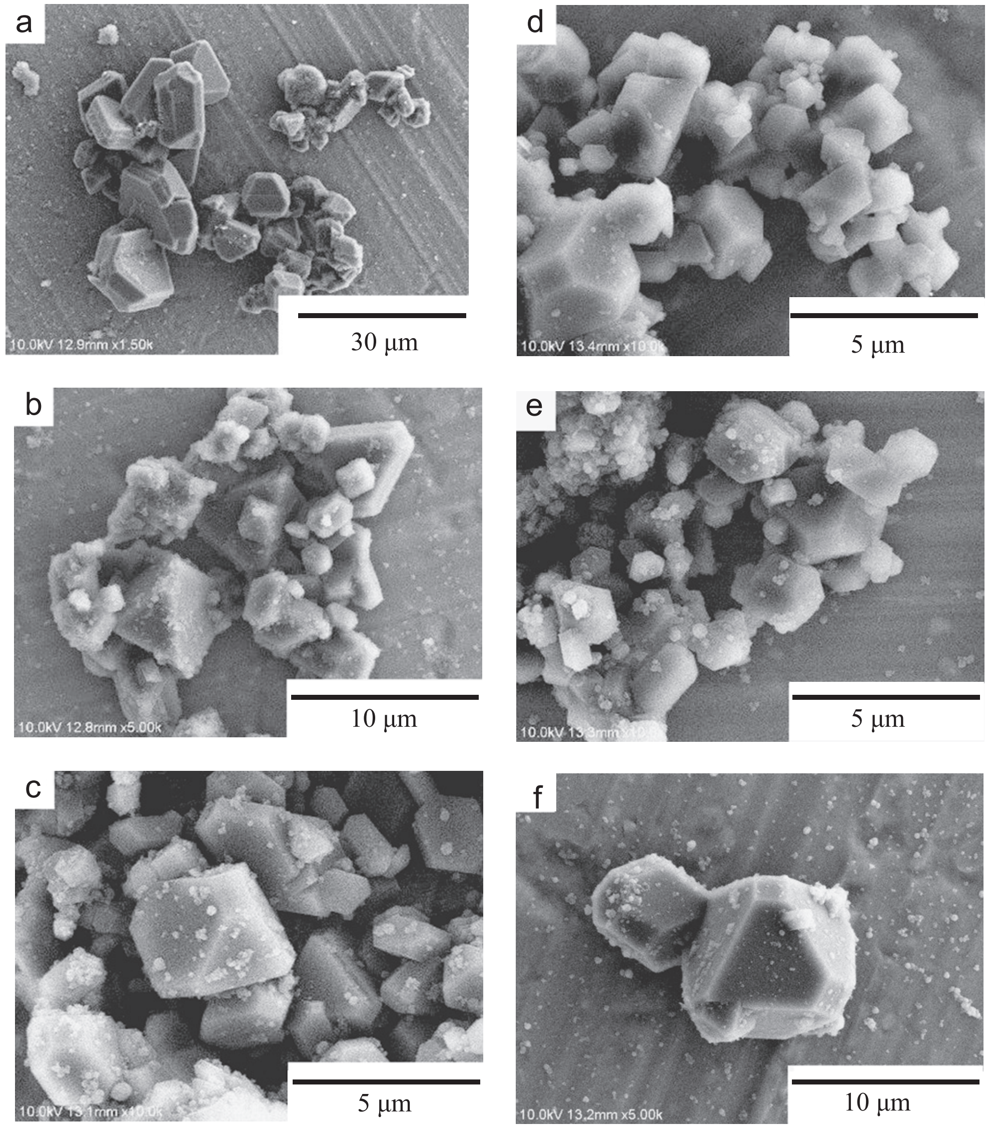

Fig. 6. Scanning electron micrographs of B_4C powders synthesized at 1550 °C using mixtures with B_4C-seed/B_2O_3=(a) 0.01, (b) 0.03, (c) 0.05, (d) 0.10, and (e) 0.20 (small B_4C seed grains), and (f) with B_4C-seed/B_2O_3=0.10 (large B_4C seed grains).

[Fig. 7(c)]. The synthesized B_4C particles consisted mainly of truncated octahedra, and rarely of thick or thin plate- and rod-like particles. This change in crystal habit may be caused by differences in the growth conditions and morphologies of the seeds. It is known that calcite and hematite, whose crystal systems are the same as that of B_4C, also show similar polyhedral and plate-like particles [14]. In addition, the planes with smaller surface areas in these B_4C particles vanished and the edges were crossed, so the morphology of the B_4C crystal could be viewed as rhombohedral.

3.3. *Effect of heat-treatment temperature on morphology of synthesized B_4C*

Fig. 8(a)–(c) shows SEM images of the B_4C powder synthesized at 1450 °C using mixtures with B_4C-seed/B_2O_3=0.01, 0.03, and 0.10 (small seed grains). The morphologies of the synthesized B_4C particles with B_4C-seed/B_2O_3=0.03 and 0.10 were mainly truncated octahedral. The B_4C powder with B_4C-seed/B_2O_3=0.01 consisted of polyhedral particles and the particles were larger than those of the B_4C powders with B_4C-seed/B_2O_3=0.03–0.20. As indicated by the existence of residual B_2O_3 in the products obtained by heat-treatment at 1450 °C [Fig. 3(a)], a number of carbon deposits were also observed by SEM as small particles of size less than 0.3 μm. The morphologies of the B_4C particles synthesized at 1450 °C and 1550 °C using a mixture with B_4C-seed/B_2O_3=0.01 frequently showed twins, and the percentage of twinned particles in the synthesized B_4C increased with increasing particle size of the synthesized B_4C powder. When a crystal grows in a highly supersaturated solution, twins are easily generated, since a large number of nuclei are present on a seed grain. In the crystal growth of B_4C from B_4C seeds,

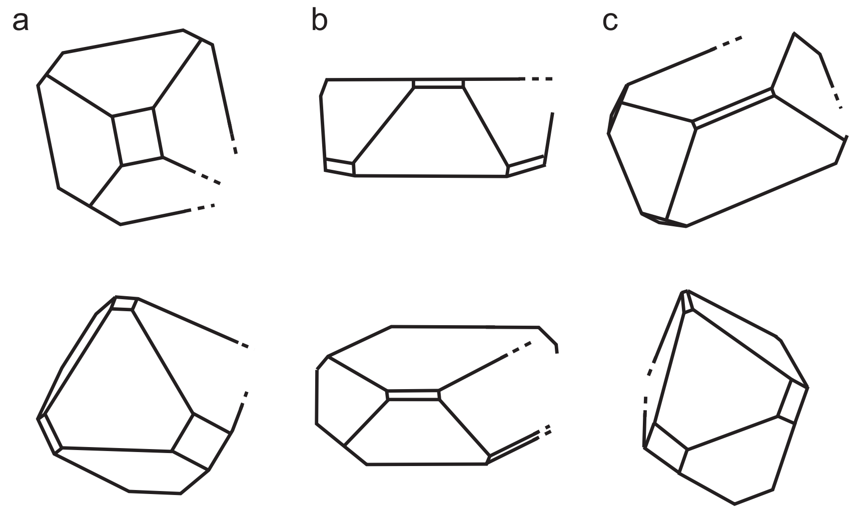

Fig. 7. Schematic illustrations of synthesized B_4C particles observed in the product obtained by heat-treatment at 1550 °C with B_4C-seed/B_2O_3=0.10 (large B_4C seed grains).

the amount of adsorbed B_4C nuclei per seed grain increases with decreasing B_4C-seed/B_2O_3 weight ratio, and this condition corresponds approximately to supersaturation of B_4C nuclei in liquid B_2O_3.

SEM images of B_4C powders synthesized at 1750 °C using mixtures with B_4C-seed/B_2O_3=0.01, 0.03, and 0.10 (small seed grains) are shown in Fig. 8(d)–(f). In the case of B_4C-seed/B_2O_3=0.01, two types of particle morphology were observed. One was dendrite-shaped aggregates of small B_4C particles, which was similar to the morphology of B_4C particles synthesized from B_2O_3–carbon black without seeds at the same temperature, reported in a previous study [6]. The high nucleation growth rate at this temperature should result in rapid production of numerous B_4C nuclei, resulting in relatively small primary particles [3,6]. The other was large polyhedral B_4C particles. The B_4C particles synthesized using a mixture with B_4C-seed/B_2O_3=0.03 mainly consisted of truncated octahedral grains. Beyond B_4C-seed/B_2O_3=0.10, the edges of the synthesized B_4C particles were rounded. A similar phenomenon was observed in our previous study for B_4C particles synthesized using excess B_2O_3 [6]. This morphology change depending on the B_4C-seed/B_2O_3 weight ratio corresponds to the increase in the calculated volatilization loss (Fig. 5). The change in morphology and suppression of the yield of B_4C in the products synthesized at higher B_4C-seed/B_2O_3 weight ratios could therefore be caused by reaction between B_4C and B_2O_3. In addition, when the starting composition of the mixture using large seeds was changed to a B_2O_3-rich composition (B_2O_3/C weight ratio=2.9, B_4C-seed/B_2O_3=0.10), and the mixture was heat-treated at 1750 °C for 3 h, the edges of the B_4C particles became rounded and the morphology was very different from that of the product from the mixture with B_2O_3/C=1.66 (Fig. 9).

4. Conclusions

B_4C powders were synthesized by a carbothermal reduction method 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 yields and morphologies of the 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 yields. The powder products obtained by heat-treatment at 1550 and 1750 °C consisted of B_4C and residual carbon. Residual B_2O_3 was also present in the powder after heat-treatment at 1450 °C. The B_4C yields of the products obtained by heat-treatment at 1450 °C using smaller seeds increased with increasing amounts of B_4C seed grains. In the case of heat-treatment at 1550 and 1750 °C using smaller seeds, 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 synthesis 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. In the case of addition of larger seeds, the yields of the products obtained by heat-treatment at 1550 °C were comparable to those obtained using smaller seeds, with B_4C-seed/B_2O_3=0.10, regardless of the added amount.

Truncated octahedral B_4C particles were synthesized selectively by addition of B_4C seed grains over a wide range of heat-treatment temperatures. The particle size of the B_4C powder decreased with increasing amounts of added B_4C seed grains. In the case of addition of smaller amounts of seed grains, the morphologies of the B_4C particles synthesized at 1450 and 1550 °C were polyhedral,

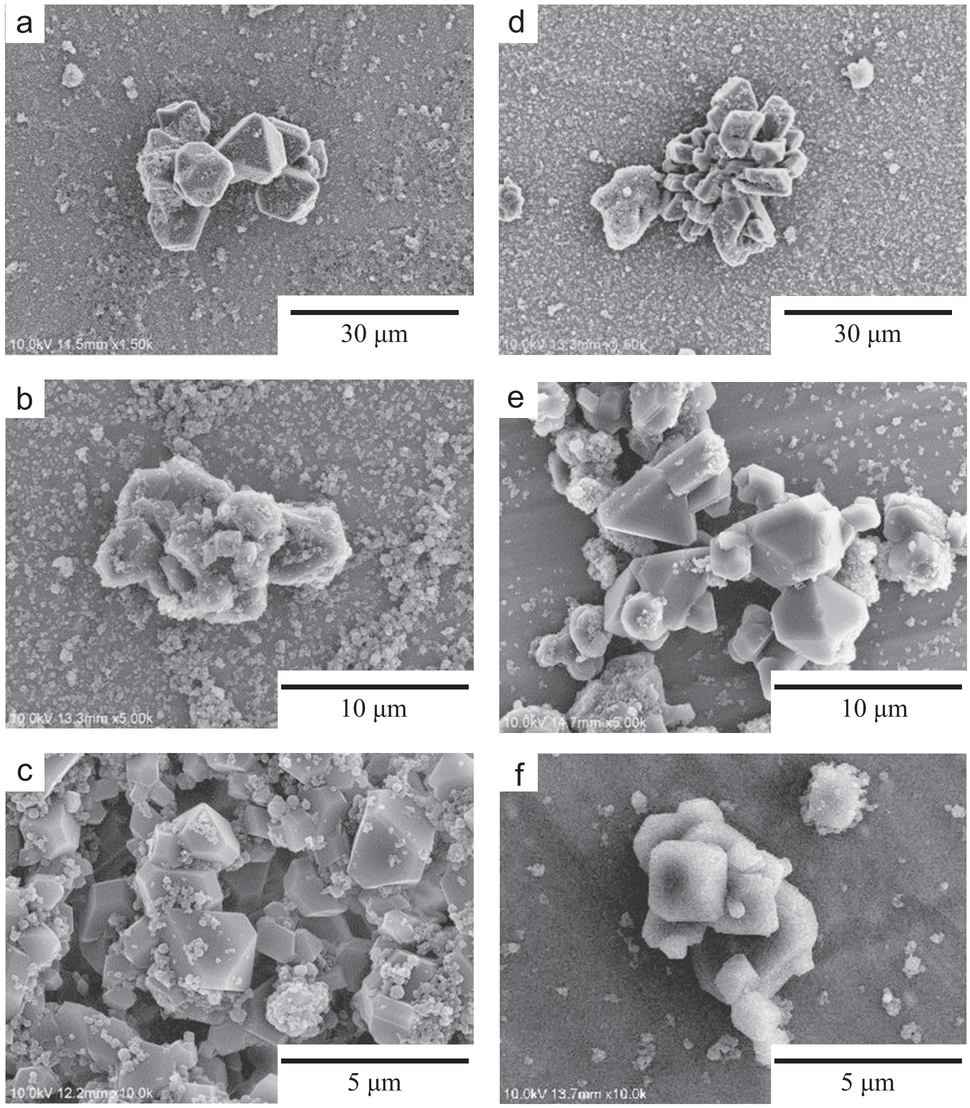

Fig. 8. Scanning electron micrographs of B_4C powders synthesized at (a)–(c) 1450 and (d)–(f) 1750 °C using mixtures with B_4C-seed/B_2O_3 = (a), (d) 0.01; (b), (e) 0.03; and (c), (f) 0.10 (small B_4C seed grains).

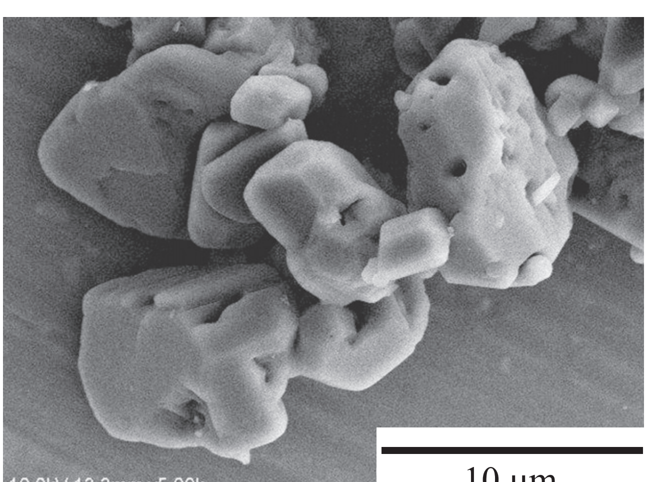

Fig. 9. Scanning electron micrograph of B_4C powder synthesized at 1750 °C using a mixture with B_2O_3/C = 2.90 and B_4C-seed/B_2O_3 = 0.10 (large B_4C seed grains).

e.g., truncated octahedra and their twins, 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 seed grains, the morphologies of the B_4C particles synthesized at 1450–1750 °C were mainly truncated octahedral and thick plate-like.

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