Microstructure in precursor formed by controlling composition of condensed boric acid-poly(vinyl alcohol) product for low-temperature synthesis of boron carbide powder

Masaki KAKIAGE,[†] Naoki TAHARA, Rie WATANABE, Ikuro YANASE and Hidehiko KOBAYASHI

Department of Applied Chemistry, Graduate School of Science and Engineering, Saitama University,
255 Shimo-Okubo, Sakura-ku, Saitama 338–8570, Japan

The dispersion state of boron oxide (B_2O_3) and carbon components in a precursor prepared from a condensed boric acid (H_3BO_3)-polyol product by thermal decomposition in air was found to be closely related to the formation of boron carbide (B_4C) powder at a low synthesis temperature. The microstructure in the precursor was fabricated by controlling the composition of a condensed H_3BO_3 -poly(vinyl alcohol) (PVA) product. The size of B_2O_3 particles dispersed in the carbon matrix of the microstructure decreased with increasing PVA content of the condensed product. Crystalline B_4C powder with a little free carbon was synthesized from a precursor with a more finely and homogeneously dispersed structure consisting of B_2O_3 particles and the carbon matrix by heat treatment at 1200°C for 5 h in an Ar flow. Furthermore, the formation and subsequent grain growth of B_4C particles were promoted even at a low synthesis temperature.

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1. Introduction

The low-temperature synthesis method of boron carbide (B_4C) powder, which is an important non-oxide ceramic with attractive properties and superior functions, has recently been investigated. The carbothermal reduction of boron oxide (B_2O_3), for which the overall reaction is given by Eq. (1), is used to produce B_4C owing to the use of inexpensive and nonhazardous raw materials, but the process is performed at a high temperature of approximately 2000°C.^{1),2)}

Carbothermal reduction using a condensed product that is made up of boric acid (H_3BO_3) and a polyol is attractive as a low-temperature synthesis method of B_4C powder.^{2)–8)} The condensed product forms a borate ester (B–O–C) bond by a dehydration condensation reaction between H_3BO_3 and the polyol. This reaction accelerates the dispersion of boron and carbon sources, and thus the synthesis temperature is reduced. However, the obtained product contains a large amount of residual carbon, which is a common disadvantage of B_4C synthesis using a polyol. We performed the thermal decomposition of a condensed H_3BO_3 -polyol product in air to control the amount of carbon to the stoichiometric ratio required for the carbothermal reduction [Eq. (1)],^{9)–13)} whereby crystalline B_4C powder with little free carbon was synthesized by heat treatment at 1250°C for 5 h in an Ar flow.^{10)–13)} The obtained thermally decomposed product consisted of highly dispersed B_2O_3 and carbon components.^{10),11),13)} Note that the synthesis temperature is expected to be lowered by improving the dispersion of the B_2O_3 and carbon components owing to the increased interface between the B_2O_3 and carbon components with superior reactivity.^{10)–12)}

Poly(vinyl alcohol) (PVA) is a typical polyol as well as a water-soluble polymer and readily forms a B–O–C bond with H_3BO_3 by dehydration condensation. Thus, PVA is useful as a carbon source for the low-temperature synthesis of B_4C powder. The morphology of the precursor obtained by the thermal decomposition of the condensed H_3BO_3 -PVA product in air exhibits the dispersion of B_2O_3 particles in a carbon matrix,¹¹⁾ which is similar to the sea-island structure of a polymer alloy. This indicates that the morphological characteristics of a matrix polymer strongly determine the morphology of the precursor.

Our previous study revealed that a precursor with a homogeneously arranged B_2O_3 /carbon structure at the nanometer scale prepared from a condensed H_3BO_3 -PVA product enables the use of a lower synthesis temperature and a shorter holding time.¹¹⁾ It is known that the phase-separated morphology of a polymer alloy is related to the volume fraction of each component. Furthermore, the number of hydroxyl groups of PVA, which react with H_3BO_3 , in a condensed product increases with increasing PVA content, increasing the dispersion of H_3BO_3 .

In this study, the desired microstructure of the B_2O_3 /carbon precursor is formed by controlling the composition of the condensed H_3BO_3 -PVA product to achieve the low-temperature synthesis of B_4C powder. We considered the effect of the PVA content of a condensed product on the microstructure in the precursor consisting of B_2O_3 particles and the carbon matrix. The formation of B_4C at a low synthesis temperature and its morphology were investigated.

2. Experimental procedure

2.1 Synthesis of B_4C powder

PVA was supplied by Kuraray Co., Ltd., Japan, for which the degrees of polymerization and hydrolysis were 320 and 98.5 mol %, respectively. H_3BO_3 (99.5%) was purchased from Wako Pure Chemical Industries, Ltd., Japan. These materials were used as received. A condensed product was prepared by the

[†] Corresponding author: M. Kakiage; E-mail: kakiage@apc.saitama-u.ac.jp

dehydration condensation of H_3BO_3 and PVA with a H_3BO_3 :PVA (hydroxyl group of PVA) molar ratio of 1:3–6. PVA was dissolved in distilled water (ca. 5 wt %) by stirring and heating in a water bath at 80°C for 1 h. The concentration of the PVA solution was kept at a constant regardless of the molar ratio. Then, H_3BO_3 was dissolved in distilled water (ca. 1–2 wt %) and added dropwise to the PVA solution. The blended solution was heated until the water evaporated, which was followed by drying at 120°C in air. The resulting product was a white solid.

Thermal decomposition in air was performed to eliminate the excess carbon component; the condensed product was placed in an alumina crucible after grinding with an agate mortar and pestle, and thermally decomposed in air. The thermal decomposition conditions (temperature and holding time) were determined with the aim of achieving the stoichiometric $\text{C}/\text{B}_2\text{O}_3$ ratio (≈ 3.5) for the carbothermal reduction [Eq. (1)]. The black precursors obtained by the thermal decomposition of the condensed products in air were ground with an agate mortar and pestle into powder form. The precursor powders are denoted P3–P6 according to the molar ratio of PVA (listed in Table 1). Each precursor powder was placed in a graphite boat and heated at 1050–1250°C for 0–20 h in an Ar flow (200 ml/min) at a heating rate of 10°C/min.

2.2 Characterization

The B_2O_3 content of the precursor powder was determined as the H_3BO_3 content by titrating a mannitol- H_3BO_3 complex with sodium hydroxide solution using phenolphthalein as the indicator. The B_2O_3 component was removed from the precursor powder by washing in hot water. A Rigaku Thermo Plus TG8120 was used for the thermogravimetric (TG) measurements of PVA and the condensed products. Heating scans were performed up to

700°C at a rate of 10°C/min in air. Scanning electron microscopy (SEM) observations of the morphologies of the precursor and product powders were conducted with a Hitachi S-4100 field-emission scanning electron microscope operated at 15.0 kV. The samples were coated with 5-nm-thick Pt-Pd before the observation. X-ray diffraction (XRD) measurements of the products were performed using a powder X-ray diffractometer (Rigaku RINT2200) operated at 40 kV and 30 mA with monochromatized $\text{Cu K}\alpha$ radiation. The B_4C peak intensity ratio [$I_{\text{B}_4\text{C}}/(I_{\text{B}_4\text{C}} + I_{\text{C}} + I_{\text{B}_2\text{O}_3})$] of the products was estimated from the main peak intensities of the B_4C [$I_{\text{B}_4\text{C}}$; (021) reflection at $2\theta = 37.8^\circ$], carbon (I_{C} ; amorphous halo at $2\theta = 23\text{--}27^\circ$), and B_2O_3 [$I_{\text{B}_2\text{O}_3}$; (031) reflection at $2\theta = 27.8^\circ$] components in the XRD pattern. CHN elemental analyses were performed by a combustion method with a gas chromatograph using a FlashEA 1112 elemental analyzer (Thermo Electron Corporation). The residual free carbon content was estimated from an amount of carbon in the product after the washing in hot water.

3. Results and discussion

The thermal behavior of the condensed products was investigated to characterize the state of each condensed product. Figure 1 shows the TG curves of PVA and the condensed products. Similar decomposition behavior was observed for all

Fig. 1. TG curves of PVA and condensed products.

Table 1. Preparation conditions and $\text{C}/\text{B}_2\text{O}_3$ ratio of each precursor

Precursor code	Molar ratio [H_3BO_3 :PVA (OH group)]	Thermal decomposition conditions	$\text{C}/\text{B}_2\text{O}_3$ ratio
P3	1:3	500°C-2 h	3.4
P4	1:4	600°C-2 h	3.4
P5	1:5	650°C-1.5 h	3.2
P6	1:6	700°C-1 h	3.3

Fig. 2. SEM images of (a, b) P3, (c, d) P4, (e, f) P5, and (g, h) P6 after removal of B_2O_3 by washing in hot water.

condensed products, which was completely different from that of PVA. Significant decomposition of the condensed products took place at 400°C, which is higher than that for PVA (300°C). This indicates the formation of B–O–C bonds by dehydration condensation. Furthermore, the decomposition corresponding to PVA was not observed for the condensed product with the highest PVA content ($\text{H}_3\text{BO}_3\text{:PVA} = 1\text{:}6$), and the weight loss attributed to the dehydration of H_3BO_3 below 200°C was not observed for the condensed product with the highest H_3BO_3 content ($\text{H}_3\text{BO}_3\text{:PVA} = 1\text{:}3$). These demonstrate the nonexistence of unreacted starting materials without B–O–C bonds in the condensed product prepared in this study.

The dispersion state of the B_2O_3 and carbon components in the precursors was investigated by SEM observation. A series of SEM images of the precursors after washing in hot water is shown in Fig. 2. The B_2O_3 component can be removed by washing the precursor powder in hot water, thus leaving the carbon component. Nanosize B_2O_3 particles were dispersed in a carbon matrix for all precursors, and the dispersibility markedly improved with increasing PVA content of the condensed product. Among the precursors, P3 had an extremely disordered structure with larger B_2O_3 particles. The pore size distributions of the precursors estimated from their SEM images are shown in Fig. 3. The pore size and its variation decreased with increasing PVA content of the condensed product. The pore size for P6, which has the smallest pores, was 50 nm or less. Therefore, the significantly improved dispersibility of B_2O_3 particles in the carbon matrix of the precursor can be clearly attributed to the PVA content of the condensed product. A network of PVA chains

Fig. 3. Pore size distributions of precursors estimated from SEM images.

Fig. 4. XRD patterns of products obtained by heat treatment of (a) P3, (b) P4, (c) P5, and (d) P6 at 1050–1250°C for 5 h in an Ar flow.

Fig. 5. Changes in B₄C peak intensity ratio for products prepared from P3–P6 by heat treatment at 1050–1250°C for 5 h in an Ar flow.

Fig. 7. Changes in B₄C peak intensity ratio for products prepared from P3 and P6 by heat treatment at 1150°C for 0–20 h in an Ar flow.

Fig. 6. XRD patterns of products obtained by heat treatment of (a) P3 and (b) P6 at 1150°C for 0–20 h in an Ar flow.

with hydroxyl groups is structured in the PVA solution. Voids with hydroxyl groups between PVA chains, i.e., the diffusion field of H₃BO₃ molecules, increase with increasing PVA content. Thus, in the preparation of the condensed product, H₃BO₃ molecules can be more finely dispersed into the network of PVA for the condensed product with higher PVA content. Consequently, the aggregation of B₂O₃ was suppressed and a precursor having a finely and homogeneously dispersed structure is fabricated.

The XRD patterns of the products obtained by the heat treatment of each precursor at 1050–1250°C for 5 h in an Ar flow are shown in **Fig. 4**. Peaks corresponding to a rhombohedral B₄C crystal were observed at 1150°C for P3 and at 1100°C for P4, P5, and P6. The starting temperature of B₄C formation is closely related to the dispersion of B₂O₃ particles in the precursor.¹¹⁾ Only B₄C peaks appeared at 1250°C for P3 and P4 and at 1200°C for P5 and P6. Changes in the B₄C peak intensity ratio of the products prepared from P3–P6 with the heat treatment temperature in the case of heat treatment for 5 h in an Ar flow are summarized in **Fig. 5**. The peak intensity ratio increased from P3, which has the poorly dispersed structure, to P6, which has the most finely dispersed structure, at the same heat treatment temperature. This demonstrates that the dispersion of the B₂O₃ and carbon components is a dominant factor in the formation of B₄C. A finely dispersed structure leads to a larger interface between the B₂O₃ and carbon components with superior reactivity, enabling the low-temperature synthesis of B₄C. From

P5 and P6, crystalline B₄C powder with a little free carbon was synthesized at 1200°C, which is the lowest temperature reported for the synthesis of B₄C powder at a holding time of 5 h using a polyol. The residual free carbon content in the product obtained by the heat treatment of P6 at 1200°C for 5 h in an Ar flow after the washing in hot water was 4.6 wt %.

The synthesis reaction of B₄C mainly occurs at the interface between the B₂O₃ and carbon components at the low synthesis temperature in order to facilitate the diffusion of reacting species. Hence, a finely dispersed precursor with a large interface is expected to readily produce B₄C at a low synthesis temperature. **Figure 6** shows the XRD patterns of the products obtained from P3 (poor dispersion) and P6 (fine dispersion) by heat treatment at 1150°C for 0–20 h in an Ar flow. Changes in the B₄C peak intensity ratio with the heat treatment time are summarized in **Fig. 7**. The formation of B₄C from P6 was saturated at a heat treatment time of 10 h. In contrast, for P3, the B₄C peak intensity ratio increased slowly with increasing heat treatment time, and small amounts of unreacted B₂O₃ and carbon were observed even after heat treatment for 20 h. The diffusion of reacting species readily occurs for the precursor with high dispersion and high homogeneity, and thus B₄C powder was synthesized at a shorter time from P6. These results demonstrate that the B₄C formation reaction occurs homogeneously in the precursor with a homogeneous dispersion and suggest that the synthesis temperature and holding time can be reduced by using a precursor with a finely and homogeneously dispersed structure consisting of B₂O₃

Fig. 8. SEM images of products obtained by heat treatment of (a) P3 and (b) P6 at 1250°C for 5 h in an Ar flow.

Fig. 9. SEM images of products obtained by heat treatment of (a) P3 and (b) P6 at 1150°C for 20 h in an Ar flow.

particles and the carbon matrix.

The SEM images of the products obtained by the heat treatment of P3 and P6 at 1250°C for 5 h in an Ar flow are shown in **Fig. 8**. The particles prepared from P6 ($D_{50} = 10.0 \mu\text{m}$) were larger than those prepared from P3 ($D_{50} = 4.8 \mu\text{m}$). Note that grain growth was observed in particles of both products. In the formation of B_4C by the carbothermal reduction, the liquid-phase reduction of B_2O_3 dominates at lower temperatures. The precursor prepared from a condensed H_3BO_3 -PVA product has a carbon matrix, thus the carbon component is structurally connected throughout the precursor. The connectivity of the carbon component in a precursor is conducive to the grain growth of B_4C since B_4C is formed by reaction of liquid B_2O_3 at the surface of the carbon component. Our previous report revealed that the structural morphology of the precursor affected the morphology of B_4C particles.¹³⁾ **Figure 9** shows the SEM images of the products obtained by the heat treatment of P3 and P6 at 1150°C for 20 h, illustrating the significant difference between the products. Although grain growth was observed in the particles of the product prepared from P6 ($D_{50} = 9.1 \mu\text{m}$), only microparticles were observed in the product prepared from P3 ($D_{50} = 0.42 \mu\text{m}$). These results imply that a finely dispersed

precursor promotes the grain growth of B_4C particles. The number of nucleation sites increased with increasing dispersion of the boron and carbon sources, thus promoting the formation of B_4C and the subsequent grain growth of B_4C particles even at a low synthesis temperature.

4. Conclusions

In this study, we investigated the effect of the PVA content of a condensed H_3BO_3 -PVA product on the formation of B_4C at a low synthesis temperature and its morphology. A precursor was formed by the thermal decomposition of the condensed H_3BO_3 -PVA product in air. The dispersibility of B_2O_3 particles in the carbon matrix of the microstructure markedly improved with increasing PVA content of the condensed product because H_3BO_3 molecules were more finely dispersed into the network of PVA chains. Crystalline B_4C powder with a little free carbon was synthesized from a precursor with a more finely and homogeneously dispersed structure by the heat treatment at 1200°C for 5 h in an Ar flow. Furthermore, the formation and subsequent grain growth of B_4C particles were promoted even at a low synthesis temperature.

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