Synthesis of Al_3BC_3 particulates by carbo-thermal reduction process—Parameter optimization and mechanism analysis

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The synthesis mechanism of Al_3BC_3 through carbo-thermal reduction process was investigated and the processing conditions were optimized using $\text{Al}(\text{OH})_3\text{-B}_2\text{O}_3\text{-C}$ as starting materials. The mass change and phase formation of the compacts were analyzed with varying temperature. Excess $\text{Al}(\text{OH})_3$ and B_2O_3 were required compared to the stoichiometric composition due to the loss of the source materials by vaporization at 1,500–1,600°C. At 1,600°C, Al_2O gas began to actively react with carbon to form Al_4C_3 on the carbon particles. Al, Al_2O and B_2O_3 gases diffused through Al_4C_3 layer and reacted with carbon at and above 1,650°C to form Al_3BC_3 . The formation of hexagonal terrace at the surface of synthesized powder indicated that the gases also reacted at the particle surface with carbon which diffused through the carbide layers. The reactions were completed after calcination at 1,725°C for 4 h or at 1,800°C for 1 h. Gas-solid reactions were the major synthesis mechanism. The optimum composition for the synthesis of the ternary compound was $\text{Al}(\text{OH})_3\text{:B}_2\text{O}_3\text{:carbon} = 0.7\text{:}1.4\text{:}0.25$ by weight.

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1. Introduction

Silicon carbide (SiC) is one of the important ceramics for structural application because it has unique combination of beneficial properties such as high hardness, strength, chemical stability, thermal conductivity and excellent thermal stability.⁽¹⁾

Preparation of highly concentrated SiC slurry and subsequent low temperature pressureless sintering of the resultant green body have been challenging topics during the last decade for the production of SiC components. However, SiC green bodies prepared by wet processing generally required very high temperatures (2,000–2,250°C) for densification.^{(2)–(4)}

Recently, Al_3BC_3 has been used as a sintering additive of SiC due to the high sintering efficiency and flexibility for wet processing.⁽⁵⁾ Highly concentrated SiC slurry containing Al_3BC_3 additive could be casted and densified either by pressureless sintering at 1,850°C or spark plasma sintering (SPS) at 1,550°C.^{(5)–(7)} The additive has potential application for SiC components having complex shapes such as SiC tubes and SiC/SiC fiber-reinforced composites.

Various efforts have been reported for the synthesis and analysis of Al_3BC_3 by using the mixture of Al, B (or B_4C) and C as starting materials.^{(8)–(16)} Hillerbrecht et al. synthesized Al_3BC_3 as small single crystals in an aluminum melt.⁽⁸⁾ Lee et al. reported that the dissolution of B_4C and C within Al melt and subsequent precipitation of Al_3BC_3 were the major synthesis mechanisms.⁽¹⁵⁾ Li et al. reported the synthesis of bulk Al_3BC_3 by reactive hot pressing and proposed the synthesis mechanism as solid-solid reactions.⁽¹⁴⁾

Metal carbides have been prepared by the carbo-thermal reduction of metal oxides, direct reaction between metal elements and carbon, and the gas phase reaction of metal-containing gases and appropriate hydrocarbons.⁽¹⁷⁾ Among the processes, carbo-thermal reduction of metal oxides is the most commonly used route for industrial production due to inexpensive raw

materials and simple process. However, in spite of the importance of the process, the synthesis of ternary carbides using carbo-thermal reduction process has been scarcely investigated.^{(18), (19)} Especially, the synthesis of Al_3BC_3 by the process has never been reported.

The present investigation reports the synthesis of Al_3BC_3 powder using the mixtures of $\text{Al}(\text{OH})_3$, B_2O_3 , and phenolic resin through carbo-thermal reduction process. $\text{Al}(\text{OH})_3$ was selected in order to reduce the price and to increase the activity of the raw powder. Phenolic resin induced homogeneous distribution of carbon source because of the high solubility in ethanol. Processing parameters such as calcination condition and the mixing ratio of the raw powders were optimized and the synthesis mechanism of the ternary carbide was established.

2. Experimental procedures

Aluminum hydroxide [$\text{Al}(\text{OH})_3$, 99.99%, 2.5 μm , Kojundo Chemical Lab. Co., Japan], boron oxide (B_2O_3 , 99.9%, 3 μm , Kojundo Chemical Lab. Co., Japan), and phenolic resin (J-325, Dainippon Ink and Chemicals Inc., Japan, carbon yield: 25%) were used as the source materials of Al, B, and C, respectively. The carbon yield of the resin was measured by TG-DTA in a former experiment.⁽¹⁵⁾ The molar ratio of the starting materials was varied as shown in **Table 1**.

The starting powders (10 g) were mixed using a ball mill with SiC ball (200 g, diameter: 10 mm), polyethylene bottle (500 ml) and ethanol for 24 h. Then, the slurries were dried with stirring using a hot plate. Thermo-gravimetric analysis (TGA, STA 409PC, Netzsch Geraetebau Inc., Germany) of the powder mixture was performed up to 1,950°C in flowing Ar atmosphere (flow rate: 20 ml/min, heating rate: 5°C/min). The powder mixtures were heated using a tube furnace at 1,000°C for 30 min in flowing Ar to change phenolic resin into carbon. After crushing using a mortar and sieving through a 100 mesh sieve, the powder mixtures were compacted into $\phi 13 \times 13$ mm pellets using a hand press under 1 MPa pressure. The pellets were placed in a graphite

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Table 1. Chemical composition (wt%) of starting materials and secondary phases formed after calcination at 1,800°C for 1 h

Abbreviation	Al(OH) ₃	B ₂ O ₃	Phenolic resin	Secondary phases
AC	0.7	0	0.9	Al ₄ C ₃
ABC1	0.7	1.3	0.9	Al ₄ C ₃ , Al ₂ O ₃
ABC2	0.7	1.35	0.95	Al ₄ C ₃
ABC3	0.7	1.4	1	—
ABC4	0.7	1.5	1	—
ABC5	0.7	1.5	1.2	Carbon
ABC6	0.7	1.7	1	—

crucible and were heated at 1,550–1,800°C for 0.5–4 h in flowing Ar using an induction furnace (FVHP-1-3, Fuji Denpa Kogyo Corp., heating rate: 75°C/min up to 1,500°C, 30°C/min above 1,500°C). For comparison, Al–B₄C–C powder mixture was also used for the synthesis of Al₃BC₃. Details on the synthesis process using Al–B₄C–C source were described elsewhere.¹⁵⁾ The phase identification of synthesized powders was performed by X-ray diffractometry (XRD, RINT-UltimaIII, Rigaku Co., Japan) using Cu Kα₁ radiation. The morphology of the synthesized Al₃BC₃ powder was observed by scanning electron microscopy (SEM, JSM-6700F, JEOL Ltd., Japan).

Aluminum, boron, carbon and oxygen content of the compound powder was measured using an inductively-coupled plasma atomic emission spectrometry (analyzed components: aluminum and boron, ICP-AES, Optima 3300DV, Perkin Elmer, Wellesley, MA), infrared absorption method (analyzed component: carbon, CS 444-LS, Leco, St. Joseph, MI) and inert gas carrying melting-infrared absorption method (analyzed component: oxygen, TC-600, Leco), respectively.

3. Results and discussion

3.1 Optimization of starting composition

The reactions to form Al₃BC₃ using Al(OH)₃, B₂O₃ and C can be described as follows;

The standard Gibbs free energy of reaction (2) could not be obtained due to the lack of the thermodynamic data of Al₃BC₃.

According to reactions (1) and (2), the theoretical molar ratio of the constituents to form Al₃BC₃ is Al(OH)₃:B₂O₃:C = 3:0.5:9. Because Al(OH)₃ and phenolic resin lose weight to form Al₂O₃ and carbon during heating, the theoretical mass ratio of Al(OH)₃:B₂O₃:phenolic resin based on reaction (2) is 0.7:0.104:1.293.

Table 1 listed the secondary phases which formed after synthesis with changing the mixing ratio of the raw materials. The optimum composition was Al(OH)₃:B₂O₃:phenolic resin (carbon) = 0.7:1.4:1 (0.25) by weight (composition ABC3). Al₄C₃ was formed when the mass ratio of Al(OH)₃/B₂O₃ was more than 0.5 because of the depletion of B₂O₃ (ABC1, ABC2). When excess B₂O₃ was added, residual B₂O₃ phase or secondary boride phase formation was not detected by X-ray analysis due to the formation of amorphous B₂O₃ and the vaporization of remaining B₂O₃ (ABC4–ABC6).²⁰⁾

3.2 Synthesis mechanism

Reaction (2) is a simplified solid-solid reaction formula. However, the actual synthesis of Al₃BC₃ was performed by various reactions between solids, liquids and gases.

Fig. 1. TGA data of the raw powder mixtures. (---: AC, —: ABC3)

Figure 1 shows the TGA data of raw powder mixtures. The dehydration of Al(OH)₃ occurred at 250–300°C. The decomposition of the phenolic resin during pyrolysis mostly occurred below 1,000°C. The mass loss of the AC and ABC3 was similar below 1,050°C except the magnitude. The ABC3 had less weight loss than the AC below 1,050°C because the ABC3 contained B₂O₃ which is thermally stable up to 1,000°C while both Al(OH)₃ and the resin lost weight in the AC. The difference of mass loss between the AC and ABC3 decreased above 1,050°C because B₂O₃ in the ABC3 began to vaporize.²¹⁾

Both the AC and ABC3 showed strong mass loss above 1,500°C due to the decomposition of Al₂O₃.^{22)–24)}

Because reaction (2) accompanies weight loss which was originated from the formation of CO gas, TGA data indicated that the formation of Al₃BC₃ does not actively occur below 1,500°C. Mass loss mostly finished at 1,750°C.

Figure 2 shows the XRD data of the ABC3 after heating up to 1,800°C for 30 min. Al₂O₃ and C were the main phases at 1,550°C [Fig. 2(a)]. The formation of B₄C by reaction (4) was reported to occur at 1,500°C;²¹⁾

However, B₄C was not identified by XRD.

The formation of Al₄C₃ began to occur at 1,600°C [Fig. 2(b)], indicating that the following reactions occurred at this temperature;²³⁾

The amount of Al₄C₃ was maximum at 1,650°C [Fig. 2(c)]. Also, Al₃BC₃ began to form at this temperature. Al₂O₃ and Al₄C₃ were completely consumed and mono-phase Al₃BC₃ was attained at 1,800°C.

TGA and XRD data indicated that the difference between the theoretical and experimentally determined optimum mass ratio of [Al(OH)₃+B₂O₃]/C (3.73 vs. 8.4) was attributed to the loss of the aluminum-based gases and B₂O₃ below 1,600°C because the gases did not actively form solid compounds at this temperature.

Figure 3 summarized the schematic of synthesis mechanisms. Below 1,050°C, Al₂O₃ particles were covered with carbon which was derived from phenolic resin while B₂O₃ melted and distributed between the particles. Excess carbon formed agglom-

erated particles [Fig. 3(a)]. The vaporization of B_2O_3 occurred above $1,050^\circ\text{C}$.

Al_2O gas was formed by reaction (3) above $1,500^\circ\text{C}$. Al_2O and B_2O_3 were mostly vaporized without forming Al_4C_3 and B_4C below $1,600^\circ\text{C}$ [Figs. 2(b) and 3(b)]. At and above $1,600^\circ\text{C}$, Al_2O and Al gases, which were formed by reactions (3) and (5), reacted with carbon to form Al_4C_3 on the surface of carbon particles by reactions (7) and (8) [Fig. 3(c)].

Two types of diffusion can occur through Al_4C_3 layer in order to continue the reduction reactions; the inward diffusion of Al and B sources or outward diffusion of C. Among them, the diffusion of aluminum sources through the carbide layer was reported to be the dominant synthesis mechanism of Al_4C_3 .²³⁾ The effective diffusivities of the components through Al_4C_3 were reported to be 0.82 and $1.31 \text{ cm}^2/\text{s}$, respectively. However, over 90% of the carbide was reported to be formed by Al_2O and only 10% by Al because the vapor pressure of Al_2O is much higher than that of Al.²³⁾

Fig. 2. XRD data of the powder mixtures after the calcinations of the ABC3 composition at (a) $1,550^\circ\text{C}$, (b) $1,600^\circ\text{C}$, (c) $1,650^\circ\text{C}$, (d) $1,700^\circ\text{C}$, (e) $1,750^\circ\text{C}$ and (f) $1,800^\circ\text{C}$ for 30 min in Ar (●: Al_2O_3 , □: Al_4C_3 , ▼: carbon, ○: Al_3BC_3 , ▲: unidentified peaks).

At $1,650^\circ\text{C}$, boron source diffused into Al_4C_3 and formed Al_3BC_3 at the boundary between Al_4C_3 and C [Figs. 2(c) and 3(d)];

Reaction (9) mainly occurred at the initial stage of synthesis because the synthesized Al_3BC_3 prevented the contact between Al_4C_3 and C.

The formation of Al_3BC_3 continued mostly by the diffusion of Al and B sources through Al_4C_3 and Al_3BC_3 to react with carbon;

Among the two reactions, reaction (10) is believed to be the major synthesis mechanism of Al_3BC_3 due to the high vapor pressure of Al_2O compared to that of Al.

When using Al, B_4C and C as source materials, the synthesis of Al_3BC_3 was reported to be dominated by solid-solid or liquid-solid reactions.^{14),15)} However, most probably the major synthesis mechanism of Al_3BC_3 during carbo-thermal reaction is gas-solid reactions by reactions (9)–(11).

Figure 4 shows the morphology of synthesized Al_3BC_3 . The particles synthesized by carbo-thermal reduction had large deviation in size [$1\text{--}20 \mu\text{m}$, Fig. 4(a)]. The average particle size of Al_3BC_3 synthesized using Al– B_4C –C at $1,800^\circ\text{C}$ was $14.1 \mu\text{m}$. The resultant particles had irregular morphology [Fig. 4(b)]. In contrast, the shape of terraces which were formed on the Al_3BC_3 powder synthesized through carbo-thermal reduction revealed the hexagonal nature of the compound [P6₃mc, Fig. 4(c)]. Ceramic powders which were synthesized through gas reactions or dissolution-precipitation within liquid reveal their crystallographic character.²¹⁾ The formation of terraces shown in Fig. 4(c) indicated that Al_3BC_3 particulates grew partly by the reactions of gas phases with carbon at the surface of Al_3BC_3 [Fig. 3(e)].

The growth of terrace by gas reactions is mainly controlled by crystal structure, temperature, and the degree of supersaturation.²⁵⁾ The nucleation and growth of crystals from vapor phases depend mainly on the supersaturation ratio between actual and equilibrium pressures.²⁶⁾ When the degree of supersaturation increases, kink sites freely nucleate and grow on low energy planes and the growth on high energy plane is restrained. At an opposite condition, high energy planes grow out and crystal habits tend to develop.²⁷⁾

Fig. 3. Synthesis mechanisms of Al_3BC_3 by carbo-thermal reduction at various temperature. (a) below $1,050^\circ\text{C}$, (b) $1,500\text{--}1,600^\circ\text{C}$, (c) $1,600\text{--}1,650^\circ\text{C}$, (d), (e) above $1,650^\circ\text{C}$ and (f) $1,800^\circ\text{C}$. (■: Al_2O_3 , ■: B_2O_3 , ■: C, ▨: Al_4C_3 , ▩: Al_3BC_3)

Fig. 4. Morphology of synthesized Al_3BC_3 powder after calcination at $1,800^\circ\text{C}$ for 1 h using (a) $\text{Al}(\text{OH})_3\text{-B}_2\text{O}_3\text{-C}$, (b) $\text{Al-B}_4\text{C-C}$ and (c) magnified view of Fig. 4(a).

The formation of hexagonal terraces shown in Fig. 4(c) indicated a two-dimensional (2D) nucleation-growth of both high and low energy planes. The crystallographic character is revealed when the growth rate of low energy plane is controlled.²⁸⁾

During the synthesis of Al_3BC_3 , the partial pressure of gases generated by, e.g., reactions (3), (5) was quite high due to the reactions between the oxides and carbon, which caused the supersaturation of the reactants for reactions (10) and (11) at the particle surface. Growth occurred both at the low and high energy planes of Al_3BC_3 . Therefore, the synthesized Al_3BC_3 powder had a rather irregular-shape although hexagonal terraces were formed on the surfaces [Fig. 3(c)].

The synthesis time to produce X-ray pure Al_3BC_3 decreased with increasing synthesis temperature; i.e., 4 h at $1,725^\circ\text{C}$, 2 h at $1,750^\circ\text{C}$ and 1 h at $1,800^\circ\text{C}$.

3.3 Properties of synthesized Al_3BC_3

Figure 5 shows the morphology of the as-synthesized powder compact. A black-colored layer formed at the top of the specimen. Al_3BC_3 powder which formed beneath the black layer

Fig. 5. Morphology of the specimen after calcination at $1,800^\circ\text{C}$ for 1 h.

Table 2. Chemical composition of the synthesized powder (wt %)

	Al	B	C	O
Stoichiometry	63.3	8.46	28.2	
Green area	59.6	8.2	30.9	1.9
Black area	34.3	4.4	33.3	24

Fig. 6. XRD data of the synthesized Al_3BC_3 powders after calcination using (a) $\text{Al-B}_4\text{C-C}$ mixture at $1,800^\circ\text{C}$ for 2 h in Ar and (b) $\text{Al}(\text{OH})_3\text{-B}_2\text{O}_3\text{-C}$ mixture at $1,725^\circ\text{C}$ for 4 h in Ar. (●: unidentified peaks, others: Al_3BC_3)

had dark green color. Table 2 summarized the weight ratio of the constituents after calcination at $1,800^\circ\text{C}$ for 1 h. The high oxygen content of the black-colored layer indicated the incomplete reaction at the top area of the powder compact. The strong decrease of Al and B contents within the black layer was caused by the vaporization of Al_2O_3 , Al and B_2O_3 gases below $1,600^\circ\text{C}$. The black surface layer suppressed the vaporization inside the powder compact, thus helped the formation of Al_3BC_3 .

The synthesized Al_3BC_3 powder contained 1.9 wt % of oxygen. Part of the oxygen was believed to be originated from the oxides or oxihydrates which were formed on the surface of Al_3BC_3 by the reaction with humidity during handling and storage.

Figure 6 shows the X-ray data of Al_3BC_3 synthesized using $\text{Al}(\text{OH})_3\text{-B}_2\text{O}_3\text{-C}$ and $\text{Al-B}_4\text{C-C}$ raw powder mixtures. $\text{Al-B}_4\text{C-C}$ powder mixture has been commonly used to synthesize Al_3BC_3 through the direct reactions between molten Al, B_4C and C.¹⁵⁾ In both cases, nearly X-ray pure Al_3BC_3 were obtained. Interestingly, small unidentified peaks were detected at 28.5° and 36.9° regardless of the types of starting materials and synthesis mechanism. The peak broadening of Al_3BC_3 synthesized through carbo-thermal reduction was larger than that made using $\text{Al-B}_4\text{C-C}$ powder, indicating that the former one had a smaller crystallite size.²⁹⁾

4. Conclusions

Mono-phase Al_3BC_3 was successfully synthesized using a mixture of $\text{Al}(\text{OH})_3$, B_2O_3 , and phenolic resin through carbo-thermal reduction process. The loss of the source materials by vaporization occurred below $1,600^\circ\text{C}$. At $1,600^\circ\text{C}$, Al_2O gas reacted with carbon to form Al_4C_3 on the carbon particles. Al_3BC_3 was formed at $1,650^\circ\text{C}$ by the diffusion of Al, Al_2O and B_2O_3 gases through Al_4C_3 layer and subsequent reaction with carbon. Hexagonal terrace at the surface of synthesized powder indicated that the gases also reacted at the particle surface with carbon. The optimum mass ratio for obtaining nearly X-ray pure compound was $\text{Al}(\text{OH})_3:\text{B}_2\text{O}_3:\text{carbon} = 0.7:1.4:0.25$. Excess $\text{Al}(\text{OH})_3$ and B_2O_3 were required due to the loss below $1,600^\circ\text{C}$. Gas-solid reaction between Al_2O , B_2O_3 gases and C was the major synthesis mechanism of the ternary powder.

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