Synthesis of Al$_3$BC$_3$ particulates by carbo-thermal reduction process—Parameter optimization and mechanism analysis

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The synthesis mechanism of Al$_3$BC$_3$ through carbo-thermal reduction process was investigated and the processing conditions were optimized using Al(OH)$_3$–B$_2$O$_3$–C as starting materials. The mass change and phase formation of the compacts were analyzed with varying temperature. Excess Al(OH)$_3$ and B$_2$O$_3$ were required compared to the stoichiometric composition due to the formation of Al$_4$C$_3$ on the carbon particles. Al, Al$_2$O and B$_2$O$_3$ gases diffused through Al$_4$C$_3$ layer and reacted with carbon at and above $1,500^\circ$C. 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 carboide 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 Al(OH)$_3$:B$_2$O$_3$:carbon = 0.7:1.4:0.25 by weight.

Key-words : Carbo-thermal reaction, Al$_3$BC$_3$, Powder, Synthesis, SiC

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$_3$BC$_3$ 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$_3$BC$_3$ 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 fiber-reinforced composites.8)

Various efforts have been reported for the synthesis and analysis of Al$_3$BC$_3$ by using the mixture of Al, B (or B$_4$C) and C as starting materials.8–14) Hillerbrecht et al. synthesized Al$_3$BC$_3$ as small single crystals in an aluminum melt.9) Lee et al. reported that the dissolution of B$_4$C and C within Al melt and subsequent precipitation of Al$_3$BC$_3$ were the major synthesis mechanisms.15) Li et al. reported the synthesis of bulk Al$_3$BC$_3$ by reactive hot pressing and proposed the synthesis mechanism as solid–solid reactions.16)

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$_3$BC$_3$ by the process has never been reported.

The present investigation reports the synthesis of Al$_3$BC$_3$ powder using the mixtures of Al(OH)$_3$, B$_2$O$_3$, and phenolic resin through carbo-thermal reduction process. Al(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 [Al(OH)$_3$, 99.99%, 2.5 μm, Kojundo Chemical Lab. Co., Japan], boron oxide (B$_2$O$_3$, 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 $13 \times 13$ mm pellets using a hand press under 1 MPa pressure. The pellets were placed in a graphite...
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–B–C–C powder mixture was also used for the synthesis of Al13BC3. Details on the synthesis process using Al–B–C–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 Kα radiation. The morphology of the synthesized Al13BC3 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 Al13BC3 using Al(OH)3, B2O3 and C can be described as follows;

\[
2\text{Al(OH)}_3(s) \rightarrow \text{Al}_2\text{O}_3(s) + 2\text{H}_2\text{O}(g),
\]

\[
3\text{Al}_2\text{O}_3(s) + \text{B}_2\text{O}_3(s) + 18\text{C}(s) \rightarrow 2\text{Al}_2\text{O}_3(s) + 12\text{CO}(g). \tag{2}
\]

The standard Gibbs free energy of reaction (2) could not be obtained due to the lack of the thermodynamic data of Al13BC3.

According to reactions (1) and (2), the theoretical molar ratio of the constituents to form Al13BC3 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). Al13C3 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).

3.2 Synthesis mechanism

Reaction (2) is a simplified solid-solid reaction formula. However, the actual synthesis of Al13BC3 was performed by various reactions between solids, liquids and gases.

![Figure 1. TGA data of the raw powder mixtures. (\ldots AC, \ldots ABC3)](image)

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 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.23) Both the AC and ABC3 showed strong mass loss above 1,500°C due to the decomposition of Al3O2.21,24)

\[
\text{Al}_2\text{O}_3(s) + 2\text{C}(s) \rightarrow \text{Al}_2\text{O}_3(g) + 2\text{CO}(g), \tag{3}
\]

Because reaction (2) accompanies weight loss which was originated from the formation of CO gas, TGA data indicated that the formation of Al13BC3 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:

\[
2\text{B}_2\text{O}_3(s) + 7\text{C}(s) \rightarrow 4\text{B}_4\text{C}(s) + 6\text{CO}(g). \tag{4}
\]

However, B4C was not identified by XRD.

The formation of Al13C3 began to occur at 1,600°C [Fig. 2(b)], indicating that the following reactions occurred at this temperature:23)

\[
\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 2\text{Al}(s) + 3\text{CO}(g), \tag{5}
\]

\[
2\text{Al}_2\text{O}_3(s) + 9\text{C}(s) \rightarrow 4\text{Al}_3\text{C}_3(s) + 6\text{CO}(g), \tag{6}
\]

\[
2\text{Al}_2\text{O}_3(s) + 5\text{C}(s) \rightarrow 4\text{Al}_4\text{C}_3(s) + 2\text{CO}(g), \tag{7}
\]

\[
4\text{Al}_2\text{O}_3(s) + 3\text{C}(s) \rightarrow 3\text{Al}_4\text{C}_3(s). \tag{8}
\]

The amount of Al13C3 was maximum at 1,650°C [Fig. 2(c)]. Also, Al13BC3 began to form at this temperature. Al2O3 and Al13C3 were completely consumed and mono-phase Al13BC3 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.

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

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Al(OH)3</th>
<th>B2O3</th>
<th>Phenolic resin</th>
<th>Secondary phases</th>
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</thead>
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<td>AC</td>
<td>0.7</td>
<td>0</td>
<td>0.9</td>
<td>Al4C3</td>
</tr>
<tr>
<td>ABC1</td>
<td>0.7</td>
<td>1.3</td>
<td>0.9</td>
<td>Al2C3, Al12O3</td>
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<tr>
<td>ABC2</td>
<td>0.7</td>
<td>1.35</td>
<td>0.95</td>
<td>Al12O3</td>
</tr>
<tr>
<td>ABC3</td>
<td>0.7</td>
<td>1.4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>ABC4</td>
<td>0.7</td>
<td>1.5</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>ABC5</td>
<td>0.7</td>
<td>1.5</td>
<td>1.2</td>
<td>Carbon</td>
</tr>
<tr>
<td>ABC6</td>
<td>0.7</td>
<td>1.7</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3 summarized the schematic of synthesis mechanisms.
erated particles [Fig. 3(a)]. The vaporization of B$_2$O$_3$ occurred above 1,050°C.

Al$_2$O gas was formed by reaction (3) above 1,500°C. Al$_2$O and B$_2$O$_3$ were mostly vaporized without forming Al$_4$C$_3$ and B$_4$C below 1,600°C [Figs. 2(b) and 3(b)]. At and above 1,600°C, Al$_2$O and Al gases, which were formed by reactions (3) and (5), reacted with carbon to form Al$_4$C$_3$ on the surface of carbon particles by reactions (7) and (8) [Fig. 3(e)].

Two types of diffusion can occur through Al$_4$C$_3$ 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$_4$C$_3$. The effective diffusivities of the components through Al$_4$C$_3$ were reported to be 0.82 and 1.31 cm$^2$/s, respectively. However, over 90% of the carbide was reported to be formed by Al$_2$O and only 10% by Al because the vapor pressure of Al$_2$O is much higher than that of Al.

At 1,650°C, boron source diffused into Al$_4$C$_3$ and formed Al$_3$BC$_3$ at the boundary between Al$_4$C$_3$ and C [Figs. 2(c) and 3(d)];

$$\text{3Al}_2\text{O}_3(g) + \text{B}_2\text{O}_3(g) + 12\text{C}(s) \rightarrow 2\text{Al}_3\text{BC}_3(s) + 6\text{CO}(g). \quad (9)$$

Reaction (9) mainly occurred at the initial stage of synthesis because the synthesized Al$_3$BC$_3$ prevented the contact between Al$_4$C$_3$ and C.

The formation of Al$_3$BC$_3$ continued mostly by the diffusion of Al and B sources through Al$_4$C$_3$ and Al$_3$BC$_3$ to react with carbon;

$$\text{3Al}_2\text{O}_3(g) + \text{B}_2\text{O}_3(g) + 12\text{C}(s) \rightarrow 2\text{Al}_3\text{BC}_3(s) + 6\text{CO}(g). \quad (10)$$

$$6\text{Al}(g) + \text{B}_2\text{O}_3(g) + 9\text{C}(s) \rightarrow 2\text{Al}_3\text{BC}_3(s) + 3\text{CO}(g). \quad (11)$$

Among the two reactions, reaction (10) is believed to be the major synthesis mechanism of Al$_3$BC$_3$ due to the high vapor pressure of Al$_2$O compared to that of Al.

When using Al, B$_4$C and C as source materials, the synthesis of Al$_3$BC$_3$ was reported to be dominated by solid-solid or liquid-solid reactions. Most probably the major synthesis mechanism of Al$_3$BC$_3$ during carbothermal reaction is gas-solid reactions by reactions (9)–(11).

Figure 4 shows the morphology of synthesized Al$_3$BC$_3$. The particles synthesized by carbothermal reduction had large deviation in size [1–20 μm, Fig. 4(a)]. The average particle size of Al$_3$BC$_3$ synthesized using Al–B$_4$C–C at 1,800°C was 14.1 μm. The resultant particles had irregular morphology [Fig. 4(b)]. In contrast, the shape of terraces which were formed on the Al$_3$BC$_3$ powder synthesized through carbothermal reduction revealed the hexagonal nature of the compound [P6$_3$$mc$, Fig. 4(c)]. Ceramic powders which were synthesized through gas reactions or dissolution-reprecipitation within liquid reveal their crystallographic character. The formation of terraces shown in Fig. 4(c) indicated that Al$_3$BC$_3$ particulates grew partly by the reactions of gas phases with carbon at the surface of Al$_3$BC$_3$ [Fig. 3(e)].

The growth of terrace by gas reactions is mainly controlled by crystal structure, temperature, and the degree of supersaturation. The nucleation and growth of crystals from vapor phases depend mainly on the supersaturation ratio between actual and equilibrium pressures. 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.
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$_3$BC$_3$, 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$_3$BC$_3$. Therefore, the synthesized Al$_3$BC$_3$ powder had a rather irregular-shape although hexagonal terraces were formed on the surfaces [Fig. 4(c)].

The synthesis time to produce X-ray pure Al$_3$BC$_3$ decreased with increasing synthesis temperature; i.e., 4 h at 1,725°C, 2 h at 1,750°C and 1 h at 1,800°C.

3.3 Properties of synthesized Al$_3$BC$_3$

Figure 5 shows the morphology of the as-synthesized powder compact. A black-colored layer formed at the top of the specimen. Al$_3$BC$_3$ powder which formed beneath the black layer had dark green color. Table 2 summarized the weight ratio of the constituents after calcination at 1,800°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$_2$O$_3$, Al and B$_2$O$_3$ gases below 1,600°C. The black surface layer suppressed the vaporization inside the powder compact, thus helped the formation of Al$_3$BC$_3$.

The synthesized Al$_3$BC$_3$ 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$_3$BC$_3$ by the reaction with humidity during handling and storage.

Figure 6 shows the X-ray data of the synthesized Al$_3$BC$_3$ powders after calcination using Al(OH)$_3$–B$_2$O$_3$–C and Al–B$_4$C–C raw powder mixtures. Al–B$_4$C–C powder mixture has been commonly used to synthesize Al$_3$BC$_3$ through the direct reactions between molten Al, B$_4$C and C.15) In both cases, nearly X-ray pure Al$_3$BC$_3$ 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$_3$BC$_3$ synthesized through carbo-thermal reduction was larger than that made using Al–B$_4$C–C powder, indicating that the former one had a smaller crystallite size.29)
4. Conclusions

Mono-phase Al$_3$BC$_3$ was successfully synthesized using a mixture of Al(OH)$_3$, B$_2$O$_3$, and phenolic resin through carbothermal reduction process. The loss of the source materials by vaporization occurred below 1,600°C. At 1,600°C, Al$_2$O gas reacted with carbon to form Al$_4$C$_3$ on the carbon particles. Al$_3$BC$_3$ was formed at 1,650°C by the diffusion of Al, Al$_2$O and B$_2$O$_3$ gases through Al$_4$C$_3$ 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 Al(OH)$_3$:B$_2$O$_3$:carbon = 0.7:1.4:0.25. Excess Al(OH)$_3$ and B$_2$O$_3$ were required due to the loss below 1,600°C. Gas-solid reaction between Al$_2$O, B$_2$O$_3$ gases and C was the major synthesis mechanism of the ternary powder.

References