Investigation of the Role of Calcium Borate in the Growth of Hexagonal Boron Nitride Particles

Shota Daiki and Toshihiro Ishikawa

Abstract — Hexagonal boron nitride (h-BN) powder is a promising thermally conductive filler in resins and controlling its particle size is important. To obtain h-BN powder with a large particle size as well as high purity and crystallinity, high-temperature heat treatment over 1800 °C in N$_2$ gas atmosphere is effective. Carbothermal reduction nitridation (CRN) involves carbothermic reduction of boric oxide in N$_2$ gas atmosphere. In CRN using a CaO promoter, h-BN particles with large sizes can be produced through a simple heat-treatment process. During CRN, CaO forms calcium borate (CaO-B$_2$O$_3$), which prevents the vaporization of B$_2$O$_3$ and promotes h-BN particle growth at high temperatures. Up to now, the effect of CaO-B$_2$O$_3$ on the growth of h-BN particles during CRN is unclear. In this study, the role of CaO-B$_2$O$_3$ in the growth of h-BN particles during CRN was clarified via experimentation using various approaches. The results led to the ideal reaction process of CRN using a CaO promoter to produce large-particle-size h-BN powder.

Keywords — Boron nitride, Heat-treatment, Particle growth.

I. INTRODUCTION

In recent years, controlling the heat generated by electronic devices has become increasingly important, leading to a greater demand for heat-dissipating materials. Some researchers have investigated to improve the thermal conductivity and electrical insulation of resins by adding ceramic fillers, such as boron nitride, Al$_2$O$_3$, and AlN [1]-[3]. Among these, boron nitride offers excellent properties, such as high thermal conductivity, high insulation resistivity, low dielectric constant, and water resistance. Thus, boron nitride powder is widely used as a suitable filler with a high-thermal-conductivity and high-insulation-resistivity in resin composite for thermal interface materials (TIMs) [1]. The crystalline structures of boron nitride can be classified into hexagonal and cubic. The former hexagonal boron nitride (h-BN) is a white powder with a thin platelet structure similar to that of graphite. Thin-platelet h-BN particles did not fill the resin well. By increasing the particle size of h-BN, it is easier to form good thermal conduction paths within the resin sheet, and high thermal conductivity can be imparted to the resin sheets. It is important to exactly control the particle size and shape of h-BN fillers to obtain a high thermal conductivity [4]. The reaction of boric oxide with melamine or urea is well-known in the industrial manufacturing of h-BN powder [5]. In contrast, carbothermal reduction nitridation (CRN) contains the reaction of B$_2$O$_3$ with C in N$_2$ gas atmosphere [6], [7]. In CRN, CaO with high-melting-point plays an important role in preventing the vaporization of B$_2$O$_3$ at temperatures over 1680 °C. It has been already reported that CaO-B$_2$O$_3$ promotes h-BN particle growth during heat-treatment process at relatively low temperatures (~1500 °C) [8], [9].

In a previous study, we proposed a modified CRN process using a CaO promoter at relatively high temperatures over 1800°C to produce highly purified and crystallized h-BN powder [10]. This reaction temperature (>1800 °C) was remarkably high compared with previously reported processes (<1500 °C). Although B$_2$O$_3$ is vaporized at high temperatures over 1680 °C, CaO effectively catch B$_2$O$_3$ to form CaO-B$_2$O$_3$ complex oxides (CaB$_2$O$_6$, Ca$_2$B$_2$O$_7$, and Ca$_3$B$_2$O$_9$). Thus, the CaO promoter plays an important role during the production process. In this study, we further investigated the effect of CaO-B$_2$O$_3$ on the h-BN particle growth at relatively high temperatures (>1800 °C) and established an industrially advantageous process.

II. EXPERIMENTAL PROCEDURE

A. Raw Materials

H$_3$BO$_3$, C, and CaO were purchased from FUJIFILM Wako Pure Chemical Co. Ltd. We mixed 450 g (6.5 mol) of H$_3$BO$_3$, 80 g (6.7 mol) of C, and 14, 21, 28, 35, 42, 56, 70, and 84 g (0.2–1.5 mol) of CaO in a ball mill for 2h (Table I). We prepared a dehydrated bulk body of raw materials. H$_3$BO$_3$ forms a dense bulk body upon dehydration. Dehydration of H$_3$BO$_3$ proceeds as follows: 2H$_3$BO$_3$→B$_2$O$_3$+3H$_2$O. The dehydrated bulk body was prepared by heat-treatment of the mixed powder at 300 °C in air for 8 h. In this study, to synthesize white h-BN powders without residual carbons, a lower mixture ratio (C/H$_3$BO$_3$=1.03) was adopted than the theoretical value (C/H$_3$BO$_3$=1.5) according to the following equation: B$_2$O$_3$+3C→2BN+3CO.

B. Treatment of Raw Materials

First, we conducted the following experiment to investigate the role of CaO-B$_2$O$_3$. The sample Ca-1.0 (bulk body of the raw materials) (Table I) was heat-treated under two types of temperature rise conditions in N$_2$ to obtain h-BN powder. Two types of raw materials were heat-treated at 1400 °C 4 h – 1500 °C 10 min and 1400 °C 4 h – 1750 °C 10 min (indicated by intermediate temperature for 4h-maximum temperature for 10 min) in N$_2$. The obtained product was washed using aqueous hydrochloric acid (2 M) to remove calcium containing residual oxides at room temperature for 8 h and was rinsed using distilled water and air-dried at 120 °C for 10h. The washed (not containing CaO-B$_2$O$_3$) and unwashed (containing CaO-B$_2$O$_3$) products were treated at 1400 °C 4 h – 1840 °C 2 h (indicated by intermediate temperature for 4h-maximum temperature for

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The obtained product was washed with a hydrochloric acid solution (2M) as described, to remove residual calcium containing oxides. These processes are illustrated in Fig. 1.

### C. Characterization of Heat-treated Products before Acid Treatment and h-BN Powder

The impurity contents in the heat-treated products before acid treatment and h-BN powder were analyzed by X-ray fluorescence (XRF) using a Rigaku instrument. The elemental distribution in the heat-treated products before acid treatment was analyzed by energy-dispersive spectroscopy (EDS) using an SU3500 (FE-SEM apparatus) operating at 1–2 kV and an SU3500 (EDS apparatus) operating at 15 kV. The crystalline structures of heat-treated products before acid treatment were analyzed by X-ray diffraction (XRD) with CuKα radiation using a Rigaku X-ray diffractometer fitted with a nickel filter. The morphologies of the heat-treated products before acid treatment and h-BN powder were analyzed by field-emission scanning electron microscopy (FE-SEM) using an S-5500 microscope operating at 1–2 kV. The particle size distribution of the h-BN powder was analyzed using a laser diffraction particle size analyzer (HORIBA). The specific surface area of the h-BN powder was analyzed by N₂-BET method using SHIMAZU equipment.

### III. RESULTS AND DISCUSSION

#### A. h-BN Particle Growth with and without CaO-B₂O₃

As mentioned, our purpose is to obtain h-BN powder with a large particle size, high purity, and crystallinity. To achieve this, we confirmed the h-BN particle growth behavior with and without CaO-B₂O₃. To clarify this, in this section, we reveal the effect of CaO-B₂O₃ at high temperatures (>1800°C). Table II summarizes the results of XRD and XRF measurements of the heat-treated product (Ca) before or after acid treatment at 1400 °C 4 h – 1500 °C 10 min and 1400 °C 4 h – 1750 °C 10 min (indicated by intermediate temperature for 4 h-maximum temperature for 10 min) in N₂.

### TABLE II: ANALYSIS RESULT OF BULK BODY FORM OF RAW MATERIALS BEFORE HEAT-TREATMENT AND AFTER ACID TREATMENT UNDER EACH HEAT-CONDITION

<table>
<thead>
<tr>
<th>Sample</th>
<th>Results of XRD</th>
<th>Results of XRF(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>17</td>
<td>39</td>
</tr>
<tr>
<td>C</td>
<td>3.5</td>
<td>40</td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500 °C bulk nitridation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>63%</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>1750 °C bulk nitridation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>87%</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>1750 °C bulk nitridation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

As summarized in Table II, in the product heat-treated at 1500 °C, C remained, but in the heat-treated product at 1750 °C, C was completely consumed. The CaO-B₂O₃ complex oxides contained in each heat-treated product were CaB₂O₄ at 1500 °C and CaB₂O₆ at 1750 °C. Furthermore, CaO-B₂O₃ complex oxides were removed by acid treatment. As shown in Fig. 2, the h-BN particles grew larger as the heat-treatment temperature increased. Plate-like particles of approximately 10 μm were observed in the product heat-treated at 1840 °C for 2 h.
Furthermore, a second heat treatment was performed on the products with and without CaO-B_{2}O_{3} at 1840 °C for 2 h in N\textsubscript{2}. As shown in Fig. 3, the heat-treated product containing CaO-B_{2}O_{3} grew h-BN particles after heat treatment at 1840 °C for 2 h in N\textsubscript{2}, but the heat-treated product without CaO-B_{2}O_{3} did not. Therefore, it was confirmed that the pure h-BN particles did not grow into 10 μm plate-like particles by high-temperature treatment (>1800 °C), but that the h-BN particles grew by high-temperature heat treatment (>1800 °C) in the presence of CaO-B_{2}O_{3}.

B. Analysis of Heat-treated Products at 1840 °C in the CRN of BN Using a CaO Promoter

Fig. 4 shows SEM images of heat-treatment product (Ca 1.0 before acid treatment) of 1400 °C for 4 h – 1840 °C for 2 h in N\textsubscript{2}.

As shown in Fig. 4, h-BN particle aggregates with a particle size of 10 μm or less (Fig. 4A, 4B) and localized aggregates of h-BN particles with a particle size of 10 μm or larger (Fig. 4C, 4D) were identified. From this result, it is estimated that there are conditions in the growth field of h-BN particles. Therefore, we investigated the heat-treatment product (Ca 1.0 before acid treatment) in detail by SEM-EDS. Fig. 5 shows SEM-EDS results of heat-treatment product (Ca 1.0 before acid treatment) with localized h-BN plate-like particles larger than 10 μm. Fig. 5 shows that B is present throughout the heat-treatment product, and N is present in the h-BN particles observed from the SEM results. Furthermore, focusing on the regions where N is absent, Ca and O are present in high concentrations. From these results, B, Ca, and O are present around the h-BN particles with significant h-BN particle growth. B, Ca, and O are composite oxides consisting of CaO and B_{2}O_{3}, based on XRD measurements, suggesting that the h-BN particles are grown with CaO-B_{2}O_{3} covering the h-BN particles.

C. Abbreviations and Acronyms

As mentioned, the growth of h-BN particles was confirmed by high-temperature heat treatment in the presence of CaO-B_{2}O_{3} around BN particles. To investigate the effect of the amount of CaO added on h-BN particle growth, the raw materials listed in Table II were heat-treated at 1840 °C for 2 h in N\textsubscript{2}. Fig. 7 shows the specific surface area and particle size distribution of BN powder prepared by varying the amount of CaO added.
As shown in Fig. 7, the specific surface area decreased as the amount of added CaO increased. The decrease in the specific surface area indicates that the single particle size increases, and the proportion of small particles decreases. Furthermore, the sample (Ca0.5, 0.75), which contained less CaO, had a larger specific surface area than the other samples. The particle size distribution of the sample (Ca0.5, 0.75), in which the amount of CaO was small, also shifted to a lower particle size distribution. The sample (Ca2.5, 3.0), in which the amount of CaO was high, had a larger D90 particle size distribution than the other samples, indicating that it contained larger particles. Fig. 8 shows SEM images of the h-BN powders prepared by varying the amount of CaO added. As shown in Figure 8, in the sample (Ca0.5, 0.75), where the amount of CaO was small, there were numerous thin plate-like h-BN particles with small particle diameters. As the amount of CaO increased, the ratio of h-BN particles with thick plate-like particles and large particle diameters increased.

Furthermore, Fig. 9 also shows that in the sample (Ca3.0) with the highest amount of CaO, particles of approximately 30 μm were observed, as if the h-BN particles themselves had agglomerated and fused. The tendency of the D90 particle size distribution of the sample (Ca3.0) to increase was confirmed, suggesting that this is not the growth of single h-BN particles, but the agglomeration or fusion of single particles. These h-BN particles exhibit promise for use as highly thermally conductive fillers in resins.

The XRF Ca concentration of the heat-treated product increased with an increase in the amount of CaO added (Table III). XRD Rietveld analysis of the heat-treated product showed that the CaO content of the remaining composite oxide increased with the amount of CaO added (Table III). However, in sample (Ca0.5, Ca0.75) with low CaO content, 98 wt% (Ca0.5) and 91 wt% (Ca0.75) from the XRD Rietveld analysis results were h-BN, but the acid-treated samples showed that 42 wt% (Ca0.5) and 45 wt% (Ca0.75) of CaO-B2O3 complex oxide remained, and the XRF results also showed the presence of Ca and O, which suggested that sample (Ca0.5, Ca0.75) of CaO-B2O3 composite oxide remained in an amorphous form (Table III).

When the h-BN weight ratio in the heat-treated product was compared with the actual BN weight ratio obtained experimentally by theoretical calculation, the theoretical value was generally higher, suggesting that B2O3 was not perfectly converted to BN (Table IV). In this theoretical calculation, it is assumed that C used as the raw material contributed 100% to the h-BN formation reaction, CaO did not lose weight before and after the reaction, and B2O3 did not change in weight owing to evaporation, except for becoming h-BN. Therefore, it was clarified that the growth of h-BN particles was affected by crystalline CaO-B2O3. Furthermore, the amount of CaO added also plays an important role in the growth of h-BN particles.

Further, Fig. 7 shows the result of surface area and particle size distribution analysis of boron nitride powder (Ca0.5–3.0).

**FIG. 7. RESULT OF SURFACE AREA AND PARTICLE SIZE DISTRIBUTION ANALYSIS OF BORON NITRIDE POWDER (CAO.5–3.0).**

**TABLE III: RESULT OF XRF AND XRD ANALYSIS OF RAW MATERIALS AFTER HEAT-TREATMENT AT 1400 °C–1840 °C 2 H.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Result of XRF analysis (wt%)</th>
<th>Result of XRD rietvelt analysis( wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>N</td>
</tr>
<tr>
<td>Ca3.0</td>
<td>37.0</td>
<td>53.3</td>
</tr>
<tr>
<td>Ca2.5</td>
<td>36.9</td>
<td>53.3</td>
</tr>
<tr>
<td>Ca2.0</td>
<td>37.2</td>
<td>52.8</td>
</tr>
<tr>
<td>Ca1.5</td>
<td>38.7</td>
<td>53.6</td>
</tr>
<tr>
<td>Ca1.25</td>
<td>37.8</td>
<td>53.7</td>
</tr>
<tr>
<td>Ca1.0</td>
<td>38.1</td>
<td>55.5</td>
</tr>
<tr>
<td>Ca0.75</td>
<td>39.4</td>
<td>54.0</td>
</tr>
<tr>
<td>Ca0.5</td>
<td>39.2</td>
<td>54.7</td>
</tr>
</tbody>
</table>

**TABLE IV: BN RATIO IN NITRIDE PRODUCT (WT%) OF MEASURED AND THEORETICAL CALCULATED VALUE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured value (Weight loss in acid treatment)</th>
<th>Theoretical calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca3.0</td>
<td>39</td>
<td>47</td>
</tr>
<tr>
<td>Ca2.5</td>
<td>41</td>
<td>51</td>
</tr>
<tr>
<td>Ca2.0</td>
<td>46</td>
<td>54</td>
</tr>
<tr>
<td>Ca1.5</td>
<td>49</td>
<td>59</td>
</tr>
<tr>
<td>Ca1.25</td>
<td>52</td>
<td>61</td>
</tr>
<tr>
<td>Ca1.0</td>
<td>62</td>
<td>64</td>
</tr>
<tr>
<td>Ca0.75</td>
<td>55</td>
<td>67</td>
</tr>
<tr>
<td>Ca0.5</td>
<td>58</td>
<td>70</td>
</tr>
</tbody>
</table>

**IV. CONCLUSION**

We clarified the necessity of CaO-B2O3 in high-temperature treatment (over 1840 °C) via CRN using a CaO promoter to obtain large-particle-size h-BN powder. We also clarified that the h-BN particles were grown with CaO-B2O3 covering the h-BN particles and the growth of h-BN particles was affected by the crystalline CaO-B2O3. The h-BN powder obtained by CRN using the CaO promoter presented herein has a large particle size and thick plate-like.

**FIG. 8. SEM IMAGE OF BORON NITRIDE POWDER (A:CAO.5)–(H:CA3.0).**

**FIG. 9. SEM IMAGE OF BORON NITRIDE POWDER (CA3.0).**

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particles and can be expected to find application as a highly thermally conductive filler in resins.

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REFERENCES


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