Synthesis of cubic boron nitride with boron nitride powder formed from triammoniadecaborane

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Cubic BN was synthesized under high temperature and pressure conditions from BN powder formed by reaction of triammoniadecaborane (TAD) with ammonia. The BN powder formed from TAD and ammonia had a low degree of ordering. The crystal lattice of the BN powder increased in regularity with increasing synthesis temperature and time for the reaction of TAD with ammonia. The conversion yield of cubic BN at 1300 °C and 6.5 GPa in the presence of AlN increased with decreasing of reaction temperature of TAD and ammonia from 1000–700 °C. Cubic BN decreased in yield with increasing reaction time of TAD and ammonia at 800 °C. BN powder pre-heat treated at 1550 °C had a crystallite size, L_c, of 22 nm, and was converted to cubic BN in a 43% yield at 1300 °C and 6.5 GPa for 10 min. The activation energy for cubic BN synthesis from BN powder–20 mol% AlN was 97 kJ mol^{-1}, when the starting BN was synthesized at 800 °C. The conversion yield of cubic BN from the disordered BN–20 mol% AlN was 100% after heat treatment at 1300 °C and 6.5 GPa for 20 min.

1. Introduction

Cubic boron nitride (BN) has extreme hardness, excellent thermal conductivity and good electrical insulation [1]. Cubic BN is synthesized through high temperature and pressure treatment of crystalline hexagonal BN using various catalysts. The epitaxial growth of cubic BN on AlN substrate-catalyst is demonstrated for the synthesis of cubic BN from hexagonal BN. Hirano et al. [2–4] reported the synthesis of cubic BN–AlN composites from hexagonal BN–AlN in high yields in the presence of reducing agents. They also synthesized the fully dense cubic BN disc of preferred orientation on polycrystalline AlN sintered substrates [5].

BN of low crystallinity is a versatile starting material for the synthesis of cubic BN sintered bodies. Hirano et al. [6] reported that borazine was pyrolysed at 100 MPa below 700 °C to yield amorphous BN, which was transformed to cubic BN–AlN sintered compact by heat treatment at 6.5 GPa.

Triammoniadecaborane $B_{10}H_{14} \cdot 3NH_3$, (TAD) consists of boron, nitrogen and hydrogen, and is an appropriate starting material for the synthesis of pure BN without any alkaline earth and halogen elements. Yogo et al. [7] reported the synthesis of BN of low crystallinity from triammoniadecaborane and ammonia at atmospheric pressure above 800 °C. Low-ordered BN was also synthesized from triammoniadecaborane and hydrazine at 600 °C and 125 MPa [8].

The present paper describes the synthesis of cubic BN in the presence of AlN from BN powder synthesized by reaction of triammoniadecaborane and ammonia. The relation between the crystallinity of the starting BN and the conversion yield of cubic BN was investigated. The disorganized BN was found to be a superior precursor to hexagonal highly crystalline BN for the synthesis of cubic BN in the presence of AlN.

2. Experimental procedure

2.1. Starting materials

Triammoniadecaborane $B_{10}H_{14} \cdot 3NH_3$ (TAD) was prepared according to the method described by Williams et al. [9]. Hexagonal highly crystalline BN ($L_c > 100$ nm) and aluminium nitride (> 99%) were commercially available. AlN powder was heat treated at 400 °C and 10 Pa for 1 h and kept under nitrogen prior to its use.

2.2 Synthesis of BN of low crystallinity

Triammoniadecaborane weighed in a BN crucible was reacted with dry ammonia at atmospheric pressure at temperatures between 700 and 1000 °C as reported [7]

$$B_{10}H_{14} \cdot 3NH_3 \xrightarrow{\text{NH}_3} BN \qquad (1)$$
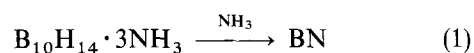
The specimen synthesized from TAD and ammonia at 800 °C was heat treated at temperatures from 1000–1550 °C for 2 h in a flow of nitrogen.

2.3. High-pressure treatment of boron nitride at 6.5 GPa

The high-pressure treatment was carried out using a girdle-type apparatus. The sample arrangement in the

pressure apparatus was the same as reported previously [8]. The pressure was calibrated at room temperature by the phase transition of Bi (2.55 GPa), Tl (3.67 GPa), and Ba (5.5 GPa). The temperature was determined on the basis of the relation of the melting points of Ag, Au and Ni at 6.5 GPa to the applied electric power. The specimen prepared from triammoniadecaborane and ammonia was mixed with aluminium nitride powder under an N_2 atmosphere, and then filled in a graphite crucible. The crucible serves as a heating element by passing the electrical current through it under pressure. The sample was treated at temperatures between 1300 and 1600 °C under 6.5 GPa from 5–30 min, and then cooled and decompressed. AlN was removed from the reaction product by treating it with hot 2N NaOH aqueous solution.

2.4. Characterization of the product

The reaction product was analysed by X-ray diffraction (XRD) analysis with CuK_α radiation. The yield of cubic BN was determined using the same calibration curve as reported previously [2]. The lattice constant $c_{0_{002}}$ and crystallite size $L_{c_{002}}$ of the specimen were determined from its 0 0 2 diffraction with highly pure Si as the internal standard [10].

The grain size of the product free from AlN was analysed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Synthesis of starting BN from TAD and ammonia

The starting BN powder was synthesized from TAD and ammonia at temperatures between 700 and 1000 °C as reported [7]. The X-ray diffraction of BN powder has two broad diffractions centred at 2θ = 25.5° and 43.0°. The former is attributed to the 0 0 2 diffraction of hexagonal BN, the latter corresponds to the 1 0 0 and 1 0 1 diffraction of hexagonal symmetry. The BN powder formed under these conditions was amorphous to X-rays. No three-dimensional regularity of the crystal lattice was formed in the BN powder. The BN powder formed at 800 °C was confirmed to have the stoichiometric ratio of B and N by elemental analysis [8].

3.2. Synthesis of cubic BN from BN powder at 1300 °C

BN powder synthesized in 3.1 was mixed with 20 mol % AlN as a substrate-catalyst [3], and then treated at 1300 °C and 6.5 GPa for 10 min in order to evaluate its properties as a starting material for the synthesis of cubic BN.

3.2.1. Effect of formation temperature of starting BN on yield of cubic BN

The conversion yield of cubic BN from the starting BN is plotted against the synthesis temperature of BN from TAD and ammonia for 5 h in Fig. 1. Cubic BN

increased in yield from 65%–86% with a decrease of synthesis temperature from 1000–700 °C.

According to Geick et al. [11], the absorption band at 800 cm^{-1} in the infrared spectrum is due to the BNB out-of-plane resonance of B_3N_3 structure. As the BNB absorption band increased in intensity on increasing the synthesis temperature [7], the BN powder formed at 1000 °C contained a larger amount of B_3N_3 structure than that formed at 700 °C.

3.2.2. Effect of synthesis time of starting BN on conversion yield of cubic BN

Fig. 2 shows the conversion yield of cubic BN and the reaction time of starting BN from TAD and ammonia at 800 °C. The yield of cubic BN decreased from 84%–72% with reaction time. The maximum yield, about 84%, was obtained when the starting BN was
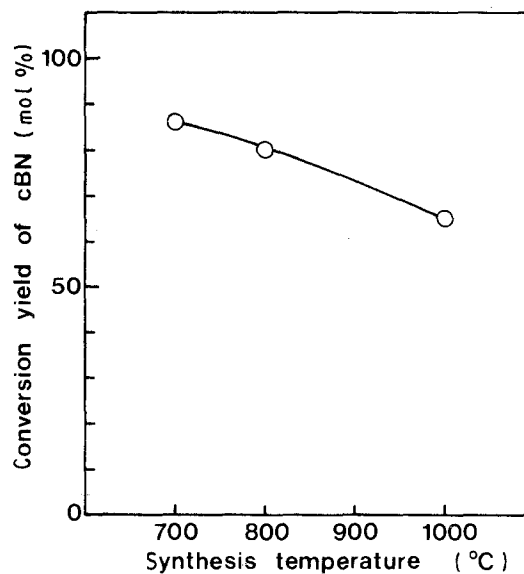

Figure 1 Change of cubic BN yield at 1300 °C and 6.5 GPa with synthesis temperature of starting BN from TAD and ammonia.
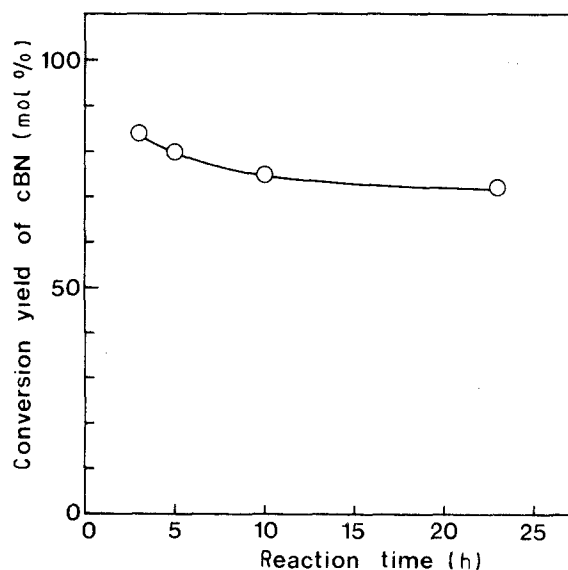

Figure 2 Variation of yield of cubic BN at 1300 °C and 6.5 GPa with synthesis reaction time of TAD and ammonia at 800 °C.

synthesized at the shortest reaction time of 3 h at 800 °C. The reaction time for the synthesis of starting BN should be longer than 3 h in order to obtain a stoichiometric boron nitride.

The intensity of BNB absorption band in the infrared spectra increased with increasing reaction time at 800 °C, and reached a constant value at the reaction time of 10 h [7]. Therefore, the yield of cubic BN depended upon the degree of B_3N_3 alignment in a starting BN, which was associated with the synthesis conditions of starting BN.

3.2.3. Effect of pre-heat treatment temperature on yield of cubic BN

The BN powder formed at 800 °C for 10 h was heat treated in a flow of nitrogen at 1000 and 1550 °C for 2 h prior to high pressure and temperature treatment at 1300 °C and 6.5 GPa. The results are summarized in Fig. 3. The yield from as-synthesized BN at 800 °C for 10 h was 75%. Cubic BN decreased in yield from 65%–53% with increasing heat-treatment temperature from 1000–1200 °C. The yield furthermore decreased to 43% after heat treatment at 1550 °C for 2 h.

The XRD profiles of starting BN and its heat-treated products at temperatures between 1000 and 1550 °C are shown in Fig. 4. The diffraction pattern of as-synthesized BN at 800 °C had broad diffractions as shown in Fig. 4a. A similar profile to Fig. 4a was observed after heat treatment at 1000 °C (Fig. 4b). At 1350 °C (Fig. 4c), the 1 0 0 diffraction at $2\theta = 41.6°$ began to separate from the broad diffraction centred at $2\theta = 43°$. This shows that the three-dimensional regularity started to form at this temperature, because the 1 0 0 diffraction reflects the stacking of the B_3N_3 plane in the c-axis direction. The three-dimensional lattice of the BN layer increased greatly in size at 1550 °C, as shown in Fig. 4d.

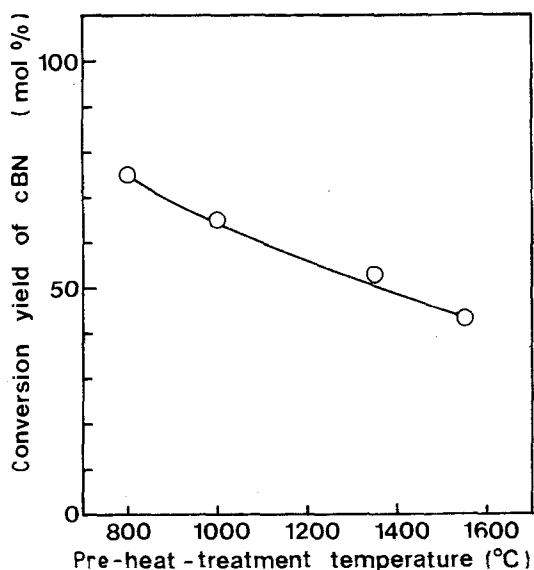Fig. 5 shows the relation between the crystallite size (L_{c002}) of starting BN and the temperature of the pre-
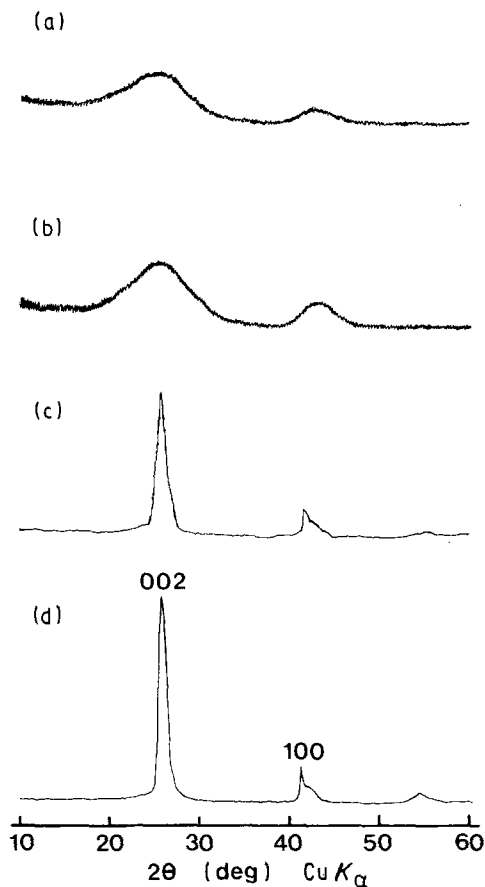
Figure 4 X-ray diffraction profiles of starting BN synthesized from TAD and ammonia under various conditions. (a) 800 °C for 10 h; (b) after heat treatment of (a) at 1000 °C for 2 h; (c) after heat treatment of (a) at 1350 °C for 2 h; (d) after heat treatment of (a) at 1550 °C for 2 h.
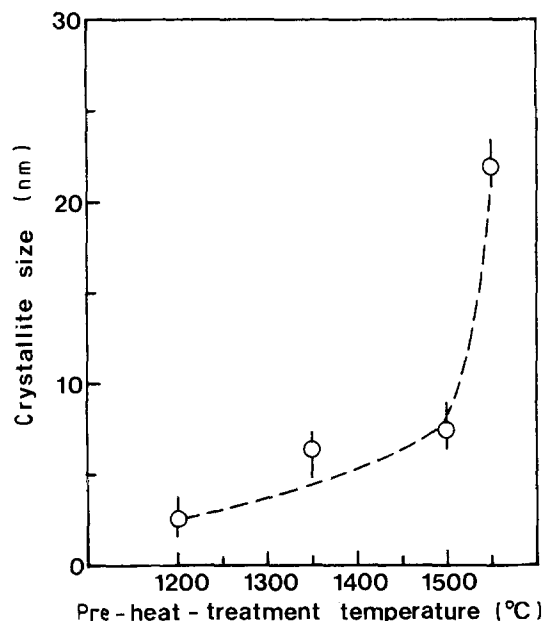
Figure 5 Change of crystallite size, L_c, of starting BN with pre-heat treatment temperature between 1200 and 1550 °C.

Figure 3 Variation of conversion yield of cubic BN at 1300 °C and 6.5 GPa with pre-heat treatment temperature of starting BN.

heat treatment under nitrogen. The crystallite size was less than 10 nm below the heat-treatment temperature of 1500 °C. However, L_c increased in size abruptly at 1550 °C. After heat treatment at 1550 °C, c_0 and L_c were 673.5 pm and 22 nm, respectively. The result

corresponds to the increase of the 1 0 0 diffraction in intensity in the BN powder heat treated at 1550 °C, as shown in Fig. 4d.

No large three-dimensional ordering of the BN layer is considered to form after a reaction time of 10 h at 800 °C. However, the different yield of cubic BN after high-temperature treatment at 6.5 GPa reflected the difference of regularity of crystal lattice of starting BN. Much higher regularity of BN pre-heat-treated at 1550 °C resulted in lower yield than that without pre-heat treatment. The results also support the advantage of using a less-ordered structure of BN as a starting material for cubic BN.

3.3. Synthesis of cubic BN under various conditions

3.3.1. Synthesis of cubic BN between 1300 and 1600 °C

The specimen synthesized from TAD and ammonia at 800 °C for 10 h was heat-treated with 20 mol % AlN from 1300–1600 °C and 6.5 GPa. The reaction time and temperature are correlated to the conversion yield of cubic BN in Fig. 6.

The reaction time required for the complete conversion of cubic BN decreased with temperature, e.g. 10 min at 1600 °C and 20 min at 1300 °C. On the other hand, highly crystalline hexagonal BN was converted to cubic BN in a 66% yield at 1600 °C and 6.5 GPa for 15 min [2].

BN of low crystallinity synthesized from TAD and ammonia was transformed to cubic BN at lower temperature and in higher conversion ratios than those of hexagonal BN with high crystallinity.

3.3.2. Grain size of cubic BN

The grain size of the cubic BN synthesized at 1600 °C and 6.5 GPa for 30 min was as large as 20 μm, when the starting BN was synthesized from TAD and am-
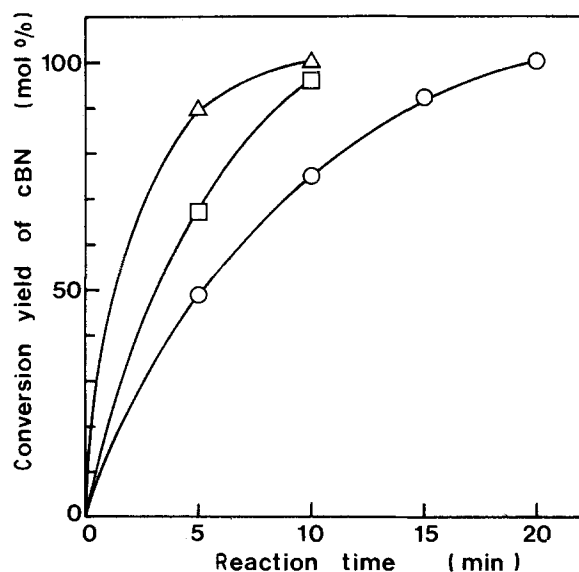
monia at 800 °C for 10 h. On the other hand, cubic BN synthesized from well-crystallized hexagonal BN at 1600 °C and 6.5 GPa for 30 min had the size about 2 μm. The size of cubic BN from the disordered BN is much larger than that from hexagonal crystalline BN. The large grain size of cubic BN results from a rapid diffusion of atoms in the BN powder during transformation.

3.3.3. Activation energy for conversion of cubic BN

The activation energy for the present conversion reaction of BN powder containing 20 mol % AlN was obtained from the Arrhenius plot shown in Fig. 7. The starting BN was synthesized from TAD and ammonia at 800 °C for 10 h. The time, τ (s), required for the conversion $\alpha = 0.8$ is plotted against the temperature.

The activation energy calculated from the slope of ln τ-T^{-1} was 97 kJ mol^{-1}, which was less than 60% of 168 kJ mol^{-1} for hexagonal highly crystalline BN–20 mol % AlN [5].

The activation energy of direct conversion of hexagonal BN to cubic BN is reported to range from 630–1050 kJ mol^{-1} [12]. The reconstructive direct transformation of hexgonal BN to cubic BN is responsible for the high activation energy without AlN.

The activity of BN powder depends upon the synthesis conditions from TAD and ammonia, which affect the crystallinity of BN powder as described in Section 3.2. The smaller activation energy of BN powder formed at 800 °C than that of well-crystallized BN is attributed to the less-ordered structure of the former than that of the latter.

Hirano et al. [5] demonstrated the growth of cubic BN disc on the most close-packed plane of nitrogen of AlN (0 0 1), which corresponded to the (1 1 1) plane of cubic BN. Similarly, the BN powder formed from TAD and ammonia undergoes the transformation involving diffusion and atomic rearrangement on to the AlN (0 0 1) substrate at 6.5 GPa above 1300 °C.

Figure 6 Molar conversion yields of cubic BN at various temperatures and reaction times under 6.5 GPa. (O) 1300 °C, (□) 1400 °C, (△) 1600 °C.
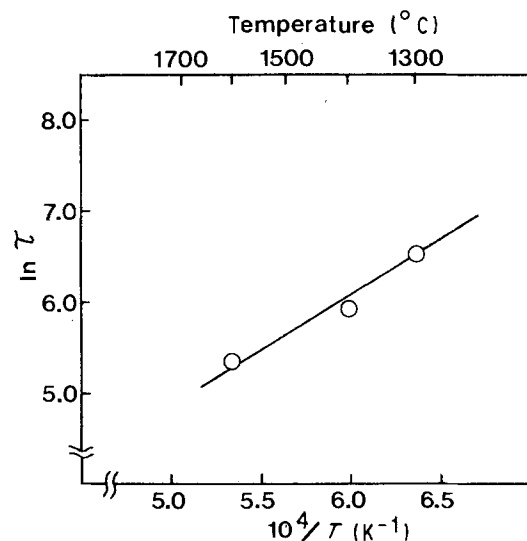

Figure 7 Arrhenius plot for cubic BN synthesis from BN powder synthesized from TAD and ammonia at 800 °C for 10 h.

Therefore, the absence of three-dimensional regularity in the disordered BN has the advantage of fast diffusion of atoms on the substrate plane of AlN.

4. Conclusions

The disorganized BN formed from triammoniadecaborane (TAD) and ammonia was converted to cubic BN using AlN. The synthesis conditions and properties of starting BN necessary for effective synthesis of cubic BN were found to be as follows.

1. The desired characteristics of starting BN for cubic BN synthesis was the randomness of B_3N_3 structure, which turned out to be amorphous to X-rays.

2. BN powder formed from TAD and ammonia at 700 °C over 5 h gave the best yield of cubic BN after heat treatment at 1300 °C and 6.5 GPa.

3. Cubic BN decreased in yield with increasing regularity of three-dimensional structure in a starting BN.

4. The activation energy of cubic BN synthesis with 20 mol % AlN from BN powder formed at 800 °C for 10 h was 97 kJ mol^{-1}.

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