

Synthesis of boron nitride from triammoniadecaborane and hydrazine under pressure

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Boron nitride (BN) of low crystallinity was synthesized from triammoniadecaborane (TAD) and hydrazine at 125 MPa below 650°C. TAD itself was pyrolysed at 600°C and 125 MPa to form a mixture of amorphous boron and boron nitride containing BH and NH bonds. The infrared spectrum of the pyrolysed product of TAD itself at 600°C and 125 MPa showed the BNB absorption at 800 cm⁻¹ due to the formation of B₃N₃ structures. The X-ray diffraction (XRD) of the reaction product from TAD and hydrazine at 600°C had broad diffractions centred at 2θ = 25.5° and 43.0° (CuKα). The BH absorption at 2500 cm⁻¹ decreased in intensity on increasing the N/B ratio from 0.3 to 0.85, and disappeared finally at a ratio of N/B = 1.3. The reaction product at 125 MPa had a porous structure. The electron diffraction of the specimen changed from faint rings to spots on circular rings after heat treatment at 800°C for 10 h. The heat-treated specimen, however, did not give sharp reflections corresponding to hexagonal BN in the XRD profile. BN of low crystallinity was transferred to cubic BN at 1200°C and 6.5 GPa in a 90% yield, which was higher than that of well-crystallized BN in the presence of AlN.

1. Introduction

Cubic boron nitride (BN) is synthesized through high temperature and pressure treatment of hexagonal BN. Various boron sources, such as boric oxide, halide, boron compound and diborane, are reacted with ammonia, urea and cyanide to yield BN of ordinary pressure phase [1, 2].

BN of low crystallinity is a versatile starting material for the synthesis of cubic BN sintered body. Hirano *et al.* [3] synthesized cubic BN-AlN composites from hexagonal BN-AlN in high yields in the presence of reducing agents. Hirano *et al.* [4] 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. Amorphous BN containing residual BH and NH bonds formed from borazine demonstrated the importance of reducing conditions as well as low crystallinity of starting BN for the synthesis of cubic BN in the presence of AlN. However, borazine is a volatile liquid, and is decomposed easily to boric acid and ammonia by air and light.

Boron cage compounds, such as derivatives of decaborane (B₁₀H₁₄), are versatile boron sources for the synthesis of BN because of their higher stability than borazine in air. Yogo *et al.* [5] demonstrated the synthesis of BN of low crystallinity from triammoniadecaborane and ammonia at atmospheric pressure above 800°C.

The present paper deals with the synthesis of BN from triammoniadecaborane and hydrazine under

pressure. One of the characteristics of pressure pyrolysis is the high yield synthesis of products. BN of low crystallinity was successfully synthesized in high yields from triammoniadecaborane and hydrazine at 125 MPa below 650°C. The formation process of BN was investigated by infrared spectroscopy. The disordered 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 B₁₀H₁₄ · 3NH₃ (TAD) was prepared according to the method described by Williams *et al.* [6]. Anhydrous hydrazine NH₂NH₂ (b.p. 113.5°C/10⁵ Pa) and aluminium nitride (> 99%) were commercially available.

2.2. Synthesis of boron nitride at 125 MPa

All pressure work at 125 MPa was carried out with a hydrothermal apparatus of the cold-seal type. TAD was dissolved in anhydrous hydrazine under nitrogen. Then the solution was sealed in a nitrogen atmosphere into a thin-walled gold capsule, 3.0 or 5.0 mm diameter and 70 mm long.

TAD and the various TAD solutions of hydrazine were pyrolysed at temperatures between 400 and 650°C and 125 MPa for 3 h. The heating rate was 10°C min⁻¹ at constant pressure of 125 MPa. The pressure was kept constant by releasing water as the pressure-transporting medium during heating. The

pressure was measured with a calibrated Heise gauge and the temperature was measured using a calibrated sheathed thermocouple set inside the pressure vessel. The sample was quenched after each experimental run.

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 is shown in Fig. 1. The pressure was calibrated at room temperature by the phase transition of bismuth (2.55 GPa), thallium (3.67), and barium (5.5). The temperature was determined on the basis of the relation of the melting points of silver, gold and nickel at 6.5 GPa to the applied electric power. The specimen prepared from triammonia-decaborane and hydrazine at 600°C was mixed with aluminium nitride powder under a nitrogen atmosphere, and then filled in a graphite crucible. The sample was treated at temperatures between 1200 and 1400°C under 6.5 GPa for 10 min, and then cooled and decompressed. The specimen was analysed by X-ray diffraction (XRD), and the yield of cubic BN was determined using the same calibration curve as reported [3].

2.4. Characterization of the product

The reaction product was analysed by XRD. The infrared (IR) spectrum of the sample was measured by a KBr disc method.

The product was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and electron diffraction analysis.

Elemental analysis of boron was carried out according to the method of Erickson and Conrad [7].

3. Results and discussion

3.1. Pressure pyrolysis of triammoniadecaborane

3.1.1. Pyrolysis of triammoniadecaborane

Triammoniadecaborane ($B_{10}H_{14} \cdot 3NH_3$, TAD) consists of boron, nitrogen and hydrogen, and is an appro-

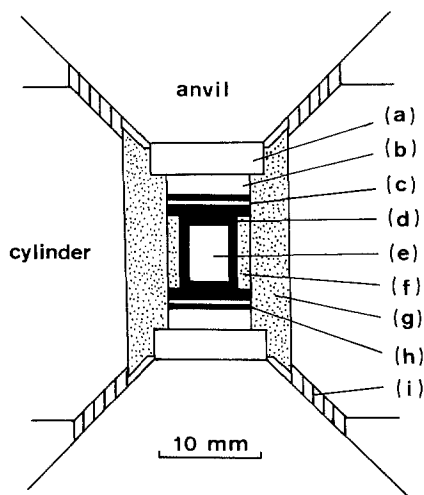


Figure 1 Sample arrangement in high-pressure apparatus: (a) WC disc; (b) steel disc; (c) molybdenum plate; (d) graphite heater; (e) sample room; (f) fired pyrophyllite; (g) pyrophyllite; (h) graphite plate; (i) composite gasket.

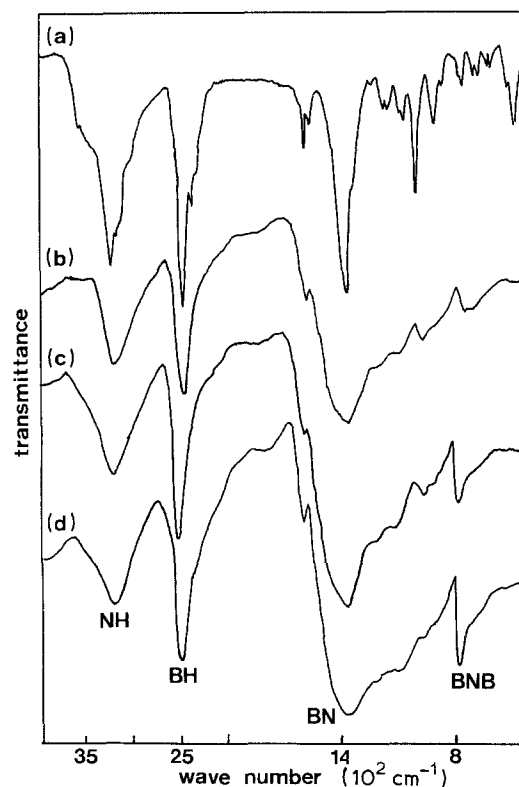


Figure 2 IR spectra of starting TAD and pyrolysed TAD at various temperatures between 550 and 650°C under 125 MPa for 3 h. (a) TAD; (b) 550°C; (c) 600°C; (d) 650°C.

priate starting material for the synthesis of pure BN without any alkaline earth and halogen elements. TAD is a white solid, and decomposes above 300°C without melting at atmospheric pressure.

TAD was pyrolysed at 550°C and 125 MPa for 3 h to produce a brown solid with a yield above 90% in weight.

3.1.2. Infrared spectroscopy

Fig. 2 shows the infrared spectra of starting TAD and its pyrolysis products at temperatures from 550 to 650°C and 125 MPa for 3 h.

TAD had the absorptions of NH at 3400 cm^{-1} , BH at 2500 cm^{-1} , and BN at 1390 cm^{-1} (Fig. 2a), which were in good agreement with those reported [6]. The pyrolysis products had absorption bands ascribed to NH, BH and BN bonds at 3400, 2500 and 1390 cm^{-1} , respectively. The BH and NH absorption bands decreased in intensity with increasing pyrolysis temperature from 550 to 650°C as shown in Figs 2b, c and d. The BN absorption at 1390 cm^{-1} changed from a sharp to a broad band after pyrolysis at 550°C (Fig. 2b). These results reveal that TAD undergoes decomposition and dehydrogenation reaction to yield a solid containing BN, NH and BH bonds.

The absorption band at 800 cm^{-1} appeared in the pyrolysis product at 600°C, and increased in intensity with increasing temperature from 600 to 650°C. The absorption band at 800 cm^{-1} is assigned to the out-of-plane B–N–B resonance of hexagonal BN [8]. The presence of the BNB absorption band shows that the B_3N_3 structure was formed by the reaction of the B_{10} cage with 3 mol NH_3 in a gold capsule. Therefore, the pyrolysis product of TAD itself is a mixture

of amorphous boron and boron nitride containing hydrogen as residual BH and NH bonds.

3.2. Synthesis of boron nitride from TAD and hydrazine

3.2.1. Reactivity of decaborane and TAD with hydrazine

Anhydrous hydrazine was used for the nitrogen source in an attempt to synthesize stoichiometric boron nitride.

Decaborane ($B_{10}H_{14}$) reacted with hydrazine very vigorously to induce a fire in air. Therefore, the reactivity of decaborane was adjusted by the formation of an adduct with ammonia ($B_{10}H_{14} \cdot 3NH_3$). TAD was found to be less reactive than decaborane, and to dissolve in hydrazine up to 36 wt % to yield uncoloured transparent solutions under nitrogen.

3.2.2. Infrared spectroscopy

The various mixture solutions of TAD and hydrazine were pyrolysed at 600°C and 125 MPa for 3 h. The IR spectra of the pyrolysis products are shown in Fig. 3.

The BH absorption at 2500 cm^{-1} decreased in intensity with an increase in the ratio of nitrogen and boron from 0.3 to 0.85 (Figs 3a to c). Finally, the BH absorption disappeared when the ratio of nitrogen and boron is 1.3 as shown in Fig. 3d. The colour of the pyrolysis product changed from brown to white with increasing N/B ratio.

The BNB absorption at 800 cm^{-1} increased in intensity with increasing N/B ratios from 0.3 to 1.3. These results show that the BH bonds of the B_{10} cage react with a sufficient amount of nitrogen compounds to yield boron nitride at 600°C and 125 MPa.

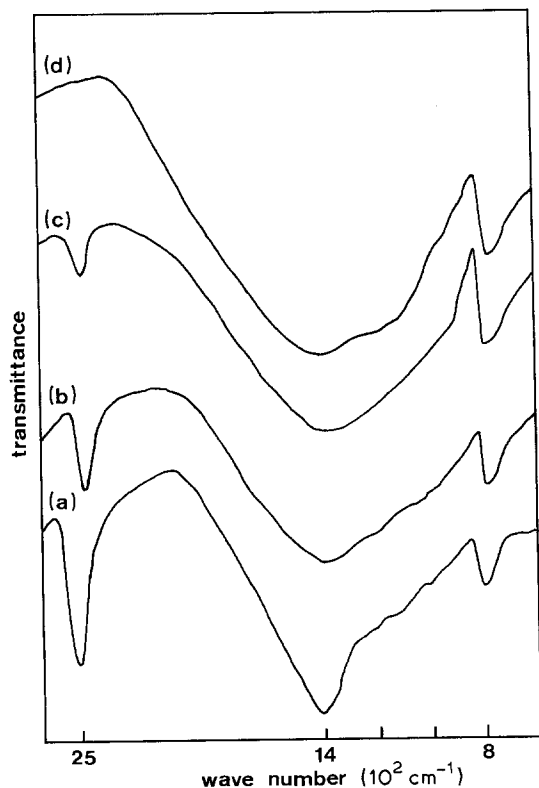


Figure 3 Change of IR spectra of reaction product formed from TAD and hydrazine with N/B ratios at 600°C and 125 MPa for 3 h. N/B = (a) 0.3, (b) 0.48, (c) 0.85, (d) 1.3.

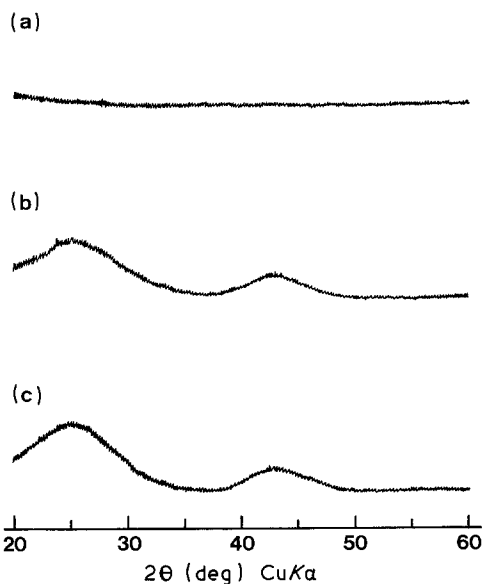


Figure 4 X-ray diffraction of pyrolysis product. (a) Pyrolysis product of TAD at 600°C and 125 MPa. (b) Reaction product of TAD and hydrazine with N/B ratio of 0.85 at 600°C and 125 MPa. (c) After heat treatment of (b) at 800°C for 10 h in a flow of ammonia.

3.2.3. X-ray diffraction studies

The XRD profile of the pyrolysis product of TAD itself at 600°C and 125 MPa for 3 h is shown in Fig. 4a. No characteristic reflection was observed in the XRD profile, although the specimen contained a small amount of B_3N_3 alignment as shown in Section 3.1.2.

When the N/B ratio of the starting material increased from 0.3 to 0.85, the XRD profile of the pyrolysis product at 600°C consisted of two broad diffractions as shown in Fig. 4b. The diffraction centred at $2\theta = 25.5^\circ$ ($CuK\alpha$) is attributed to the 002 diffraction of hexagonal symmetry. The 100 and 101 reflections of hexagonal boron nitride correspond to the diffraction centred at $2\theta = 43.0^\circ$.

The specimen was subsequently heat-treated in a flow of ammonia at 800°C for 10 h. The XRD profile of the product is shown in Fig. 4c. The crystallinity of the product is apparently comparable with that before heat treatment.

3.2.4. Electron diffraction studies

When a hydrazine solution of TAD with the N/B ratio of 0.85 was pyrolysed at 600°C and 125 MPa, the electron diffraction of the product showed faint ring patterns.

The product was successively reacted with ammonia at 800°C for 10 h to yield a white solid. The electron diffraction pattern of the white solid is shown in Fig. 5. Distinct spots appeared on the series of circular rings after heat treatment. This result shows some crystallinity is present, although the orientation is random. The product is polycrystalline boron nitride, with hexagonal symmetry. However, no large three-dimensional lattice was found in the product as shown in Fig. 4c.

The elemental analyses of the product showed that the product heat-treated at 800°C for 10 h in a flow of

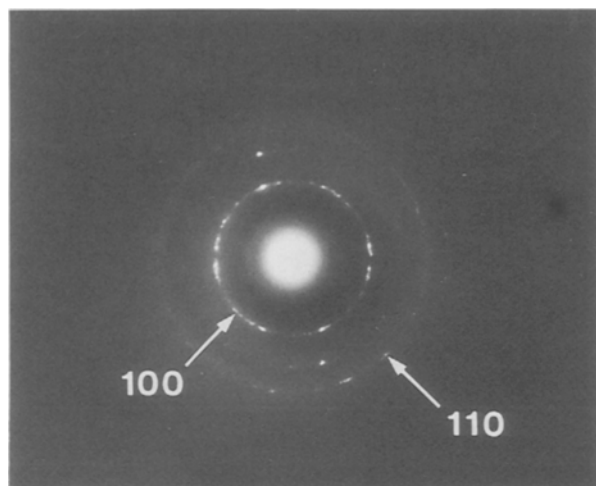


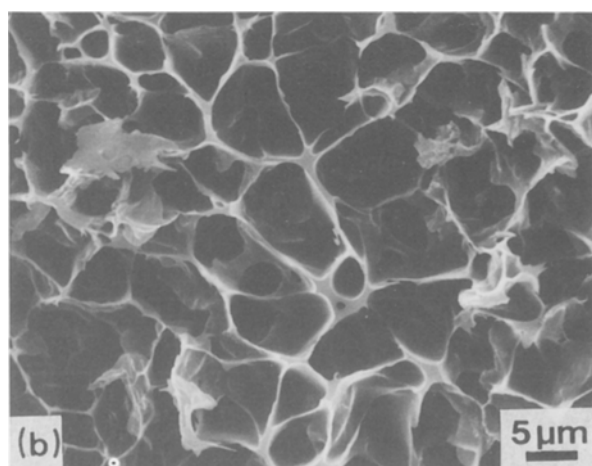
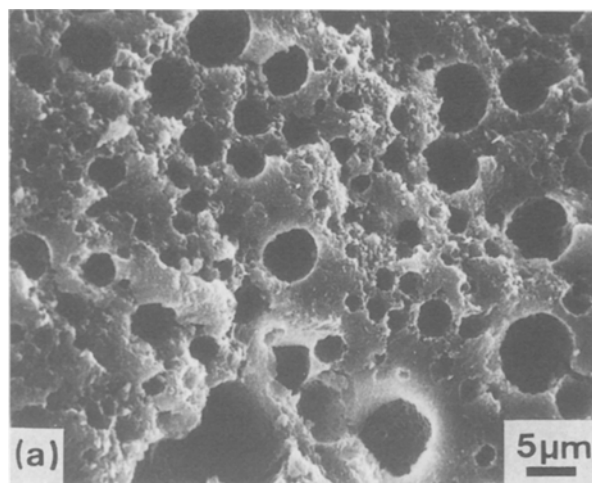
Figure 5 Electron diffraction of boron nitride shown in Fig. 4c.

ammonia contained $42.0 \pm 1.0\%$ of boron (calculated for BN, 43.56%).

TAD reacted with ammonia above 800°C at atmospheric pressure for more than 5 h to yield BN of low crystallinity [5], whereas disorganized BN was synthesized from TAD and hydrazine at 600°C and 125 MPa for 3 h in a closed system.

3.2.5. Morphology of the pyrolysis product

The morphologies of the pyrolysis product of TAD itself at 400 and 650°C under 125 MPa for 3 h are shown in Figs 6a and b, respectively. The number of



pores increased with increasing pyrolysis temperature from 400 to 650°C .

Fig. 6c shows the morphology of the reaction product from TAD and hydrazine at 600°C and 125 MPa with the N/B ratio of 0.85.

Gas phases trapped in the matrix during pyrolysis could form such pores in the product. The generation of gases proceeds more rapidly with increasing pyrolysis temperature, although the pressure suppresses the formation of gas phases. The viscosity of phases during pyrolysis is considered to be extremely high.

3.3. Synthesis of cubic BN

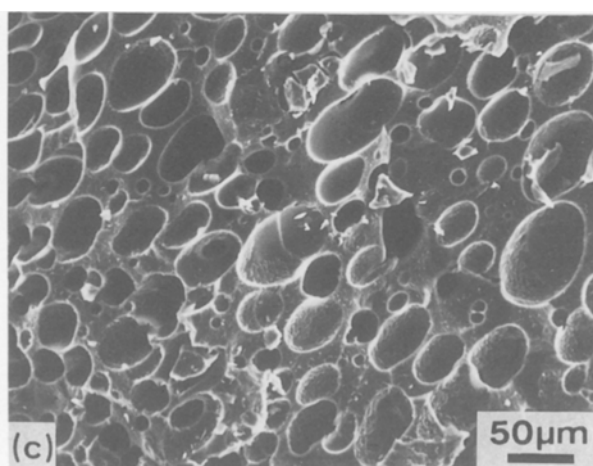
The specimen formed from TAD and hydrazine was heat-treated at 6.5 GPa in order to elucidate its properties as the starting material for cubic BN synthesis.

The specimen synthesized in Section 3.2.4 was mixed with 20 mol% AlN as a substrate-catalyst [3], and then treated at 1200°C and 6.5 GPa for 10 min. The XRD analysis showed that BN of low crystallinity was transformed to cubic BN in a 90% yield. In addition, the disordered BN was completely converted to cubic BN at 1400°C and 6.5 GPa for 10 min. On the other hand, highly crystalline-hexagonal BN was converted to cubic BN in a 66% yield at 1600°C and 6.5 GPa [3].

The growth of cubic BN was demonstrated to proceed on the most close-packed layer of AlN (001) plane [3, 9]. The active substrate plane of AlN is easily oxidized to Al_2O_3 without reducing agents, such as benzene and borazine [3, 9–11]. When amorphous BN synthesized from borazine was used as a starting BN, residual BH and NH bonds provided the reducing conditions during high temperature and pressure treatment [4]. Similarly, the residual NH bonds confirmed by IR spectroscopy in the present BN of low crystallinity acts as a reducing agent during transformation to cubic BN.

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

Figure 6 Morphologies of pyrolysis product formed under 125 MPa for 3 h. (a) Pyrolysis product of TAD at 400°C . (b) Pyrolysis product of TAD at 650°C . (c) Pyrolysis product of TAD and hydrazine with N/B ratio of 0.85 at 600°C .



three-dimensional regularity of the disordered BN has an advantage of the fast diffusion of atoms on the substrate plane of AlN.

4. Conclusions

Boron nitride of low crystallinity was synthesized successfully in high yields by the reaction of tri-ammoniadecaborane (TAD) and hydrazine at 125 MPa below 650°C. The synthesis conditions and properties of BN were found to be as follows.

1. TAD itself was pyrolysed at 600°C and 125 MPa to yield a brown solid containing a small amount of B₃N₃ structure.

2. Boron nitride synthesized from TAD and hydrazine had a low degree of ordering, which showed broad diffraction corresponding to those of hexagonal BN in the XRD profile.

3. Practically stoichiometric BN was synthesized by pressure pyrolysis of TAD and hydrazine followed by heat treatment at 800°C in a flow of ammonia.

4. The disorganized BN was transformed to cubic BN in a 90% yield after heat treatment at 1200°C and 6.5 GPa for 10 min in the presence of AlN.

References

1. K. A. SCHWETZ and A. LIPP, *Ber. Deut. Keram. Ges.* **56** (1979) 1.

2. Gmelin, "Handbuch der anorganischen Chemie", Bd. 13, Borverbindungen Teil 1 (Springer-Verlag, Berlin, 1974) p. 1.
3. S. HIRANO, T. YAMAGUCHI and S. NAKA, *J. Amer. Ceram. Soc.* **64** (1981) 734.
4. S. HIRANO, T. YOGO, S. ASADA and S. NAKA, *ibid.* **72** (1989) 66.
5. T. YOGO, S. MATSUO and S. NAKA, *Yogyo Kyokai Shi* **95** (1987) 94.
6. J. WILLIAMS, R. L. WILLIAMS and J. C. WRIGHT, *J. Chem. Soc.* (1963) 5816.
7. S. L. ERICKSON and F. J. CONRAD, *Talanta* **18** (1971) 1066.
8. R. GEICK, C. H. PERRY and G. RUPPRECHT, *Phys. Rev.* **146** (1966) 543.
9. S. HIRANO, N. FUJII, A. FUJII and S. NAKA, "Advances in Ceramics", Vol. 26 (American Ceramic Society, Westerville, Ohio, 1989) in press.
10. S. HIRANO, S. HON and S. NAKA, "High Pressure Research and Industry", Proceedings 8th AIRAPT Conference, Vol. 1 (1982) p. 376.
11. S. HIRANO, S. HON and S. NAKA, *Jpn. Soc. Mater. Sci.* **33** (1984) 1355.

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