BCN Ceramics from Pyrrolidine-Borane Complex

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Pyrrolidine-borane complex was prepared from pyrrolidine and borane-dimethyl sulfide complex as starting material and BCN ceramics were prepared at 1273 K in 0.1 MPa under Ar or NH₃. The BCN ceramics were amorphous structure and they were consisted of trigonal and tetragonal B–N bonds by FT-IR and ¹¹B-NMR measurements. BCN ceramics usually have only trigonal bond. The chemical compositions of the BCN ceramics were BC_{1.5}N_{0.4} and BC_{0.9}N_{0.4} obtained at 1273 K under Ar and NH₃ atmosphere, respectively. Electrical conductivity of the BCN ceramics indicated a semiconductive property.

(Received October 1, 1999; Accepted June 22, 2000)

Keywords: pyrrolidine-borane complex, BCN ceramics, preceramics, pyridine-borane complex

1. Introduction

Precursor method has been focused on advanced route to ceramics.^{1–3}) Organic compounds are used as starting materials, and this method leads organic compounds to advanced ceramics by passing pyrolytic conversion processes; the easier structural control of the organic compounds, the easier compositional and functional tailoring of the ceramics. The CVD method is widely used to synthesize BCN ceramics.^{4–7}) However, bulk forming and large-scale preparation are difficult using this method. Bulk formation is necessary to evaluate various properties of BCN ceramics. Therefore, the precursor method has been focused on to resolve these problems.⁸) Bill *et al.* reported that BCN ceramics were prepared from a pyridine-borane complex using this method.^{9–11}) Amorphous ceramics of BC₄N and BN compositions were prepared at 1323 K under Ar and NH₃, respectively. The boron coordination bonds of BC₄N and BN were trigonal and existed as B–N bonds in the ceramics. The heat-treated specimen under Ar atmosphere exhibited semiconductive properties, and the energy gap was 0.07 eV. The specimen under NH₃ atmosphere is an insulator. When piperazine-borane complex is the starting material, the composition was BC₂N at 1323 K under Ar atmosphere and contained trigonal B–N boron atoms identical to the pyridine-borane complex. However, the other heterocyclic compounds can not be examined as starting materials because these starting materials are not available on a commercial basis. Therefore, the objective of this work is to prepare a new pyrrolidine-borane complex from the reaction of pyrrolidine and borane-dimethyl sulfide complex as a first stage. In this study, the authors investigate the structural correlation between the precursor and ceramics.

2. Experimental

2.1 Synthesis of pyrrolidine-borane complex

0.1 mol (5.0×10^{-5} m³) of borane-dimethyl sulfide complex in 2 kmol m⁻³ toluene was dropped into 0.1 mol (1.0×10^{-5} m³) of pyrrolidine at 1273 K in 0.1 MPa Ar and the solution was stirred for 24 h and cooled using ethanol with dry ice.

The toluene was removed and a pyrrolidine-borane complex was obtained as the precipitation product.

2.2 Synthesis of preceramics

The pyrrolidine-borane complex obtained was heated continuously at 373 K for 5 h in 0.1 MPa Ar, then at 473 K for 10 h, at 573 K for 24 h, and at 673 K for an additional 24 h, which is shown in Fig. 1. The colorless and transparent liquid changed to a brown liquid and then to a brown solid. The brown solid obtained was milled ($<75 \mu\text{m}$), and pyrrolidine-borane preceramic powder was prepared. The green compact was used by CIP (cold isostatic pressure) method.

2.3 Synthesis of BCN ceramics

The powdered pyrrolidine-borane preceramics were heated at 1273 K for 2 h (heating rate: 250 K h^{-1}) in Ar (purity, 99.99%) and NH₃ (purity, 99.9%) (flow rate, $5.0 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}$, 0.1 MPa). The specimen was washed by ethanol, and BCN ceramics were prepared. The ceramics were about $5.0 \times 10^{-3} \text{ m}$ in diameter and $7.0 \times 10^{-3} \text{ m}$ in height.

2.4 Analysis

The analysis of the ceramics obtained was evaluated

Fig. 1 Synthesized condition of pyrrolidine-borane preceramics.

by thermo gravimetric analysis (TGA) (Sinku-Riko TCD-9800A; carrier gas, Ar; flow rate, $5.0 \times 10^{-5} \text{ m}^3 \text{ min}^{-1}$; heating rate, 523 K h^{-1}), gas chromatograph (Yanaco G3810 TCD; Column, Porapack N; carrier gas, He; flow rate, $5.0 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}$), Fourier transform infrared (FT-IR) (Jasco FT-IR 5300 type fourier transform infrared spectroscopy), ^{11}B solid state nuclear magnetic resonance (NMR) (Jeol JNM-GX270), elemental analysis (N, O, Horiba Oxygen/Nitrogen analyzer 550, 650 series; C, S, Carbon/Sulfur analyzer 510, 511, 512), Raman spectroscopic (Jeol NRS-2000, laser, 300 mW; exposure meter, 60 s; integration number, 10 times; argon laser, 514.5 nm) and X-ray diffraction (XRD) ($\text{CuK}\alpha_1/40 \text{ kV}/20 \text{ mA}$, $2\theta = 10\text{--}80$ degree).

3. Results and Discussion

3.1 Preceramics derived pyrrolidine-borane complex

The FT-IR spectra of the pyrrolidine-borane complex and preceramics are shown in Fig. 2. N–H bonds (3180 cm^{-1}) and B–H bonds (2300 cm^{-1}) exist in the complex. However, both N–H and B–H bonds in the preceramics disappear in the pyrolytic process. Trigonal B–N bonds (defined as $\text{B}(\text{sp}^2)\text{--N}$) of h-BN, and tetragonal B–N bonds (defined as $\text{B}(\text{sp}^3)\text{--N}$) of the c-BN, are also observed in Fig. 2.^{12,13} Trigonal and tetragonal B–N bonds exist in both the complex and preceramics. The absorption intensity of h-BN around 1390 cm^{-1} is strong and that of c-BN is very weak.¹⁴ The trigonal B–N bond absorption of the preceramics is weak, as shown in Fig. 2. Tetragonal B–N bonds also exist in the preceramics, but it is difficult to discuss the ratio of $\text{B}(\text{sp}^3)\text{--N}$ to $\text{B}(\text{sp}^2)\text{--N}$ based on the FT-IR results. The results of the ^{11}B solid state NMR measurement are shown in Fig. 3. The preceramics show a single symmetrical resonance identical to that of c-BN.¹⁵ The trigonal B–N bonds are the same as h-BN¹⁵ and tetragonal B–N bonds and

Fig. 2 FT-IR spectra of pyrrolidine-borane complex (c), preceramics (d), h-BN (a) and c-BN (b).

coexist in the preceramics, as shown in Fig. 2.

The molar chemical compositions of the pyrrolidine-borane complex and the preceramics were $\text{B}_1\text{C}_4\text{N}_1\text{H}_{12}$ and $\text{B}_{1.0}\text{C}_{2.6}\text{N}_{0.2}\text{H}_{5.0}$. The chemical compositions of the pyridine-borane complex and the preceramics were $\text{B}_1\text{C}_5\text{N}_1\text{H}_5$ and $\text{B}_{1.0}\text{C}_{3.7}\text{N}_{0.9}\text{H}_{7.3}$.¹⁶ The nitrogen in the pyrrolidine-borane preceramics decreased compared to the pyridine-borane preceramics. Pyrolysis of the pyrrolidine-borane preceramics may progress further because there are no conjugated double bonds in the pyrrolidine-borane complex as starting material. The bonds involving hydrogen, such as B–H, C–H, and N–H, decreased in the pyrrolidine-borane preceramics compared with pyridine-borane preceramics.

3.2 BCN ceramics

Figure 4 shows the thermogravimetric change during pyrolysis. The ceramic yield is about 60% by heat treatment up to 1273 K . A rapid decrease in weight occurs around 673 K . The pyrrolidine-borane preceramics give off hydrocarbon (ethane

Fig. 3 ^{11}B solid state NMR spectra of pyrrolidine-borane preceramics (c), h-BN (a) and c-BN (b).

Fig. 4 TGA curves of pyrrolidine-borane preceramics in Ar.

and ethylene) gases at this temperature, which were detected by gas chromatograph. FT-IR and ^{11}B solid state NMR measurements were performed to determine the structural change of the pyrrolidine-borane preceramics. The FT-IR spectra of the BCN ceramics were obtained under both Ar and NH_3 by heat treatment at 1273 K, which are shown in Fig. 5. The peaks are indistinct from pyrrolidine-borane preceramics because of the broadening and decreasing of the absorption. The existence of trigonal B–N bonds can be confirmed when compared with 1390 and 810 cm^{-1} of h-BN as the standard. However, it is not clear whether tetragonal B–N bonds exist.

Fig. 5 FT-IR spectra of pyrrolidine-borane preceramics (c), BCN ceramics at 1273 K (d, e, f and g), h-BN (a) and c-BN (b).

Fig. 6 ^{11}B solid state NMR spectra of pyrrolidine-borane preceramics (c), BCN ceramics at 1273 K (d, e and f), h-BN (a) and c-BN (b).

The ^{11}B solid state NMR spectra are demonstrated in Fig. 6. The split peaks at 0 and 30 ppm of the BCN ceramics prepared from pyrrolidine-borane at 1273 K under both Ar and NH_3 can be considered to be trigonal B–N bonds. The FT-IR (Fig. 5) and ^{11}B -NMR (Fig. 6) suggest that trigonal and tetragonal B–N bonds coexist, and trigonal B–N bonds of the ceramics increase with increases of the heat treatment temperature.^{17,18} These increases are thought to be due to the thermal stability of trigonal B–N bonds under atmospheric pressure. However, the BCN ceramics, which derived from pyridine-borane complex at the same temperature and in the same atmosphere, have trigonal B–N bonds only, which are shown in Fig. 6.¹⁶

The results of the chemical composition analysis are shown in Table 1. The specimens heated at 1273 K under Ar and NH_3 atmospheres decrease in both carbon and hydrogen compared with pyrrolidine-borane preceramics, due to the formation of hydrogen and hydrocarbon gases. The B/N ratio of the preceramics is higher than that of the BCN ceramics. A part of boron reacted with a very small amount of oxygen and B_2O_3 was formed. The chemical analysis measurement was performed after dissolving and removing B_2O_3 by ethanol. Therefore, the B/N ratio in the BCN ceramics is relatively decreased. There is more nitrogen in the ceramics because there was almost no NH_3 gas formation during 1273 K heating.

Figure 7 shows Raman spectra of BCN ceramics from pyrrolidine- and pyridine-borane preceramics at 1273 K under

Table 1 Chemical composition of pyrrolidine-borane preceramics and BCN ceramics (molar ratio).

	B	C	N	H
Preceramics	1.0	2.6	0.17	5.6
1273 K, Ar	1.0	1.5	0.40	0.42
1273 K, NH_3	1.0	0.90	0.40	0.66

Fig. 7 Raman spectra of BCN ceramics from pyrrolidine-borane (a) and pyridine-borane (b) in Ar.

Fig. 8 X-ray diffraction patterns of BCN ceramics derived from pyrrolidine-borane preceramics at 1273 K in Ar (a) and in NH_3 (b).

Fig. 9 Electrical conductivities of BCN ceramics prepared at 1273 K in Ar.

Ar. The spectra show a layered structure. The results of X-ray diffraction are shown in Fig. 8. The typical halo patterns observed show graphite-like turbostratic structures for 1273 K products. The patterns exhibit the (002) diffraction ($2\theta = 25^\circ$), characterized as interlayer spacing and (100) diffraction. The graphite-like turbostratic structure of pyrrolidine-borane-derived BCN ceramics is similar to other BCN ceramics obtained from corresponding heterocyclic compounds.

The sign of Seebeck coefficient for BCN ceramics from pyrrolidine- and pyridine-borane were negative in the measured from room temperature to 1073 K, which indicated the electron contributed to carrier conduction in the ceramics. Figure 9 shows the electrical conductivities of BCN ceramics measured by a direct current two-terminal method. The other BCN ceramics obtained at 1273 K under Ar from the pyridine-borane complex are also shown for comparison. The electrical conductivity increases, which is shown as a semi-conductive property. The difference in the electrical conductivity of both ceramics is a result of the difference in their carbon content. The orders of electrical conductivities are not high compared with graphite. The existence of B–N bonds may inhibit the conductivity by a carbon network.

Mott's plots are often used to examine a conduction mechanism.^{19–21} Figure 10 shows Mott's plots for the two types of BCN ceramics. Hopping conduction is dominant in the BCN ceramics from pyrrolidine-borane, as evidenced by a

Fig. 10 Mott's plots of BCN ceramics prepared at 1273 K in Ar.

minus straight line inclination. In contrast, the inclination is not a completely straight line in the case of BCN from pyridine-borane. This is thought to be mainly because of the difference in carbon content as the difference in conductivity appears. All six-membered rings that consist of carbon in the parts caused by relatively much carbon, like a BCN from a pyridine-borane complex, may lead to higher conductivity by passing through at that point. However, boron and nitrogen atoms, which act as impurities in conduction in the other parts, may contribute to expressing hopping conduction.

4. Conclusion

Turbostratic $\text{BC}_{1.5}\text{N}_{0.4}\text{H}_{0.42}$ and $\text{BC}_{0.9}\text{N}_{0.4}\text{H}_{0.66}$ ceramics were prepared from pyrrolidine-borane complex at 1273 K under Ar and NH_3 . Both BCN ceramics were graphite-like turbostratic structures that consisted of trigonal and tetragonal B–N bonds.

Acknowledgments

The authors wish to thank Prof. Dr. S. Shimada of Hokkaido University for the ^{11}B -NMR measurements, and thank Dr. M. Suzuki of Hokkaido National Industrial Research Institute (HNIRI) for carbon and nitrogen analysis, and thank Mr. T. Hoshi of Nittestu Cement Co. Ltd. for the hydrogen and boron analysis. This research was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture under contract Nos. 10137201, 09229203 and 08243203 and a Sasakawa Scientific Research Grant.

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