

Growth pressure-temperature region of cubic BN in the system BN-Mg

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The growth pressure-temperature region of cBN in the system BN-Mg was determined under the conditions up to 8 GPa and 2300° C. Hexagonal BN with different oxygen contents (1.9 wt % for R-type and 7.9 wt % for N1-type) was used as a starting material. The lower temperature limit of the cBN region obtained from the R-type is about 1380° C under pressures of 6 to 8 GPa. This limit can be compared with the eutectic point in the system hBN-Mg₃B₂N₄. The data suggest that cBN crystals grow through the dissolution and precipitation process from a eutectic liquid. The cBN region obtained from the N1-type is located at higher temperatures than that of the R-type, the lower limit of which is reached at about 1700° C at 6 GPa. MgO and/or Mg₃(BO₃)₂ are formed as by-products in such a system. The finding implies that Mg₃B₂N₄, a solvent of BN, reacts with oxide impurities (especially B₂O₃) by the following reaction; Mg₃B₂N₄ + $\frac{3}{2}$ O₂ = 3MgO + 2BN + N₂ or Mg₃B₂N₄ + 3O₂ = Mg₃(BO₃)₂ + 2N₂. It is deduced that the cBN growth region shifts towards higher temperatures depending on the effect of oxygen.

1. Introduction

A convenient method of converting hexagonal boron nitride (hBN) to cubic boron nitride (cBN) involves the use of a suitable catalyst at high pressures and temperatures. Magnesium is well known as a typical catalyst selected from the series consisting of alkali and alkaline earth metals.

Kudaka *et al.* [1], Ushio *et al.* [2] and Fukunaga *et al.* [3] reported on the growth *P-T* region of cBN in the system BN-Mg. However, their experimental results differ. The discrepancy of these data appears to be caused by the fact that no information on the reaction between BN and Mg at high pressures had been established. The present authors have recently found a eutectic relationship between hBN and Mg₃B₂N₄ at 2.5 GPa employing differential thermal analysis [4].

Thus, the present work aims to examine the growth *P-T* region of cBN in the system BN-Mg under the conditions up to 8 GPa and 2300° C and to investigate the effect of the oxygen contained in hBN.

The precipitation of cBN from molten Mg₃B₂N₄ was deduced from the lower temperature

limit of the cBN growth region obtained in the present study. The effect of oxygen in this system was discussed in relation to the stability of Mg₃B₂N₄.

2. Experimental details

High pressure and high temperature experiments were carried out by use of a belt-type apparatus. As shown in Fig. 1, a gasket assembly is modified from that designed by Hall [5]. By the use of the outer laminated paper gasket of large diameter, the pressure generated reached 12 GPa at room temperature. Detailed description of this assembly has already been reported [6].

Dummy cells for pressure and temperature calibrations are shown in Fig. 2. The pressure was calibrated by detecting the electrical resistance change in Bi (2.55, 2.7, 7.7 GPa), Ba (5.5, 12 GPa) and Sn (9 GPa) at room temperature. The flat strip of the calibrant metal is placed parallel to the anvil faces in the centre of the cell. The transition pressure was confirmed to be reproducible within an accuracy of 3%. Temperatures up to 1600° C are measured using a Pt-Pt/13% Rh thermocouple

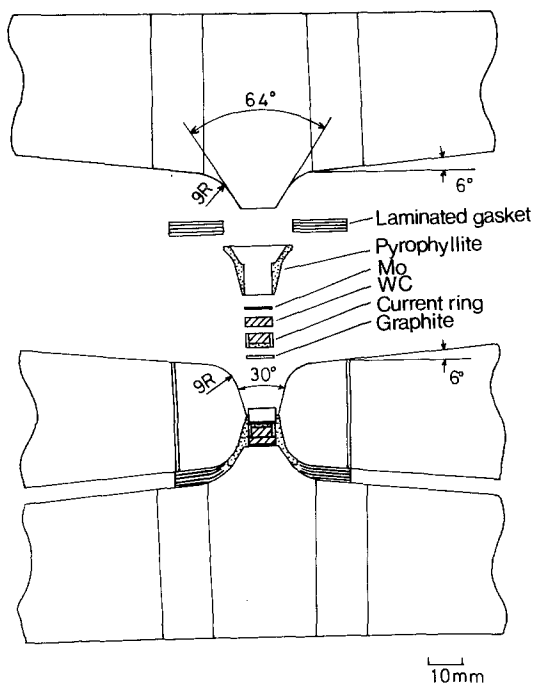


Figure 1 Schematic view of cell and gasket assembly.

of 0.3 mm diameter, the hot junction of which is located at the centre of a tubular carbon heater. No correction was made for the pressure effect on the emf of the thermocouple. In actual runs, the temperature of the sample was evaluated from the power input through the carbon heater, and which had been previously calibrated and extrapolated as a function of temperature. The accuracy of temperature measurements was estimated to be about 30°C.

Fig. 3 shows the sample assembly for high pressure-temperature experiments. In these exper-

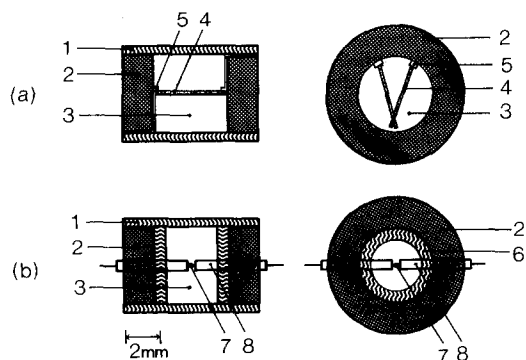


Figure 2 Cross-section of dummy cell used for the determinations of (a) pressure, and (b) temperature. 1 Graphite disc, 2 pyrophyllite, 3 hBN disc, 4 calibrant (Bi and Ba/Sn), 5 Au-electrode, 6 graphite heater, 7 hot junction (Pt/Pt-13% Rh), 8 Al_2O_3 tube.

iments, the sample was subjected to conditions up to 8 GPa and 2300°C. The pressure and temperature were held at the predetermined levels for 30 min. After this, the temperature was decreased rapidly by turning off the supplied power to the carbon heater prior to the release of pressure.

Recovered samples were examined by means of powder X-ray diffraction with filtered $CuK\alpha$ radiation. Cubic BN crystals were obtained by leaching in dil. HCl and subsequently in $NaF-H_2SO_4$ solution. Some samples were examined by single crystal X-ray technique using a Weissenberg camera. The crystal habit and the surface structure of cBN were observed under an optical microscope and a scanning electron microscope (SEM).

3. Results

3.1. Starting materials

Two types of hot-pressed hBN, R-type and NI-type, supplied from Denka Co were used as starting materials.

Fig. 4 shows the SEM photographs of the fractured surface of both types of hBN. In the figure discrete grains with the platelet form can be seen. The grain size was about 10 and 15 μm and the apparent densities were 2.02 ± 0.01 and $1.96 \pm 0.02 \text{ g cm}^{-3}$ for the R- and NI-type, respectively.

Fig. 5 shows the powder X-ray diffraction patterns for both types of hBN. They were of high crystallinity, because the diffraction peaks of (100) and (101) were completely resolved. The calculated values of the graphitization index (G.I.) were 1.56 and 1.39 for R- and NI-types, respectively, where $G.I. = \text{area} [(100) + (101)] / \text{area} (102)$ [7]. These values were smaller than the ideal value of 1.60. These results were caused by the effect of preferred orientation and it was thought that the graphitization of each hBN was almost complete. No extra peaks from impurities

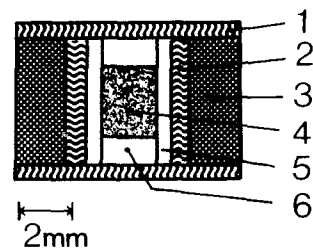


Figure 3 Arrangement of Mg and hBN in the reaction cell. The cylindrical pyrophyllite holder is placed in a belt-type apparatus. 1 Graphite disc, 2 graphite heater, 3 pyrophyllite, 4 magnesium, 5 hBN sleeve, 6 hBN disc.

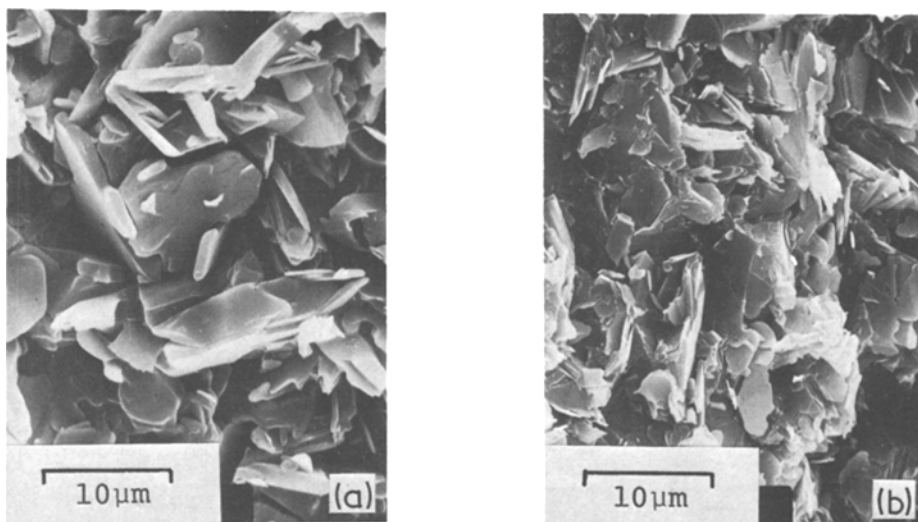


Figure 4 SEM photographs of hBN, for (a) NI-type and (b) R-type.

were found between $2\theta = 10^\circ$ and 90° when $\text{CuK}\alpha$ radiation was employed.

The cation impurities detected by emission spectrochemical analysis were less than 100 ppm. Oxygen contents in the R- and NI-type hBN measured by neutron activation analysis were 1.9 ± 0.1 and 7.9 ± 0.4 wt %, respectively.

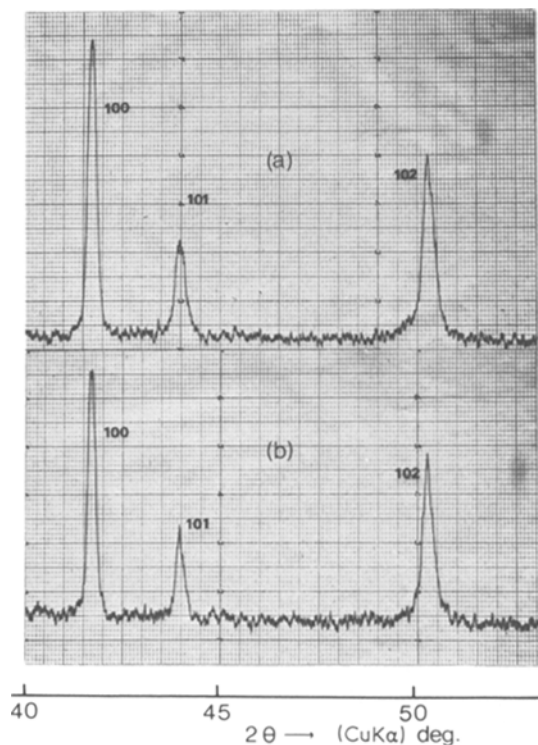


Figure 5 Powder X-ray diffraction patterns of hBN, for (a) NI-type and (b) R-type.

Magnesium rod of 99.9% purity obtained from Furukawa Magnesium Co was used as a catalyst for the conversion of hBN into cBN.

3.2. Growth pressure—temperature region of cBN

A conventional quenching method was employed in the determination of the growth region of cBN. The results of this experiment are summarized in Fig. 6. In this figure, circles and triangles correspond to the NI- and R-type hBN, respectively. Open marks indicate the runs where cBN could be successfully grown, while solid marks are those where there was no observation of cBN by X-ray diffraction. Corresponding to the two cases, two growth P - T boundaries are drawn by solid lines.

The lower temperature limit of cBN formation for the NI-type, 1700°C at 6 GPa, was about 300°C higher than that for the R-type. Two previous sets of data [1, 3] (curves a and b) on the growth region of cBN agree well with the results for the NI-type. Fukunaga *et al.* [3] have used hBN containing 4 wt % oxygen. For the data of Kudaka *et al.* [1], no information on the oxygen content was available. However, the hBN used by them probably contained a large amount of oxygen, because obvious peaks identified as MgO were observed in their X-ray powder patterns.

The content of cation impurities, graphitization index, degree of crystallinity and apparent density were almost the same in the present hBN samples, while the oxygen content of the R-type was

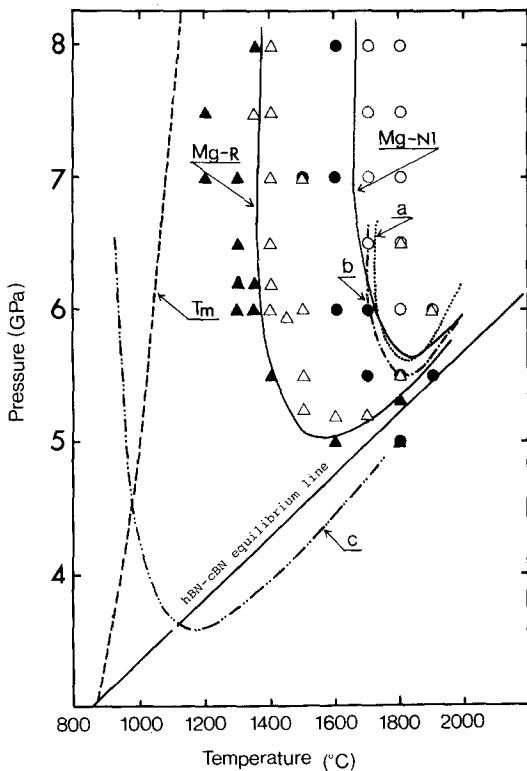


Figure 6 Growth P - T regions of cBN. Curves (a), (b) and (c) show the data by Fukunaga *et al.* [3] Kudaka *et al.* [1] and Ushio *et al.* [2], respectively.

remarkably less than that of the NI-type. On the basis of this, it becomes evident that the pressure and temperature necessary for the formation of cBN decrease comparatively when the oxygen content of hBN decreases.

Ushio *et al.* [2] have reported the growth P - T region of cBN which was lower than that of the R-type (curve c). The lower temperature limit given by them was lower than the estimated melting temperature of Mg (T_m).^{*} However, in the present experiments, it was checked that no visible reaction was detected between Mg and BN at several different P - T conditions near curve c in Fig. 6.

Ushio *et al.* used a different assembly in which hBN and Mg powders were mixed [1, 3]. For all our experiments using the powder mixture, no cBN crystal was observed within the possible

region of cBN formation reported by Ushio *et al.* Their results presumably contained an uncertainty of temperature measurement, because they used a platinum foil heater which is easily deformed and tends to cause a large temperature gradient in the sample.

the runs at a temperature lower than that of cBN growth;

(1) In the runs of R-type, no visible change was found in the samples.

(2) In the runs of NI-type, MgO and a small amount of $Mg_3(BO_3)_2$ were formed in Mg lumps, above about 1400° C.

3.3. Observation of cBN crystals

Cubic BN crystals grew everywhere a Mg lump was situated. The crystals were 0.1 to 0.3 mm in size and black or transparent brown in colour. When the crystal size was large, cBN crystals commonly took irregular and blocky shapes. In the runs of R-type, two types of crystal habits were found by controlling the P - T conditions. One was an octahedron and the other was a truncated tetrahedron. This change in crystal habit was very sensitive to temperature and appears to occur at about 1650° C and 6 GPa. At higher temperatures, truncated tetrahedron crystals were predominant.

Fig. 7 shows one of the $\{111\}$ surfaces of a truncated tetrahedron. This crystal was grown at 6.5 GPa and 1800° C. A single-spiral pattern of high steps is found as shown in the figure. This kind of growth step is parallel to the edges of the $\{111\}$ surfaces.

Fig. 8a and b shows the $\{111\}$ surfaces of an octahedron. The growth conditions for the crystals in (a) and (b) were 6.5 GPa, 1600° C and 6.5 GPa, 1700° C, respectively. The surface of a cBN crystal obtained from the R-type (Fig. 8a) is smooth compared to that obtained from the NI-type (Fig. 8b). Generally, cBN crystals of good quality grew only in the low oxygen containing system.

In the NI-type system, detectable amounts of MgO and $Mg_3(BO_3)_2$ were observed co-existing with a crystal such as shown in Fig. 8b. The

^{*}The melting temperature of Mg with pressure (T_m) is drawn in Fig. 6 and reported by Kennedy and Newton [8] up to 4.5 GPa. It can be calculated using Kraut and Kennedy's relation [9], above 4.5 GPa, as follows; $T_m = T_m^0 [1 + C(\Delta V/V_0)]$ where T_m^0 is the melting temperature under atmospheric pressure, $\Delta V/V_0$ is the isothermal dilatation and C is a constant. $\Delta V/V_0$ was taken from the data by Bridgeman [10] and C was determined from the data of Kennedy and Newton, up to 4.5 GPa.

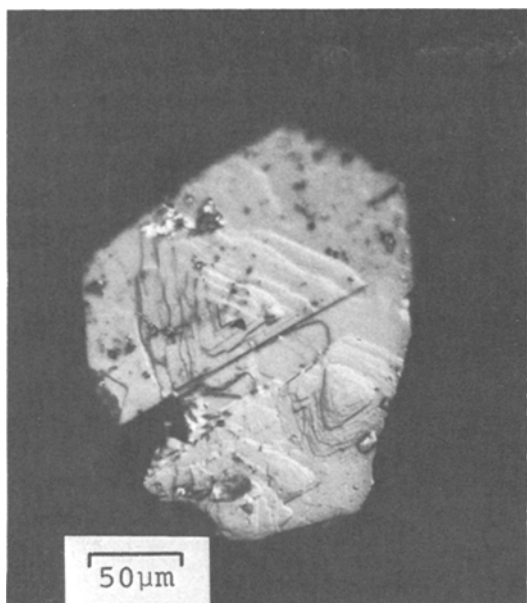


Figure 7 Spiral patterns on the truncated tetrahedral surface of cBN.

roughness on the surface was probably formed by the oxides which inhibited the development of the surface of cBN.

4. Discussion

4.1. Intrinsic growth P – T region of cBN in the system BN–Mg

The growth P – T region of cBN was remarkably extended over lower temperatures in the case

when hBN with low oxygen contents was used. The region obtained by R-type is considered to be almost intrinsic.

Recently, we have detected $Mg_3B_2N_4$ as one phase in the system B–Mg–N. A eutectic of the system hBN– $Mg_3B_2N_4$ was measured to be $1295 \pm 7^\circ C$ at 2.5 GPa by differential thermal analysis (DTA) [4]. The lower temperature limit of the cBN growth region obtained from the R-type was about $1380^\circ C$ in the pressure range 6 to 8 GPa. Therefore, it is suggested that the growth of cBN was performed through the dissolution and precipitation process in a eutectic liquid of the system BN– $Mg_3B_2N_4$.

Previous reports ignored the effect of oxygen on the growth P – T region of cBN. The growth of cBN was obstructed by the formation of oxides such as MgO and $Mg_3(BO_3)_2$.

These conclusions were derived from the discussion in Section 4.2.

4.2. The lower temperature limit of the cBN growth region

According to the solvent–catalyst scheme of Wentorf [11] and by DeVries and Fleischer [12], the lower temperature limits of the cBN growth region must correspond to one of the eutectic points in the system of the BN–catalyst. Magnesium or its compounds in the system B–Mg–N are possible catalysts of cBN formation. However, no reaction between BN and Mg was found at a

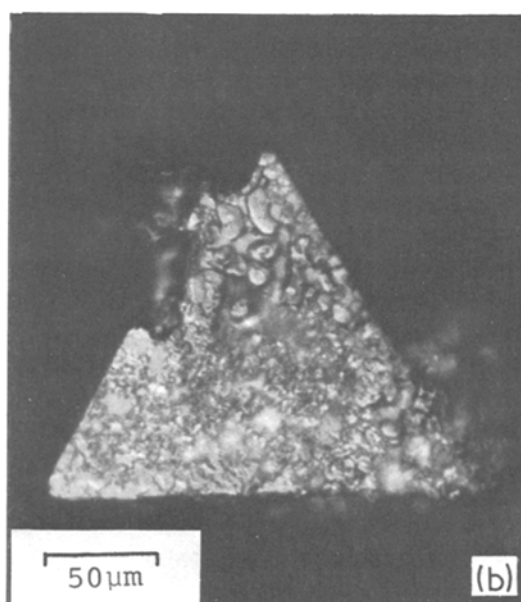
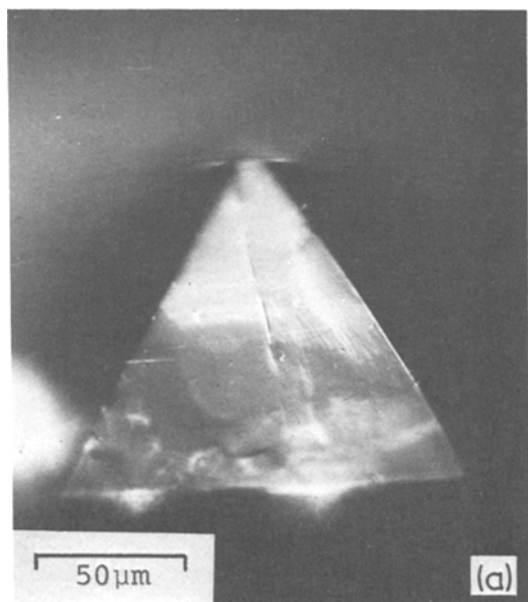


Figure 8 The $\{1\ 1\ 1\}$ surface structures of cBN crystals in the runs using (a) R-type and (b) Ni-type.

temperature a little higher than the melting point of Mg.

Filonenko *et al.* [13] reported the formation of a mixture of MgB_2 and Mg_3N_2 during the synthesis of cBN under the conditions of 4 to 7 GPa and 1500 to 2200 K in the system B–Mg–N. It is also difficult to consider that both compounds function as a catalyst–solvent. This is attributed to the following reasons; MgB_2 is a thermally unstable product; it decomposes into other borides such as MgB_6 and MgB_{12} above $1050^\circ C$ in air [14]. According to the data of Bradley *et al.* [15], Mg_3N_2 does not melt but dissociates at $2300^\circ C$ and 4.6 GPa. In addition, it was confirmed that no conversion of hBN into cBN was found using MgB_4 at 7 GPa and $1900^\circ C$.

The present authors have recently found that $Mg_3B_2N_4$ was formed in synthesis from the reaction between molten Mg and hBN above $1150^\circ C$ at 2.5 GPa [4]. DTA results showed that a eutectic relationship between hBN and $Mg_3B_2N_4$ was established at $1295 \pm 7^\circ C$ and 2.5 GPa. The precipitation of hBN from such a eutectic liquid was detected at temperatures higher than $1300^\circ C$. These data strongly support that $Mg_3B_2N_4$ has a function as a catalyst for cBN growth in the system BN–Mg under conditions appropriate for the thermodynamic stability of cBN. The lower temperature limit of the cBN growth region obtained from the R-type corresponds with a eutectic of the system cBN– $Mg_3B_2N_4$ at a given pressure. This is one reason why we consider that the intrinsic growth region of cBN is only determined from the oxygen-free reaction system.

4.3. Effect of oxygen on the cBN growth region

Oxygen impurities (especially B_2O_3) contained in the system react with $Mg_3B_2N_4$ as follows; $Mg_3B_2N_4 + 3/2 O_2 = 3 MgO + 2 BN + N_2$ or $Mg_3B_2N_4 + 3 O_2 = Mg_3(BO_3)_2 + 2 N_2$. Because $Mg_3B_2N_4$ is consumed by the above reaction, the formation of cBN diminishes or halts. At a sufficiently high temperature above the eutectic point of BN– $Mg_3B_2N_4$, the amount of liquid increases and the residual liquid which does not suffer from the effect of oxygen can act as catalyst–solvent.

Thus, it is deduced that the lower temperature limit of the cBN formation shifts towards a higher temperature in high oxygen containing system, for example, in the case of runs using the NI-type.

In the system BN–Li, no drastic effect of oxygen on the growth region of cBN was found and no compounds such as LiO_2 or/and Li-borates were obtained as by-products. $Mg_3B_2N_4$ can neither be prepared in air nor in N_2 gas, but is slowly decomposed in humid air. It may be understood from the behaviour described above that the instability of $Mg_3B_2N_4$ in oxygen forms a striking contrast to that of Li_3BN_2 under high pressure–temperature conditions.

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