

Formation mechanism of cBN crystals under isothermal conditions in the system BN-Ca₃B₂N₄

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Cubic BN was synthesized by treating hexagonal BN (hBN) in the presence of Ca₃B₂N₄ which acted as a flux for BN. After the high pressure and temperature treatments, cBN was obtained in a part of hBN layer initially charged, but hardly in the flux layer. The grains of cBN were precipitated accompanied with the advance of Ca₃B₂N₄ flux into hBN zone. From these observations, it can be deduced that hBN dissociated beneath the thin layer of flux advanced, and crystallized as cBN under an isothermal condition. In this system, the mechanism was basically the same as that of the diamond growth in the metal flux such as nickel and cobalt. Namely, the crystal growth of cBN was governed by the difference of solubility between hBN and cBN in a melted Ca₃B₂N₄, because of the eutectic relation between BN and Ca₃B₂N₄. For the nucleation process, two types of features were observed; one was the preferential nucleation at the boundary of hBN-flux, and the other was the homogeneous nucleation in the part of hBN layer initially charged.

1. Introduction

Although cubic BN (cBN) has a lower hardness than diamond, it is stronger than diamond against corrosion of iron family element at high temperature. Therefore, it shows substantially superior mechanical properties to those of diamond when used for grinding and cutting a material containing nickel, cobalt or iron.

It has been common to prepare the cBN crystals by treating hexagonal BN (hBN) in the presence of a catalyst. Typical catalysts have been known to be alkali metals, alkaline earth metals and their nitrides such as lithium, magnesium, calcium, Li₃N, Mg₃N₂, Ca₃N₂ and so on. Incidentally, it is desirable to find out the growth conditions that yield good cBN crystals with a size and morphology suitable for practical use. However, the growth mechanism of cBN is still a subject of discussion.

DeVries and Fliescher [1] have proposed the following formation mechanism of cBN in the

system Li₃N-BN; the formation of cBN begins with the reaction between hBN and Li₃N to form Li₃BN₂ at a high pressure and temperature. Subsequently, hBN is dissolved into the liquid Li₃BN₂, and is precipitated as cBN. Recently, Endo *et al.* [2] reported that Me₃B₂N₄ (Me = alkaline earth elements) was available for preparing cBN. Me₃B₂N₄ has a eutectic with BN under a high pressure and temperature. This system seems to be convenient for investigating the growth mechanism of cBN as compared with the other systems previously reported, because there are no heterogeneous reactions between hBN and the metals or the nitrides.

This experiment was carried out to clarify the growth mechanism of cBN under an isothermal condition in the BN-Ca₃B₂N₄ system, and to investigate how to govern the process of nucleation and growth of cBN crystals as a function of pressure and temperature.

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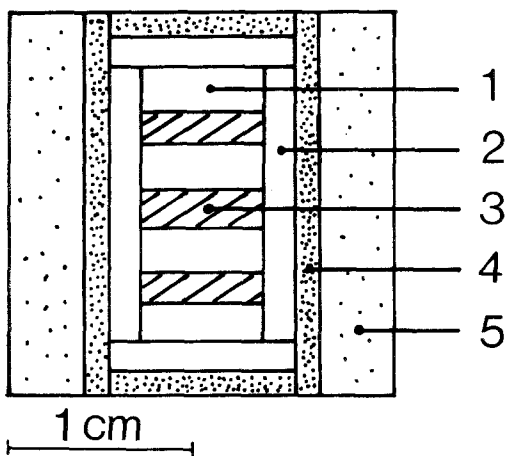


Figure 1 The reaction chamber, 1: hBN disc, 2: hBN cylinder, 3: $\text{Ca}_3\text{B}_2\text{N}_4$ flux, 4: graphite heater, 5: NaCl pressure medium.

2. Experiment

2.1. Preparation of starting materials

Hexagonal BN powder and the sintered body was baked in a flowing N_2 gas at 2100°C in order to remove oxygen impurity, since the oxygen influences the nucleation and growth of cBN [3]. According to a radio activation analysis, the oxygen content of the hBN was reduced to less than 0.3 wt %.

$\text{Ca}_3\text{B}_2\text{N}_4$ was prepared by the following procedure; calcium metal was purified by a conven-

tional sublimation technique and exposed to N_2 gas for the preparation of Ca_3N_2 . The Ca_3N_2 was mixed with hBN, then baked at about 1100°C in N_2 gas. The detailed conditions were previously described in [4].

Prior to these procedures, the N_2 gas was purified of oxygen to 1 ppm or less by using an active copper column.

2.2. High pressure and temperature experiments

The high pressure and temperature experiments were performed by using a belt-type apparatus. Fig. 1 shows a typical cell assembly of this experiment. $\text{Ca}_3\text{B}_2\text{N}_4$ and hBN were alternatively piled in the hBN sleeve for forming the reaction zone. Carbon heater and NaCl as pressure medium were heated at 2000 and at 250°C , respectively, in vacuo for removing absorbed impurity such as water, prior to assembling the reaction cell.

Fig. 2 shows experimental conditions of high pressure and temperature synthesis. The pressure was estimated by the electrical changes of bismuth, thallium and barium induced by the phase transformation at room temperature. The temperature was measured by the e.m.f. of a Pt/13%Rh–Pt thermocouple. Since the pressure practically increased as the temperature increased, the values were corrected from the growth P – T (pressure–

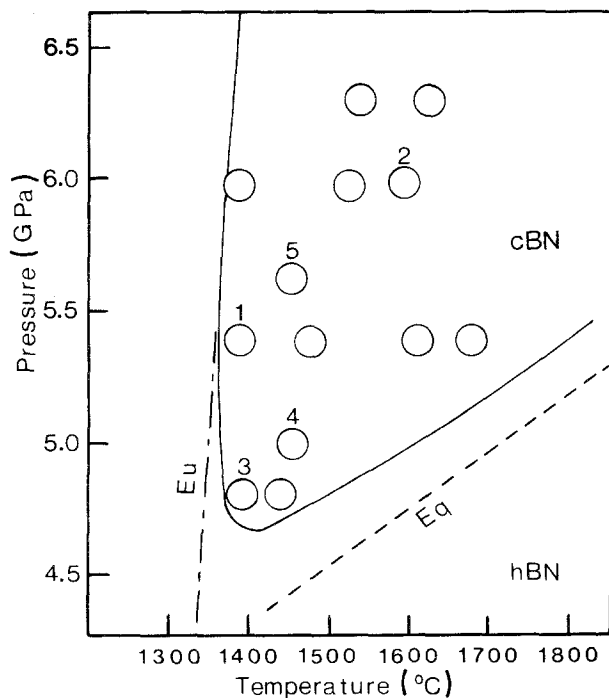


Figure 2 Growth P – T region of cBN in the system BN – $\text{Ca}_3\text{B}_2\text{N}_4$. \circ : experimental point in the study, Eu: eutectic temperature of BN – $\text{Ca}_3\text{B}_2\text{N}_4$, Eq: equilibrium line between pure hBN and cBN.

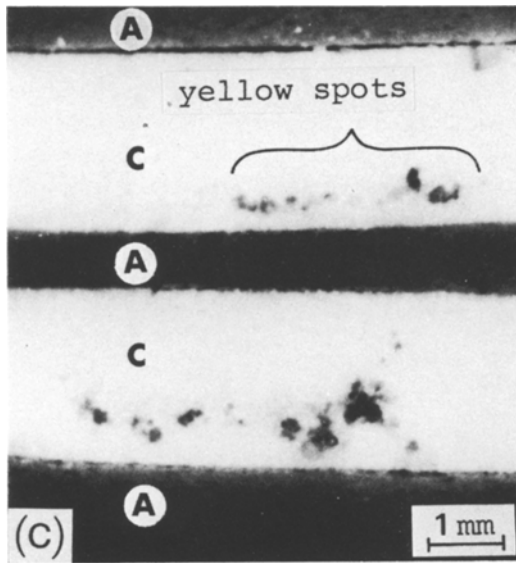
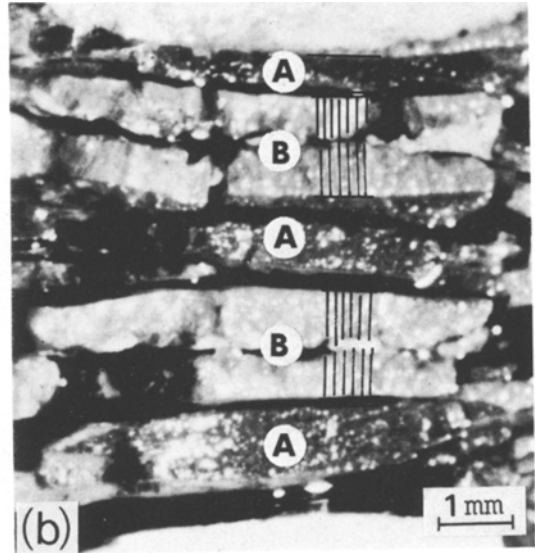
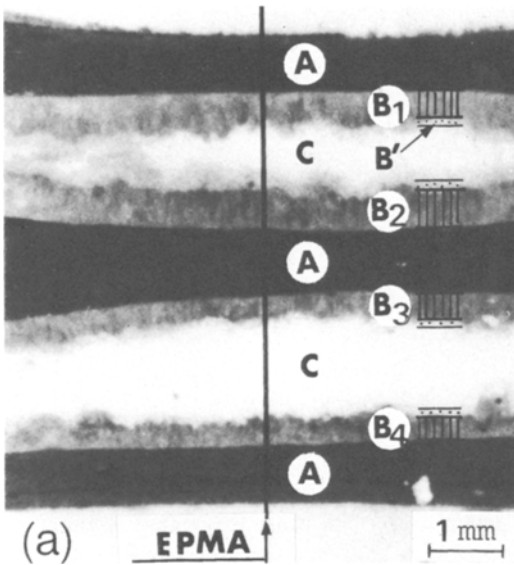


Figure 3 Vertical section of the reacted sample, showing typical aspects of the cBN formation by sectional colouring (microphotograph). (a) Sample 1 (1350° C, 5.4 GPa), (b) sample 2 (1600° C, 6.0 GPa) and (c) sample 3 (1400° C, 4.8 GPa). Colouration A: brown (flux zone), B: yellow (cBN zone), B': pale yellow, C: white (hBN zone).

probe microanalysis (EPMA) after washing off the paraffin with acetone and drying in a nitrogen gas stream.

3. Experimental results

3.1. Circumstance of cBN precipitation

3.1.1. Colouring of the reaction zone

The shape of the reaction zone was deformed by the volume change, which resulted from the transformation of hBN into cBN. However, it seems that the isostatic pressure was effectively applied to the reaction zone because the NaCl pressure medium melted under the condition for cBN growth.

Fig. 3 shows the vertical section of the reaction zone. By the difference of colouring, two types of cBN deposition were recognized. One was observed in sample 1 prepared at 1340° C and 5.4 GPa. In Fig. 3a, there are sectional zones having individual colours such as brown (A), yellow (B), pale yellow (B') and white (C). The other type was observed in sample 3 (shown in Fig. 3c). This sample was prepared at 1400° C and 4.8 GPa. The yellow and pale yellow zone was observed nowhere, but spots of such a colouration were widely distributed in the white zone.

Besides these profiles, there were some vari-

temperature) conditions of diamond in the Co–C system reported by Strong and Tuft [5] and Kennedy and Kennedy [6].

After treating the sample at the designed P – T conditions for 30 min, it was cooled to room temperature before the applied pressure was released.

2.3. Observation of recovered sample

Since the $\text{Ca}_3\text{B}_2\text{N}_4$ easily reacts with moisture in the air to make $\text{Ca}(\text{OH})_2$, the recovered sample was immediately immersed into the liquid paraffin and cut along the centre axis by using an ultrasonic cutter. The section of sample was observed under an optical microscope, and examined by scanning electron microscopy (SEM) and electron

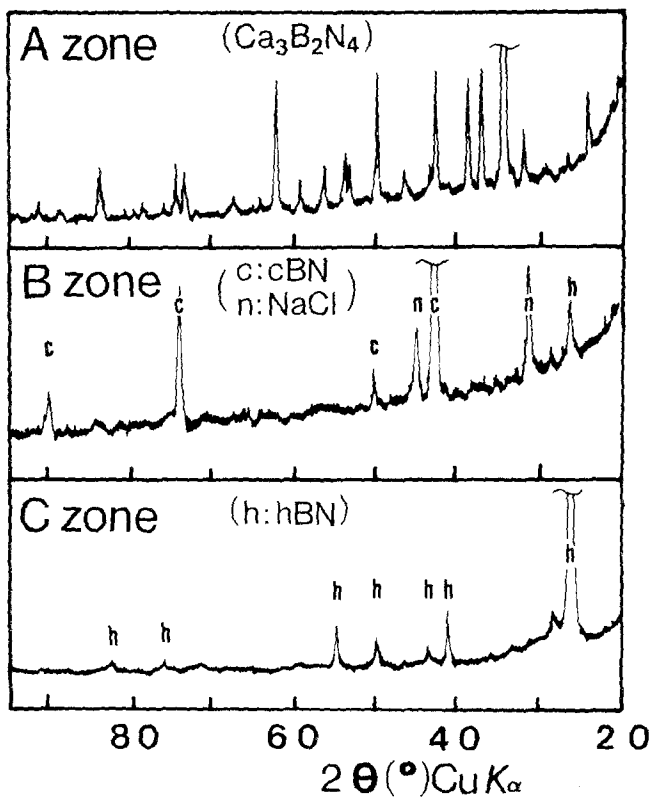


Figure 4 X-ray diffraction patterns of each zone in the sample 1 (see Fig. 1a).

ations of the first type. In some cases the B zone was directly in contact with the C zone due to the lack of B' zone. In others the hBN layer completely changed into a cBN layer as shown in Fig. 3b. This shows that the conversion rate was markedly enhanced by the increase of temperature and pressure.

3.1.2. Identification of each zone

After the sample was crushed in a liquid paraffin, the individual zone was classified according to the colouring, and identified by a X-ray diffraction technique. Fig. 4 shows the X-ray diffraction patterns characterizing each zone of sample 1.

As the results indicate, the brown zone A corresponds to $\text{Ca}_3\text{B}_2\text{N}_4$ and the white zone C corresponds to hBN. Then, the yellow zone B was composed of cBN crystals with a small amount of $\text{Ca}_3\text{B}_2\text{N}_4$ and NaCl, and they accompanied hBN in the B' zone. In this context, the yellow spots observed in sample 3 were also identified as cBN crystals.

3.1.3. Distribution of the flux $\text{Ca}_3\text{B}_2\text{N}_4$

In order to know the elements distribution, EPMA was done along the line drawn in Fig. 3a. Fig. 5 shows that calcium was intensely detected in the

brown zone A and hardly at all in the white zone C. In zones B and B' calcium was detectable, but its amount decreased abruptly. Since the position of calcium was equal to being $\text{Ca}_3\text{B}_2\text{N}_4$, it is clear that $\text{Ca}_3\text{B}_2\text{N}_4$ advances toward the hBN layer (zone C).

In the case of sample 3 (Fig. 3c) calcium was also observed around cBN crystals in the yellow and pale yellow spots.

Sodium accompanied with chlorine was occasionally found in zones B and B'. Its distribution has no relation with that of $\text{Ca}_3\text{B}_2\text{N}_4$. Hexagonal BN reduced the volume beyond 37% when transformed into cBN. Therefore, it was plausible that NaCl could penetrate and condense between cBN grains through the growth process of cBN. This fact was also confirmed by the X-ray diffraction peaks of NaCl. When a molybdenum foil was placed between the reaction zone and the NaCl pressure medium in order to separate them from each other, no contamination of NaCl was observed and a difference in the profile from the former was hardly found.

3.1.4. Profile of the vertical section

Fig. 6 shows the SEM photograph of the vertical section of the sample 1. In this figure, it is clear

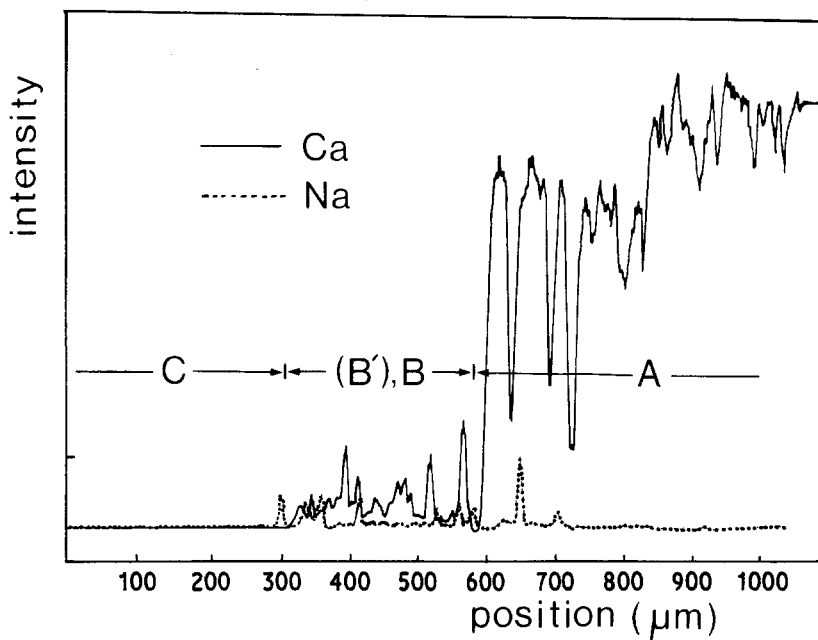


Figure 5 Distribution of calcium and sodium in the reaction zone, examined by EPMA along the line shown in Fig. 3a.

that the sectional surface of zone A is quite smooth, but that of zone B is rough. The profiles are due to the difference in hardness between them. Moreover, the shape of cBN in the zone reflects on the latter feature.

A supplemental flabby layer is found between zone A and zone B. It seems that this is caused by

drastic asymmetrical expansion between cBN and $\text{Ca}_3\text{B}_2\text{N}_4$ when the pressure was released. According to the EPMA etc, the layer is substantially the same as zone A in composition, but is more reactive to moisture as if the $\text{Ca}_3\text{B}_2\text{N}_4$ is in the form of a fine powder.

3.2. Morphology of cBN crystals

After washing the flux with dilutes HCl, the morphology of cBN was examined using SEM.

As shown in Fig. 7a, cBN crystals elongated in the direction of the hBN layer (zone C) were observed. The lateral faces of the crystals show an irregular shape, but their tops show an acute and regular form with sharp edges and smooth surfaces. Fig. 7c shows the magnified profile of the elongated crystals in the B zone, facing to the B' zone. As such a shape of cBN crystals was dominantly formed, there was a probability that the liquid phase of $\text{Ca}_3\text{B}_2\text{N}_4$ worked. A face, developed up to about $30\ \mu\text{m}$, was observed. The elongated crystals should aggregate on each other, because they could not be separated by leaching them with acids.

Fig. 7d shows the profiles of zones B' and C. Cubic BN crystals having regular morphology were occasionally found on the side of zone C, where it was composed of a consecutive body of B'. Since zone C was only constituted by hBN, it can be presumed that cBN crystals grew under the influence of a diluted flux that penetrated into

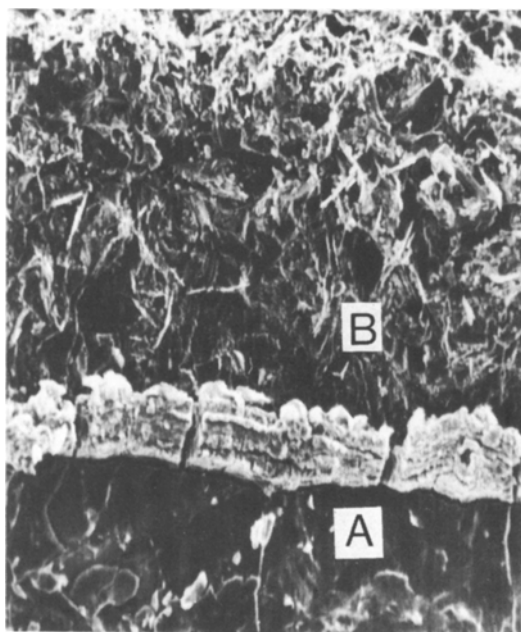


Figure 6 Section of the sample 1 showing flabby layer between A and B zone (SEM photograph).

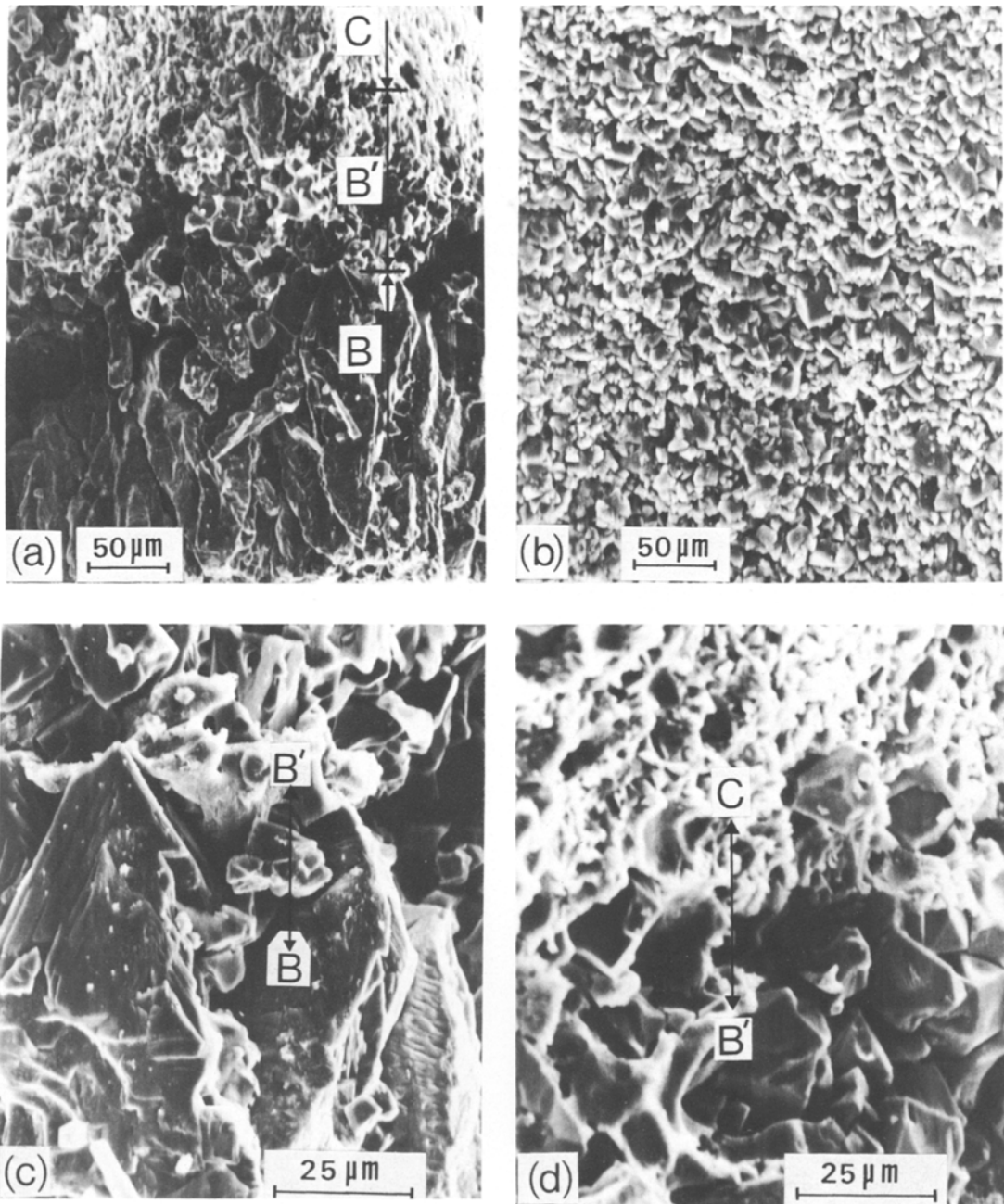


Figure 7 Fractured surface of sample 1 after the flux was washed away by diluted HCl (SEM photograph). (a): general aspect, (b): cBN crystals in the B zone facing the flux zone C, viewed from the flux side, (c) : magnified side view of the cBN crystals in the B zone, (d): euhedral crystals in the B' zone.

zone C. In sample 3 (Fig. 3c), isolated crystals are also observed in the hBN layer. Its shape is regular and has the well known euhedral morphology.

4. Discussion

4.1. Behaviour of $\text{Ca}_3\text{B}_2\text{N}_4$

The flux layer almost kept the original shape after

the high pressure and temperature treatments, but the hBN layer partially changed to cBN crystals at the surface that contacted with the flux layer. The zone of cBN given as B_1 , B_2 , B_3 and B_4 were nearly equivalent in dimension. This implies that the cBN crystals grew effectively under the isothermal conditions. The flux $\text{Ca}_3\text{B}_2\text{N}_4$ was not

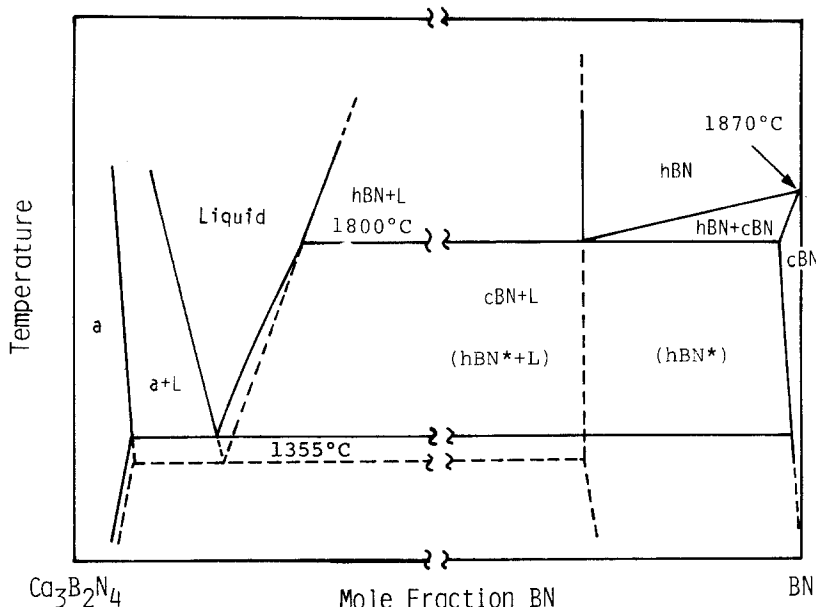


Figure 8 Composition-temperature diagram of the BN-Ca₃B₂N₄ system.

changed in crystal structure, but turned from white to brown in colour. According to the foregoing observation, it is clear that the flux did not lose the capability for cBN growth, but was probably discoloured by the dissolution of a foreign species such as BN and NaCl.

4.2. Binary system of Ca₃B₂N₄-BN

After high pressure and temperature treatments, no product except BN and Ca₃B₂N₄ was found in the reaction zone. This suggested that the chemical reaction for producing cBN favorably progressed on the composition between Ca₃B₂N₄ to BN.

As shown in Fig. 8, the composition-temperature relationship at 5.4 GPa is composed on the basis of the data reported by Endo *et al.* [2]. They showed that the lower temperature limit of cBN growth was about 1370°C at 5.4 GPa, and Ca₃B₂N₄ had a eutectic with hBN at 2.5 GPa and 1310°C.

Hexagonal BN has a larger solubility to the flux than cBN under the thermodynamic stable condition for cBN, and the eutectic temperature between Ca₃B₂N₄ and hBN must be somewhat lower than that between Ca₃B₂N₄ and cBN, as shown in Fig. 8. Cubic BN crystals were grown after the liquid phase of Ca₃B₂N₄-BN was formed, hence the lowest temperature for the growth should be equal to, or higher than, the eutectic temperature of Ca₃B₂N₄-hBN. Therefore, when changes with pressure by linear relationship, the eutectic temperature is approximately estimated

on the line tying 1310°C at 2.5 GPa to the lowest temperature of the growth *P-T* region as shown in Fig. 2. Thus the temperature at 5.4 GPa is about 1355°C.

The equilibrium temperature between cBN + liquid and hBN + liquid (A) was also estimated from the higher temperature limit of cBN growth, and was about 1800°C at 5.4 GPa. As the equilibrium temperature-pressure between hBN and cBN (B) was calculated by the following equation; $P(\text{GPa}) = 0.00256T(\text{K}) - 0.0888$. It was 1870°C at 5.4 GPa. However, it can not be determined experimentally given what chemical process occurred between (A) and (B).

The growth mechanism of cBN was appropriately interpretable on the basis of the diagram shown in Fig. 8. Under the isothermal condition where cBN grew, the growth of cBN was driven by the solubility difference between hBN and cBN. At the boundary of the hBN layer and the flux layer, hBN dissolved into the flux and crystallized as cBN behind the thin layer of flux. Consequently, the thin layer of flux seemingly advanced into the hBN layer. The observation of cBN growth in sample 1 reflected on the scheme described above.

4.3. Nucleation of cBN

The flux, Ca₃B₂N₄ diffused throughout the cBN layer and extended down to the boundary of hBN and cBN. As shown in Fig. 7a, the elongated crystals of cBN were often observed along the axis

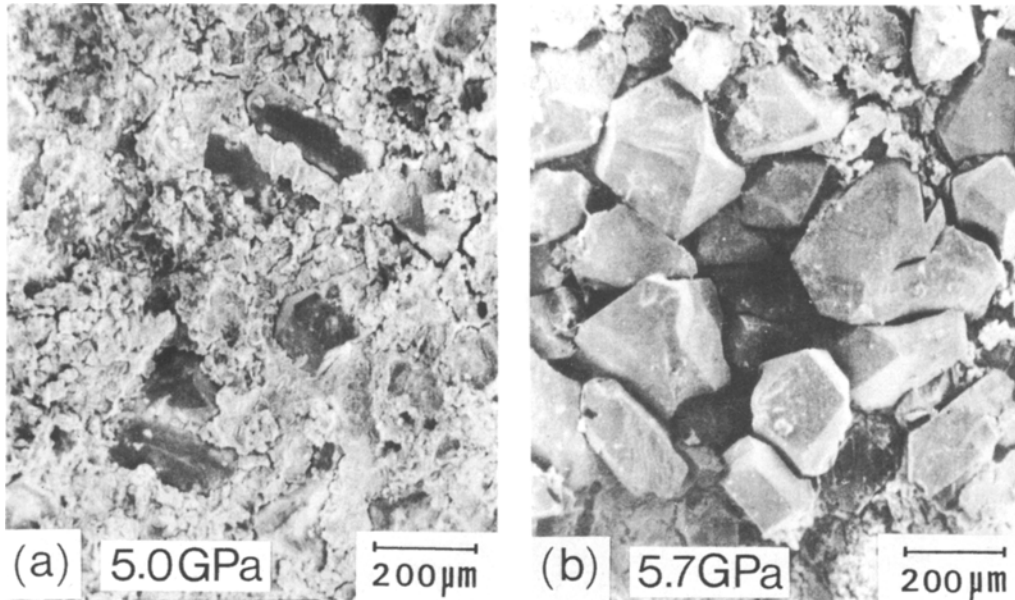


Figure 9 Blocky crystals of cBN formed under different pressure conditions at a temperature 1450° C, showing the pressure dependence of the values (SEM photograph). (a) Sample 4 (5.0 GPa) and (b) sample 5 (5.7 GPa).

perpendicular to the flux layer, and the shape of the top was that common to the euhedral morphology and that of the lateral was irregular. This seems to express how the driving force of the flux promptly gave rise to the nucleation and successive growth of cBN. As seen in Fig. 7b, the elongated crystals appeared to be small crystals grown together where they faced zone A.

From these features, it could be assumed that nuclei of the cBN crystals were preferentially formed nearby the hBN layer at the initial stage, while hBN was dissolved in the flux.

The isolated grains of cBN were sometimes observed near the boundary of zones B and C as shown in Fig. 7d. They have a regular morphology with smooth surfaces. Samples were subjected to the different pressure conditions of 5.0 and 5.7 GPa at 1450° C. Fig. 9 shows the number of cBN grains that changed as the function of pressure.

Hanneman [7] has previously reported the theoretical aspect of the pressure effect on the homogeneous nucleation. According to his analysis, as pressure increases, the nucleation rate markedly increases in the homogeneous system. Consequently, the foregoing observation coincides with this analysis. It can be visualized that the nucleus of cBN was formed in the flux after the BN species was supersaturated and the growth of cBN successively took place. However, the distinctive thin

layer of the flux was not detected on the growth front by EPMA. This profile is somewhat different from that of diamond growth. The diamond grains were almost covered with a metal thin film saturated by carbon [8]. It can be estimated that a weakness of the surface tension of the flux on cBN brings out the foregoing observation, besides the viscosity of $\text{Ca}_3\text{B}_2\text{N}_4$ is lower than that of metal.

In the case of sample 3, cBN crystals with euhedral morphology were found in the part surrounded by hBN, before the cBN layer was formed at the boundary of the hBN and flux layers. It could be confirmed by EPMA that such crystals had a skin of $\text{Ca}_3\text{B}_2\text{N}_4$. It can be assumed that cBN crystals were formed by homogeneous nucleation and growth. This fully implied that the diluted flux played some important role in growing cBN. A further study on the behaviour of the flux is worth considering.

Cubic BN was rarely precipitated in the flux zone, the so-called zone A. Owing to a small temperature gradient, a sufficient amount of hBN was hardly transported by the flux. In other words, there is the probability that a cBN crystal of a larger size could be obtained by using the seed crystal of cBN when a suitable temperature gradient is generated in the flux zone. The process described above has clearly included controlling the homogeneous nucleation.

5. Conclusions

Under the isothermal condition, the cBN crystals were formed under control by the thin film growth mechanism, just like diamond growth with the film of metal. At the boundary of hBN and the flux, the cBN crystals precipitated by the process of preferential nucleation and growth. This was discussed on the basis of the formation of elongated cBN crystals. Whereas, when hBN slowly dissolved in the flux which advanced into the hBN layer, cBN crystals with euhedral morphology precipitated. This process was established through homogeneous nucleation and growth. The number of cBN crystals were remarkably dependent on the super-pressure which was evaluated as the difference from the hBN-cBN equilibrium pressure.

As the other profile, the cBN crystals were formed like islands in the hBN layer, and covered with the hull, made of $\text{Ca}_3\text{B}_2\text{N}_4$. It could be concluded that the nucleus of cBN was indispensably formed in the diluted flux. The growth mechanism is now the subject of further discussion.

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*Received 6 December 1982
and accepted 24 February 1983*