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The synthesis of cBN using $Ca_3B_2N_4$

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The phase relation of the system Ca–B–N was investigated at a pressure of 2.5 GPa by both differential thermal analysis (DTA) and a quenching method. When BN reacted with Ca at temperatures higher than 1150° C, $Ca_3B_2N_4$ was formed together with small amounts of Ca_3N_2 and CaB_6. The system of $Ca_3B_2N_4$–BN has a eutectic relationship at 1316° C and 2.5 GPa. The synthesis of cBN was established by using $Ca_3B_2N_4$ under the thermodynamic stable conditions of cBN. It could be seen that cBN crystals grew repeatedly in $Ca_3B_2N_4$ melt, which advanced into the hBN layer. The cBN crystals obtained in this way were of outstanding purity and of good quality. This indicated that hBN dissolved and precipitated as cBN in $Ca_3B_2N_4$ melt without any appreciable change of molar boron/nitrogen ratio. In the system of Ca–B–N, the low-temperature limit of cBN formation was closely related to the eutectic relationship between BN and $Ca_3B_2N_4$.

1. Introduction

The study of the reaction between BN and a catalyst has attracted much attention in the practical synthesis of cBN. DeVries and Fleischer [1] have briefly derived general considerations for the growth mechanism of cBN from nitrides of various kinds. In particular, an interpretation was given that the growth P–T region of cBN was closely related to the stability of a complex or a compound formed in the ternary system of *M*–B–N (where *M* is an alkaline earth metal). In addition, there were two mechanisms for forming cBN, which were dependent in part on the break-up of a complex or a compound, and which were based on the eutectic relationship between BN and a binary compound such as Li_3BN_2. However, no information was experimentally obtained with regard to which compounds were useful as the solvent of BN in this system. Therefore, since it was noted [1] that cBN did not form when Li_3BN_2 itself melted or decomposed, it must be concluded that DeVries and Fleischer were of the opinion that neither $Mg_3B_2N_4$ nor $Ca_3B_2N_4$ showed a eutectic relationship with BN, and decomposed.

Recently, Endo *et al.* [2] showed that the system of $Mg_3B_2N_4$–BN resulted in a eutectic relationship at 1295° C and 2.5 GPa, and that hBN precipitated from a liquid phase of $Mg_3B_2N_4$. $Mg_3B_2N_4$ was formed through the reaction between BN and Mg, and herein the low-temperature limit of cBN formation in the system of Mg–BN was closely connected with a eutectic of $Mg_3B_2N_4$–BN.

On the basis of these works, the present work was undertaken to determine the phase relation of Ca–B–N, and then to find out the compound which acted as the solvent of BN. In addition, the synthesis of cBN was practiced in order to clarify the growth mechanism of cBN.

2. Experimental procedure

2.1. Starting materials

Hexagonal BN in hot-pressed form was supplied by Denkikagaku Co. as starting material. In order to minimize the oxygen impurity-content the as-supplied BN was baked at 2050° C for 7 h in flowing N_2 gas. The result of a neutron activation analysis showed that the quantity of oxygen impurity reduced to less than 0.3 wt % in hBN.

$Ca_3B_2N_4$ was prepared by the method described in [3]: either Ca or CaH_2 was intimately mixed with hBN in molar ratio Ca : BN of 3 : 2, corresponding to a formula of $Ca_3B_2N_4$. This mixture was fired in the hBN crucible at 800 to 950° C for 12 h, and subsequently at 900 to 1150° C for 20 h in dried N_2 or NH_3 gas.

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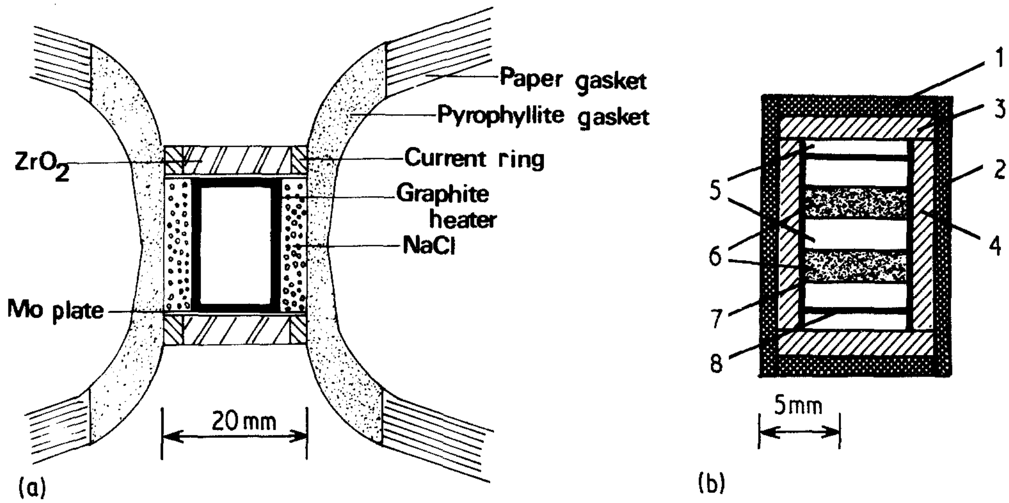

Figure 1 Cross-sectional diagram (a) of the general cell assembly and (b) the details of the cell construction used in the synthesis experiments. (1) Graphite disc, (2) graphite heater, (3) NaCl disc, (4) NaCl sleeve, (5) hBN disc, (6) catalyst, (7) Mo capsule and (8) Mo disc.

2.2. Apparatus and procedure

2.2.1. *Differential thermal analysis (DTA)*

DTA measurements at 2.5 GPa were carried out by using a piston–cylinder apparatus with bore diameter 12.7 mm. The same assembly was used as that described in [2]. After the sample was compressed by a load equivalent to 2.5 GPa, DTA analysis was conducted up to 1600° C on both heating and cooling cycles. Al_2O_3 was used throughout as a reference material. Temperatures were measured using two pairs of Pt/Pt–13 % Rh thermocouples, and controlled at heating and cooling rates of 35 to 40° C min^{-1}.

2.2.2. *The synthesis of cBN*

High pressure/high temperature treatments were performed under conditions of 4.4 to 6.5 GPa and 1180 to 1800° C for 20 to 120 min by a belt-type apparatus of bore diameter 25 mm. Fig. 1 shows a typical construction of cell assemblies.

Pressure was calibrated on the electrical transitions for Bi (2.55 and 2.7 GPa), Tl (3.7 GPa) and Ba (5.5 GPa) at room temperature. The temperature of sample was estimated from the electric power through the carbon heater and calibrated by inserting a Pt/Pt–13 % Rh thermocouple in the cell. The pressure effects of e.m.f. were uncorrected. Otherwise, the actual pressure and temperature generated in the sample were revalued from the growth pressure–temperature conditions of diamond on comparing with the data reported by Strong and Tuft [4], and by Kennedy and Kennedy [5]. The values of pressure and temperature obtained were estimated to be accurate to within ± 0.2 GPa and ± 25° C.

The sample obtained by a conventional quenching method was examined using the X-ray diffraction technique. After leaching in diluted HCl and subsequently in $NaF–H_2SO_4$, cBN crystals were observed under an optical microscope and a scanning electron microscope (SEM).

3. Results and discussion

3.1. DTA measurements

DTA at 2.5 GPa was conducted in the systems of Ca–BN, Ca_3N_2–BN and $Ca_3B_2N_4$–BN, respectively. Each sample was submitted to more than five heating–cooling cycles to check the reproducibility of results. Besides a broad peak near 1150° C, four sharp peaks were observed at 1412, 1316, 1062 and 1032° C, which enabled the phase diagram of the Ca–B–N system to be drawn.

When BN reacted with Ca under conditions of 1200° C and 2.5 GPa for 30 min, $Ca_3B_2N_4$ was formed as the main product. The chemical composition should slightly deviate from the line joining Ca and BN, so that smaller amounts of Ca_3N_2 and CaB_6 were simultaneously obtained. In this context, it was postulated that one broad endothermic change in the region of 1150 to 1190° C could be assigned to the reaction between Ca_3N_2 and BN for forming $Ca_3B_2N_4$. The peak at 1412° C was so great in intensity that it could be identified as the peak corresponding to the melting of $Ca_3B_2N_4$. On being heated up to 1600° C no further phase changes were seen.

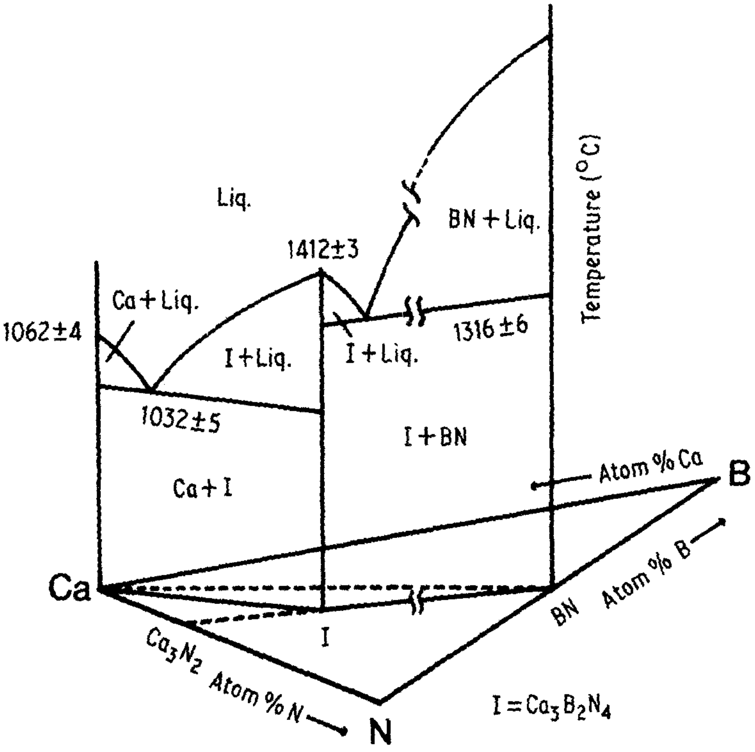

Figure 2 The phase relationship in the ternary system of Ca–B–N at 2.5 GPa.

In Ca–BN system, two endothermic peaks were observed at 1062 and 1032° C. As the peak at 1062° C remarkably decreased in intensity after an iterative run, this could be assigned to the melting temperature of Ca, which was about 70° C lower than that given by Jayaraman *et al.* [6] (≃ 1132° C at 2.5 GPa). The value they obtained was measured using an alumel–chromel thermocouple. Therefore, the present value was not grossly in error after consideration of the larger pressure effect on the e.m.f. of Pt/Pt–13 % Rh thermocouple. It was convincingly estimated that the peak at 1032° C could be assigned to the eutectic in the system of Ca–$Ca_3B_2N_4$.

On the basis of the above discussion, it was reasonable to assign the peak at 1316° C to the eutectic point in the system of $Ca_3B_2N_4$–BN. Furthermore, when the sample was subjected to conditions of 1350° C and 2.5 GPa for 20 min, the precipitation of hBN was frequently observed within the bulk of $Ca_3B_2N_4$. This profile was very similar to that of the Mg–B–N system.

Summarizing the DTA results with endothermic change, the phase diagram of the Ca–B–N system at 2.5 GPa can be described as shown in Fig. 2. The eutectic compositions are arbitrarily represented.

3.2. The synthesis of cBN

3.2.1. Pressure–temperature conditions for synthesis

Fig. 3 shows the experimental pressure–temperature (*P*–*T*) conditions of all runs in the $Ca_3B_2N_4$–BN system (circles) and Ca–BN system (triangles).

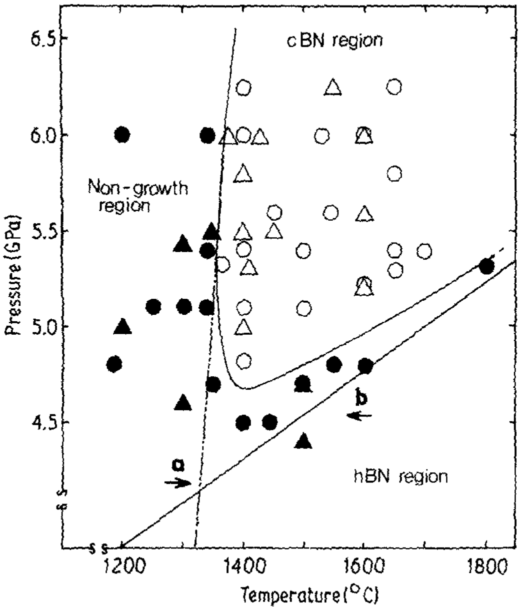

Figure 3 The growth *P*–*T* region of cBN.

In this figure, the open marks indicate the run where cBN could be successfully grown, while the solid marks indicate the runs without the formation of cBN, observed by X-ray diffraction analysis. The growth areas of cBN in both systems were similar, shown by the solid line in Fig. 3. This indicated that by-products formed in the system of Ca–BN were not apparently affected in the *P–T* region of cBN formation.

The low-temperature limit of cBN formation was about 1350° C in the ranges of 5 to 6.5 GPa. It was possible to assume that the low-temperature limit was governed by the initial formation of a liquid in the $Ca_3B_2N_4$–BN region. Therefore, the slope shown by arrow **a** was estimated to be $23 \pm 7°\,C\,GPa^{-1}$ with reference to the eutectic temperature of 1316° C at 2.5 GPa. This value was not far different from that of the system $Mg_3B_2N_4$–BN, which was $28 \pm 3°\,C\,GPa^{-1}$. The line indicated by arrow **b** shows the equilibrium boundary between hBN and cBN, which was estimated by several thermodynamic functions.

DeVries and Fleischer [1] reported the data on the *P–T* region of cBN formation using Ca_3N_2. This disclosed that the low-temperature limit was extended to 1000° C at 6 GPa, and the low-temperature boundary showed a negative coefficient with pressure. Moreover, their work makes no mention of the grain size, purity or water content of the hBN used as starting material. The profile of the cBN growth area obtained from their work was substantially different from that found from this work.

According to the discussion in a previous paragraph, it should be considered that the reaction of BN and Ca_3N_2 took place to form $Ca_3B_2N_4$ under high pressure and temperature conditions. Consequently, it was expected that the *P–T* growth region of cBN formation in the system of Ca_3N_2–BN might be similar to that in the $Ca_3B_2N_4$–BN system. From a kinetic point of view, it was difficult to say that the process for forming $Ca_3B_2N_4$ could homogeneously progress. So far, there was no evidence for the production of "complex" having a composition in the region of Ca_3N_2–$Ca_3B_2N_4$.

In contrast, Wakatsuki *et al.* [7] pointed out that the low-temperature limit decreased up to 1200° C at 6 GPa when hBN in very fine powder form was used without any catalyst. Kobayashi [8] has reported that the limit also decreased to 800 to 1000° C at 6 GPa when water and boric acid were used as catalysts. The *P–T* region of cBN formation shown in [1] unexpectedly resembled the data described above. The present work also failed to establish that the synthesis of cBN with Ca_3N_2 at 6 GPa and 1000 to 1350° C takes place.

Care must be taken to ensure that Ca_3N_2, used as the catalyst, is not handled in air before treatment under high pressure and temperature conditions, since it may be vigorously hydrolysed by moisture; alternatively, some water confined in the hBN starting material can fulfill the function of catalyst. These points must be considered before the intrinsic *P–T* region of cBN formation can be determined. In particular, the data shown in [1] hardly considered the mechanism of cBN formation from the solvent resulting from the negative coefficient of the low-temperature limit with pressure.

3.2.2. The appearance of cBN growth

The synthesis of cBN was demonstrated using $Ca_3B_2N_4$ as the solvent of BN. Fig. 4 shows the appearance of cBN growth. This sample was subjected to treatment at 1540° C and 5.6 GPa for 30 min. The growth of cBN was mostly noticeable in the region of the initial hBN layer; it was seen that cBN grew beneath the thin film of solvent, which advanced into the hBN layer. As a result, the difference in solubility of hBN and cBN might be effectively applied as a driving force for the formation of cBN at the fixed pressure and temperature of the experiment. X-ray diffraction analysis showed that the zone of $Ca_3B_2N_4$ had not suffered from decomposition through the growth of cBN.

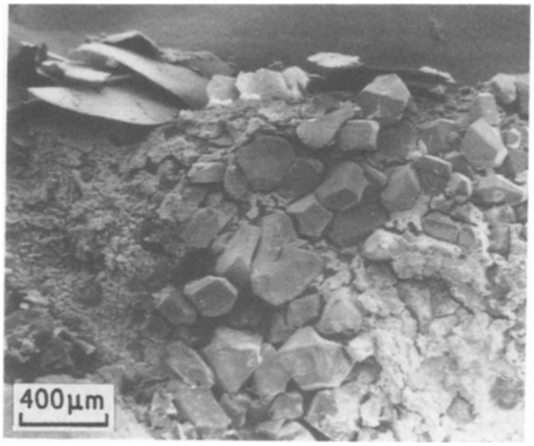

Figure 4 The appearance of cBN precipitated from $Ca_3B_2N_4$ as a solvent of BN.

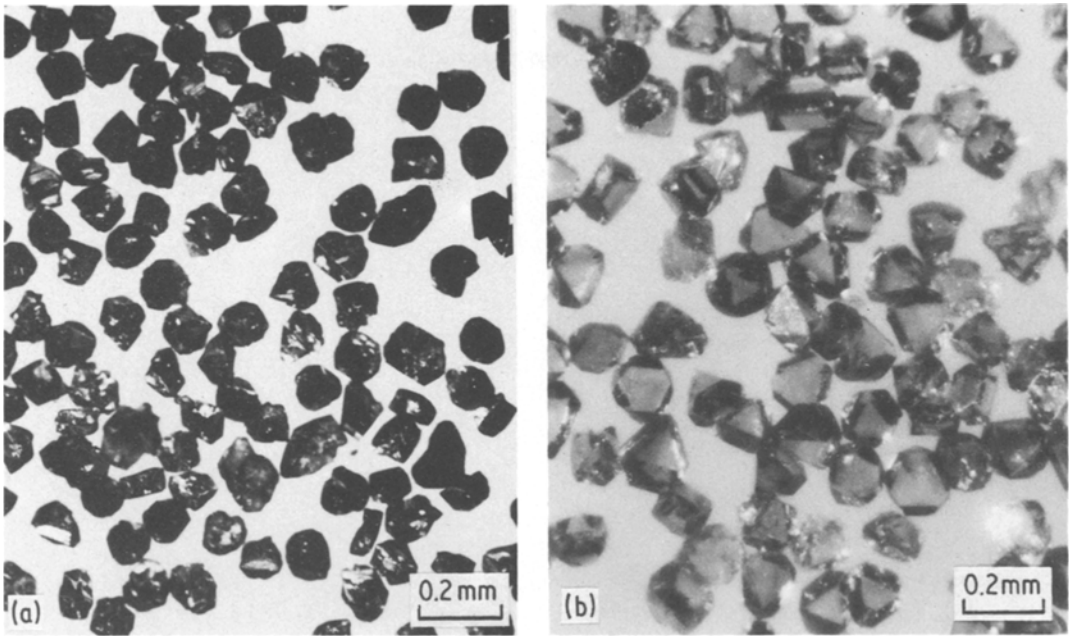

Figure 5 Cubic BN crystals synthesized (a) with Ca at 5.5 GPa and 1450° C and (b) with $Ca_3B_2N_4$ at 5.6 GPa and 1450° C.

Sheet-like crystals were occasionally observed in the zone of $Ca_3B_2N_4$, and were identified, from X-ray diffraction analysis, to be hBN. A more detailed consideration of the film growth mechanism will be published elsewhere.

3.2.3. Microscopic observation of cBN

In order to demonstrate the distinctive advantages for the use of $Ca_3B_2N_4$ as catalyst more clearly, a comparative observation of cBN crystals leached in diluted HCl and $NaF-H_2SO_4$ solution was conducted.

Fig. 5a shows the microphotograph of cBN crystals synthesized using Ca at 5.5 GPa and 1450° C. They are black or dark brown, opaque and of an irregular morphology. According to the chemical analysis of boron, it was suspected that liberating boron or borides were confined to the cBN crystals; this could be the reason why CaB_6 or boron-rich phases were compelled to form, thus producing $Ca_3B_2N_4$. Therefore, the by-products prevented the growth of cBN crystals of high purity.

Fig. 5b shows the cBN crystals synthesized using $Ca_3B_2N_4$ at 5.6 GPa and 1450° C. As can be seen, they are yellow in colouring, quite transparent and of a regular morphology; they show higher purity and quality than the crystals synthesized using Ca, described above.

It could be deduced that hBN dissolved into the $Ca_3B_2N_4$ melt and precipitated as cBN without any appreciable change of molar boron/nitrogen ratio. This was consistent with the observation that any inclusion impregnated into cBN could not be seen. The cBN crystals were mostly truncated octahedral in shape but occasionally adopted a twinned plate-like shape.

Fig. 6 shows a SEM photograph of cBN crystals synthesized with $Ca_3B_2N_4$ at 5.4 GPa and 1700° C for 20 min. They were typically tetrahedral in shape composed of $\{111\}$ and $\{100\}$ faces. Although there was some uncertainty as to the exact positon of the morphology boundary, it appeared that the morphology of cBN was distinctly changed from octahedral to a tetrahedral as the temperature increased at a given pressure. This morphological trend of cBN was less different from that reported previously using Ca.

4. Conclusions

Study of Ca–B–N was performed at 2.5 GPa, and construction of the phase diagram of Ca–B–N, which was indispensable for discussing the growth mechanism of cBN, was undertaken. It could be

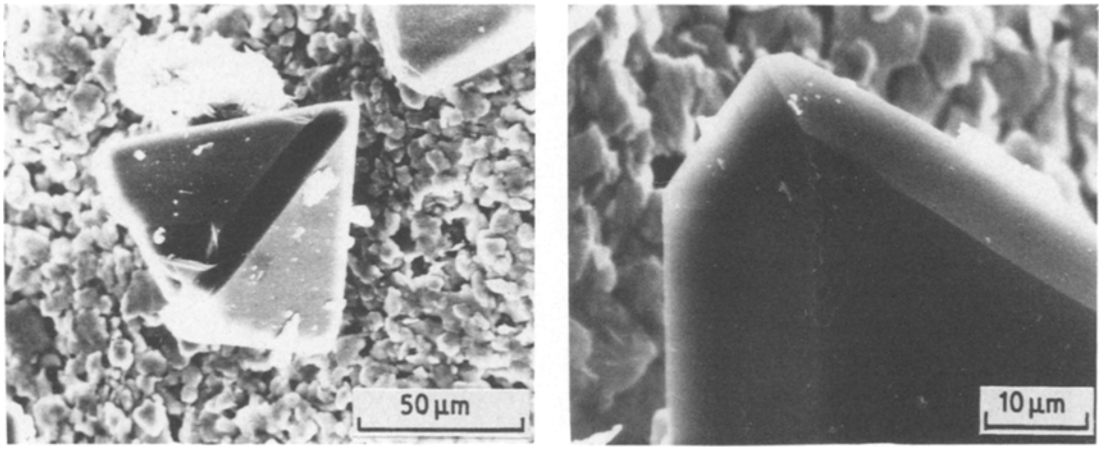

Figure 6 Cubic BN crystal synthesized with $Ca_3B_2N_4$ at 5.6 GPa and 1700° C.

seen that Ca and Ca_3N_2, known to be available catalysts for the formation of $Ca_3B_2N_4$, never directly fulfilled the function of a solvent of BN. As a result, the growth mechanism of cBN was clarified with regard to the eutectic between BN and $Ca_3B_2N_4$.

As described by DeVries and Fleischer [1], there was a eutectic relationship between BN and Li_3BN_2(W), which was a high-pressure phase. However, $Ca_3B_2N_4$ could be readily prepared at atmospheric pressure; moreover, it was relatively more stable than Ca and Ca_3N_2 in air. This contributed to the elimination of the problem arising from the hydrolysis of the catalyst. This stability makes the handling of $Ca_3B_2N_4$ in an industrial operation greatly favourable.

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