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Growth mechanism of cubic BN using Li_3BN_2 solvent under high pressure

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ABSTRACT

The pressure and temperature region of the cubic BN precipitation was studied using Li_3BN_2 as synthetic solvent over the pressure and temperature range from 3.5 to 6 GPa and 1100 to 1800 °C for a duration of 0.3–11 h. The pressure and temperature region of cubic BN formation in the BN-Li_3BN_2 was bounded by lowest temperature line and highest temperature line of cubic BN formation at constant pressure value. We determined these lines as P(GPa) = [T(°C)/30] − 37 for the lowest temperature line and P(GPa) = [T(°C)/465] + 0.79 for the highest temperature boundary between cubic and hexagonal BN. The recovered samples reacted at pressure lower than about 5 GPa were mixture of re-crystallized hexagonal BN and cubic BN crystals. Meta-stable hexagonal BN grew rapidly in the cubic BN stable pressure and temperature region and cubic BN was grown slowly in the meta-stable hexagonal BN matrix.

1. Introduction

The cubic BN (cBN) powders synthesized under high pressure and high temperature (HPHT) are utilized for the grinding abrasives and for the starting powders of sintered cutting tools for ferrous materials. In this study, hexagonal BN (hBN) was used as a starting material. Transformation process from hBN to cBN under HPHT was normally carried out using the solvent of BN to reduce synthetic pressure of cBN. Typical solvents employed in the HPHT synthesis of cBN are alkali or alkaline earth boron nitrogen compounds. Among them, Li_3BN_2 is a typical solvent presently used in the industrial production of cBN powders.

Since pioneer work by Wentorf [1], pressure–temperature (P–T) regions of cBN growth using Li_3BN_2 as solvent have been reported by the several authors [2–7]. The P–T regions of cBN growth presented by the previous reports, showed threshold pressure (lower pressure limit of cBN formation) at about 5 GPa. The P–T condition of 4.5 GPa and 1400 °C was located in the cBN stable region, but no clear results for the formation of cBN in the previous reports. If we examine in the system of graphite and Fe–Ni–Co solvent, diamond can be detected in the diamond stable region within very short reaction time. Lowest temperature limit of the cBN formation determined by the previous researchers was scattered from 1050 °C to 1600 °C [3–7].

In the present study, we report new P–T region of cBN growth based on the HPHT experiments ranging 3–6 GPa and 1100–1800 °C with reaction time of 0.3–11 h. We carried out HPHT experiment employing about one order of magnitude longer reaction time than that adopted by previous researchers. Present results showed sharp demarcated line between cBN growth region and hBN stable region and the line was agreed with reported equilibrium phase boundary line between hBN and cBN [8]. It was confirmed that cBN growth was carried out in the BN-Li_3BN_2 system without limitation of threshold pressure of cBN crystallization.

In the present study, we also discuss on the nucleation and growth mechanism of cBN in the system hBN-Li_3BN_2. The nucleation of cBN was started in the re-crystallized hBN (We denote as Rc-hBN in this paper), which formed by the reaction between starting hBN and molten Li_3BN_2 solvent. The nucleation density of cBN was controlled by the excess pressure from equilibrium pressure. The volume percent of fine cBN crystals was increased at high excess pressure. It is deduced that difficulty of cBN detection below about 5 GPa is mainly due to slow nucleation and growth rate of cBN in the Rc-hBN matrix.

2. Experimental

2.1. Starting materials and HPHT experiments

We used hot-pressed hBN disk (N1 grade, Denka, Japan) which contained 2 wt% of oxygen as starting material. The Li_3BN_2 powder was synthesized using 1:1 molar mixture of Li_3N and BN powder at 1100 °C for 5 h in a nitrogen gas. The product was identified as Li_3BN_2 by X-ray powder diffraction (XRD) patterns.

HPHT experiments were carried out at pressures of 3.5 to 6 GPa at temperatures from 1100 to 1800 °C using modified belt type high pressure apparatus with a bore diameter of 25 mm [9]. We used the sample cell formed from NaCl + 10 wt% of CaO stabilized ZrO_2 powder mixture. The size of the cell was 21 mm in diameter and 17.6 mm of length. Graphite heating element of 12 mm of outer diameter and 1 mm of thickness was inserted on the center of the sample cell. The

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NaCl sample container of 7 mm of inner diameter and 8 mm of length was placed at the center of graphite heater sleeve. The assembled sample layer of hBN disk/Li_3BN_2 solvent/hBN disk was placed in the sample container.

The sample was compressed to the designed pressure at room temperature and then the sample was heated to reaction temperature with heating rate of 60–80 °C/min. The reaction time was set in the range of 0.3 to 11 h. Temperature variation during the reaction was estimated within 10–20 °C.

The calibration of the sample pressure was carried out based on the diamond–graphite phase equilibrium line [10]. We determined minimum P–T points of diamond formation using graphite–Ni, —Co and –invar system. Detected P–T points of the diamond formation were converted to the observed press load and heating power to the graphite heater [9]. The reproducibility of the pressure of the belt type apparatus used in the present experiments was within about 2% [9]. Pressure decrease due to the volume change from hBN to cBN was also accompanied in the experiment. We used 21 mm diameter and 17.6 mm length sample cell of compressed NaCl powder. The size of the hBN sample used was 7 mm diameter and 6 mm of length. The estimated pressure decrease by the volume contraction of the phase transformation from hBN to cBN was about 0.4%. Temperature estimation from the in-put power to the heater contained error within 3–4% due to the variation of the in-put power.

Recovered reacted samples were examined mainly by optical microscope and scanning electron microscope (SEM). Identification of cBN crystal was easy because cBN grains are yellow in color and they scratched on glass plate. Rate of cBN conversion was estimated volume fraction of cBN grains in the sample.

3. Results and discussion

3.1. Observation of cBN crystals by optical microscope

The photograph of an optical microscope of Fig. 1 shows a sample reacted at 4.2 GPa and 1285 °C for 2 h. The layer of the solvent Li_3BN_2 was located between two hBN disks but it was dissolved by hot water before taken a photograph. Central zone of the hBN disk was mixture of Rc-hBN and cBN crystals. Upper and lower ends of the hBN disks were un-reacted gray hBN (UR-hBN) zones. The recovered samples reacted at lower pressure than about 5 GPa, are normally contained Rc-hBN and cBN crystals. The amount of cBN crystals was increased with increase of pressure and reaction time. The cBN crystals are precipitated in the Rc-hBN matrix and no cBN crystals in the un-reacted hBN zone for all samples examined in this study. The cBN crystals were precipitated disorderly and no selectivity of cBN growth at the interface between hBN source and Li_3BN_2 solvent.

The Rc-hBN was crystallized by the reaction between molten Li_3BN_2 solvent and starting hBN. The temperature of the gray UR-hBN zones shown in Fig. 1 was estimated lower than about 1230 °C (lower than liquid formation temperature of Li_3BN_2 rich components) due to temperature gradient in the sample.

In Fig. 2, we showed the sample contained large amount of cBN crystals. The sample was reacted at 4.2 GPa and 1300 °C for 6 h. The sample showed dense cBN crystals of about 80 μm in size cBN. The data suggested that rate of reaction from Rc-hBN to cBN at 4.2 GPa and 1300 °C was slow but the reaction from Rc-hBN to cBN continued with keeping constant reaction temperature.

3.2. The growth P–T region of cBN

In Fig. 3, we illustrated the P–T regions of cBN, Rc-hBN and UR-hBN phases identified by the quenched samples. The close square marks in the figure showed the P–T conditions of cBN precipitated in the quenched samples. As noted in the previous section, almost quenched samples in the cBN region contained Rc-hBN. The relative amount of cBN in the samples was changed with pressure, temperature and the duration of the reaction. The open square in the cBN region denoted no cBN was found in the sample. The P–T condition of this sample was close to minimum pressure and temperature of cBN growth. Small variation of pressure and temperature may prevent cBN growth.

The open circle marks located in the lower temperature region were identified as gray UR-hBN and Rc-hBN crystals were not detected in the

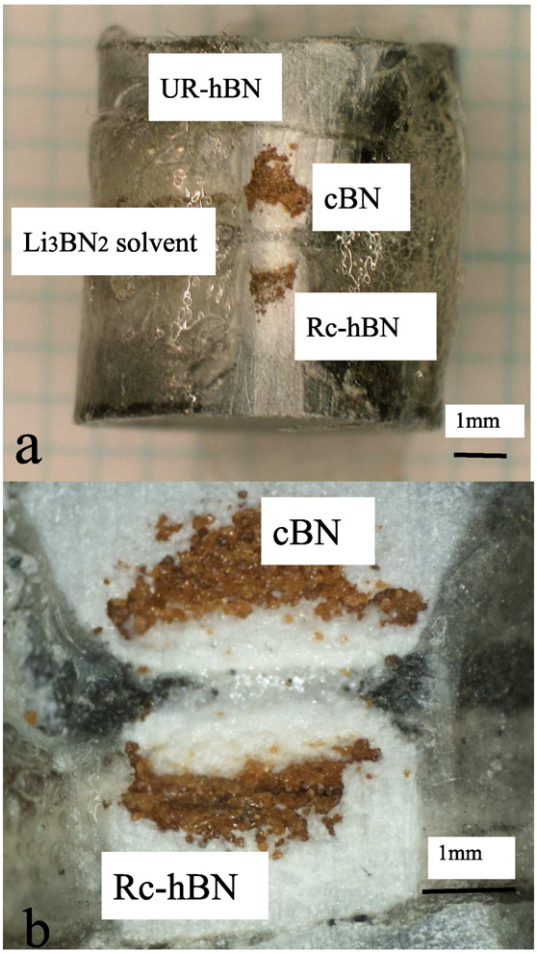

Fig. 1. a) Sample reacted at 4.2 GPa and 1285 °C for 2 h. b) Enlarged image of the sample (a). The cBN crystals were found in the Rc-hBN zone. No cBN crystals were detected in the un-reacted gray hBN (UR-hBN) zone. The distribution of the cBN crystals in the Rc-hBN matrix was not uniform. Ring shape region of cBN crystals was observed in this sample.

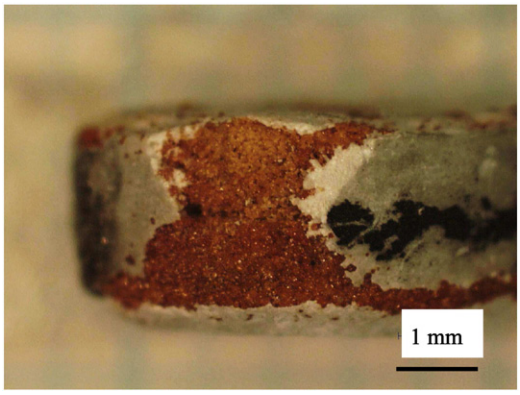

Fig. 2. Precipitated cBN crystals were covered full volume of starting hBN disk. The sample was reacted at 4.2 GPa and 1300 °C for 6 h. Small amount of Rc-hBN layer was remained in the periphery of the hBN source.