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Phase Transformation of Amorphous Boron Nitride under High Pressure

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Amorphous boron nitride (BN) powder was prepared by mechanically milling hexagonal BN and used as a starting material for studying BN phase transformation behavior. Fabricated amorphous BN (aBN) powder was significantly reactive with humidity in the air. When it was kept under a dry nitrogen atmosphere without H_2O or O_2, the phase transformation from aBN to cubic BN (cBN) occurred at 7.7 GPa at temperatures above 2200 °C, whereas aBN powder treated in air transformed into cBN at 5.5 GPa at temperatures above 1500 °C. These observations suggest that H_2O has a strong catalytic effect on the phase transformation behavior of aBN. Without H_2O, the phase transformation from aBN to cBN is rather difficult to achieve compared with transformations starting from other crystalline phases of BN. The cBN powder produced from aBN consists of fine grains smaller than 100 nm, which are superior in purity to those obtained via the conventional route using an alkali-earth metal/solvent system.

Introduction

Cubic boron nitride (cBN) is the second hardest material, after diamond, and is superior to diamond in terms of chemical resistance to ferrous alloy. Abrasive and sintered bodies of cBN are, therefore, important for industrial applications, particularly as cutting tools for steel materials.[1] Cubic BN powders are usually produced from hexagonal BN (hBN) by using a solvent, such as the alkali metal/BN compound Li_3BN_2, at high pressure (HP) and high temperature (HT), such as 5 GPa and 1500 °C.[2] Commercial cBN powders are mass-produced in this way, and fine-grained powder is prepared by crushing the fabricated cBN grains.

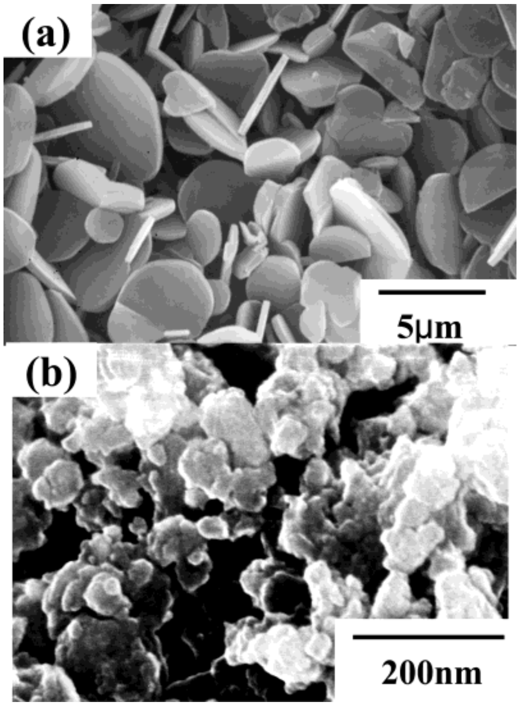

Figure 1. SEM images of hBN and milled aBN powders. (a) hBN and (b) aBN treated by planetary milling for 50 h.

On the other hand, direct transformation of cBN from a low-pressure form of BN has been successfully performed at 7.7 GPa without the use of any catalyst.[3−8] Translucent cBN sintered bodies have also been fabricated by starting from the low-pressure form of BN and also from cBN powders without additives.[4,5] These bodies exhibit superior mechanical properties compared to conventional sintered bodies of cBN with binder.[5,8−10] Thus, the process of fabricating the binderless high-purity cBN polycrystalline form has already been established in the 7.7 GPa region.

There is a basic demand for preparing fine-grained cBN powder for use as an abrasive and also as the starting material of the sintered body. The commercially

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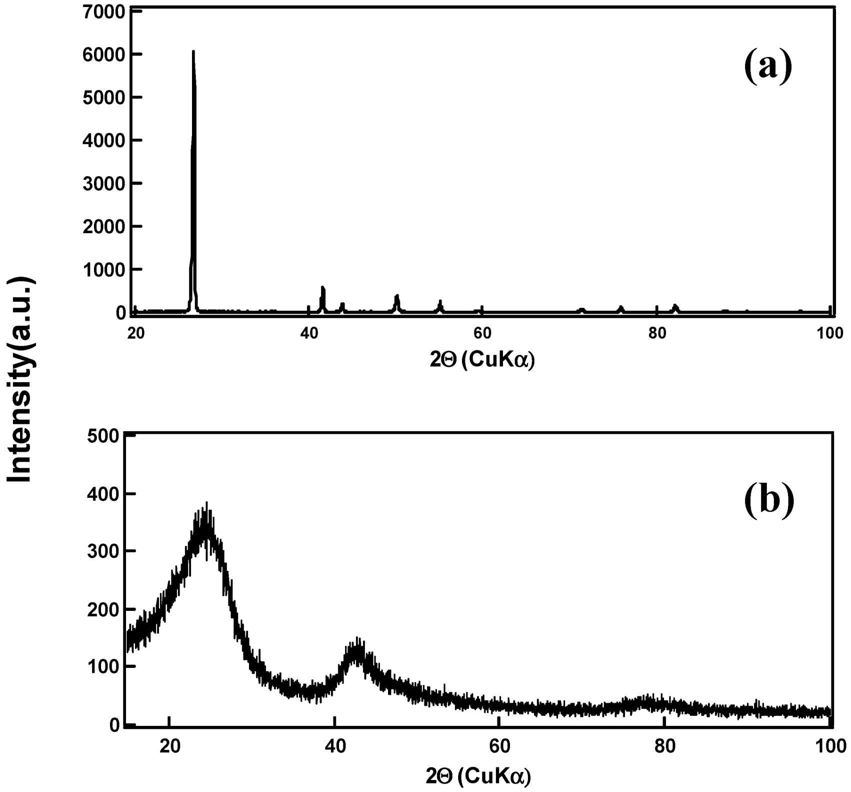

Figure 2. XRD profiles of hBN and milled aBN powders. (a) hBN and (b) aBN treated by planetary milling for 50 h.

available cBN powder is synthesized with solvent and graded into appropriate particle sizes. Because the ordinary grain size of cBN powder obtained using the conventional process is larger than several micrometers, fine-grained cBN powder with submicrometer grains is obtained by crushing the larger-grained powder. The powder, therefore, has residual solvent components, as well as cracking and residual strain caused by the crushing process.

From the viewpoint of product purity, the synthesis of cBN powder by the direct transformation process should, therefore, be a promising approach, because it is solvent-free. However, the products recovered under these synthesis conditions were sintered and formed aggregates, because high temperature (above 1800 °C) is required for the phase transformation. Mechanical crushing of the sintered bodies was still necessary to prepare fine-grained cBN powders. Thus, it can be seen that the conventional process for obtaining fine-grained cBN powder still has room for improvement in terms of purity as well as crystallinity.

It has been pointed out that the initial crystallinity of the starting BN material affects its phase transformation behavior.[11−17] Using amorphous BN (aBN)[12] and turbostratic BN (tBN)[13−15] as the starting materials, cBN crystals have been obtained in the region of 1000 °C and 7 GPa. These previous studies suggest promising routes for obtaining fine-grained cBN powder, because of the lower synthesis temperature of 1000 °C, which avoids sintering. However, the properties of the fabricated cBN powders were not adequately described. The effect of ball milling on the phase transformation behavior in starting powders of hBN was also examined. It has been shown that the hexagonal−cubic transformation under HP was substantially facilitated by ball milling; e.g., under 7.7 GPa, the formation of cBN starts at 1250 °C with premilled hBN powders, but it starts at 1450 °C with nonpremilled powders.[16] According to high-resolution transmission electron microscopy (HRTEM), the transformation was facilitated by a mechanochemical effect. To strengthen this effect, powders of hBN were ball-milled even more strongly to obtain aBN.[17] Recently, the preparation of aBN by this method and its phase transformation behavior were reported.[18] Although the mechanism of the phase transformation from aBN to cBN was inferred from an analysis of the recovered products,[18] the aBN powder prepared in this system was affected by H_2O from atmospheric humidity. It has been pointed out that water has a catalytic effect on the formation of cBN from hBN under HP.[19,20] Care must be taken in interpreting the phase transformation behavior of aBN, because elimination of the H_2O

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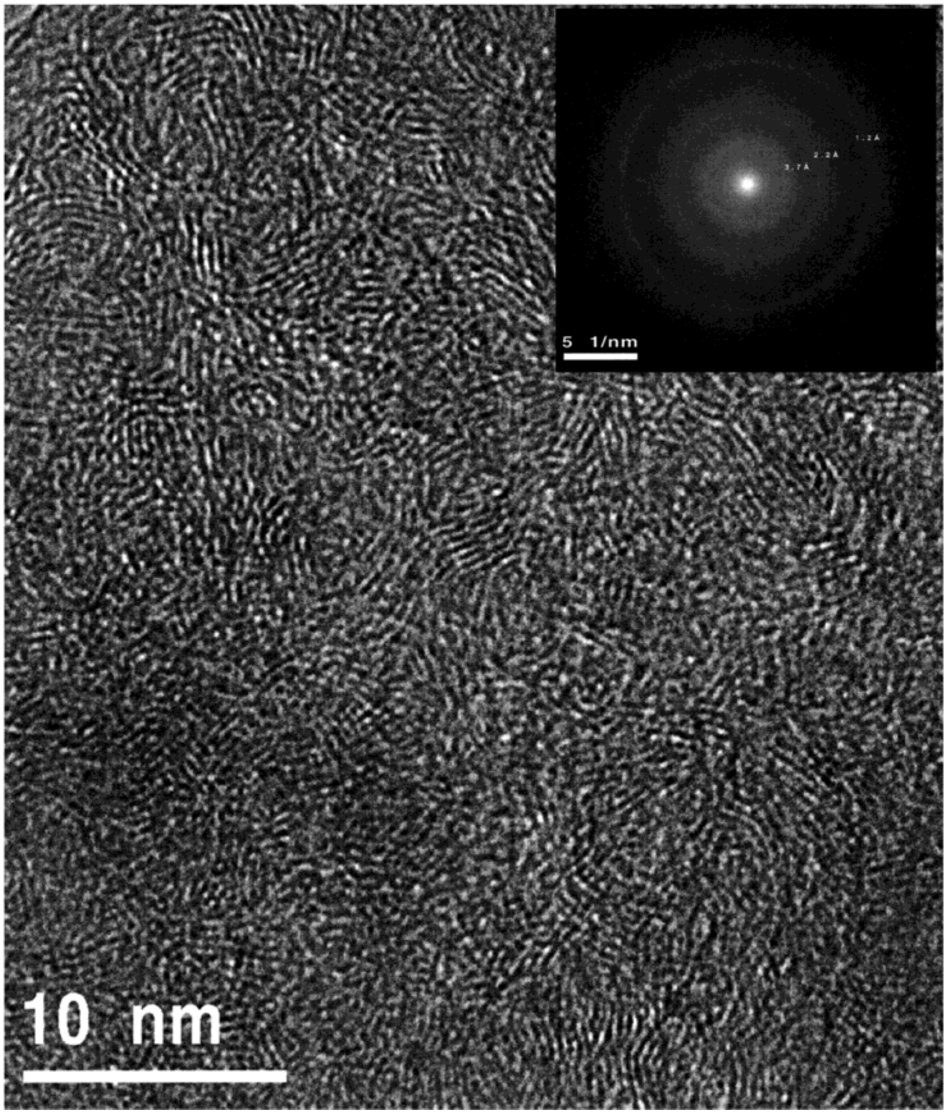

Figure 3. HRTEM image of milled aBN powder treated by planetary milling for 50 h.

component from the aBN system was not reported. No practical investigations of the behavior of aBN under HP without H_2O as a catalytic component have been performed. A reexamination of the synthesis of cBN from the amorphous state is, therefore, required to fully understand its mechanism and to develop a new route for obtaining fine-grained cBN powder.

In this study, we prepared two types of aBN powder. One was treated in dry nitrogen atmosphere free from H_2O and oxygen. The other was treated in air with ambient humidity. The purpose of this study was to observe the intrinsic phase transformation behavior of aBN under HP.

Experimental Section

Preparation of Amorphous BN. The amorphous BN (aBN) powders were prepared by mechanical milling of hBN. Planetary milling was applied to hBN powders for 50 h by using WC−Co alloy balls and a chamber (Fritsch type P-5). Figure 1a and b shows scanning electron microscope (SEM) images of the starting hBN and milled BN powders, respectively. X-ray diffraction (XRD) profiles of the powders are shown in Figure 2. As shown in Figure 1, the apparent feature of the milled powder changed from initial hexagonal platelets to coagulated particles smaller than 50 nm. An HRTEM image shows that the milled BN powder consisted of nanoscale crystals (less than 3 nm) and amorphous phases, as shown in Figure 3. The amorphous halo pattern of the electron diffraction pattern (EDP, Figure 3 inset) is in accordance with the broad XRD profile in Figure 2b.

Prior to milling, a commercially available starting hBN powder [average grain size of 5μm, Shin-etsu co., Ltd, h(10)f type, shown in Figure 1a] was heated at 2100 °C under a nitrogen atmosphere so as to suppress the major impurity of oxygen to less than 100 ppm. Chemical analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) showed that the milled BN powder had no discernible contamination (below 50 ppm) from the milling equipment.

The milled powder was extremely reactive, so it was easily affected by humidity in the air. Upon exposure to air, the powder immediately released heat and ammonia gas and also increased in weight, changing from pure aBN to aBN/H_2O. To prepare aBN powder free from water and oxygen, all of the following processes for preparing aBN powder and encapsulating it for HP treatment under a dry nitrogen atmosphere using a glovebox were performed: (1) The milling chamber was sealed by using copper gasket so as to tightly enclose the atmosphere in the chamber. (2) The starting hBN powders were encapsulated into the chamber with dry nitrogen. (3) After being milled, aBN powders were removed from the milling chamber and encapsulated in the Ta capsule for the HP treatment in the globe box. Because the Ta capsule was mechanically sealed tightly, the aBN powder prepared by the

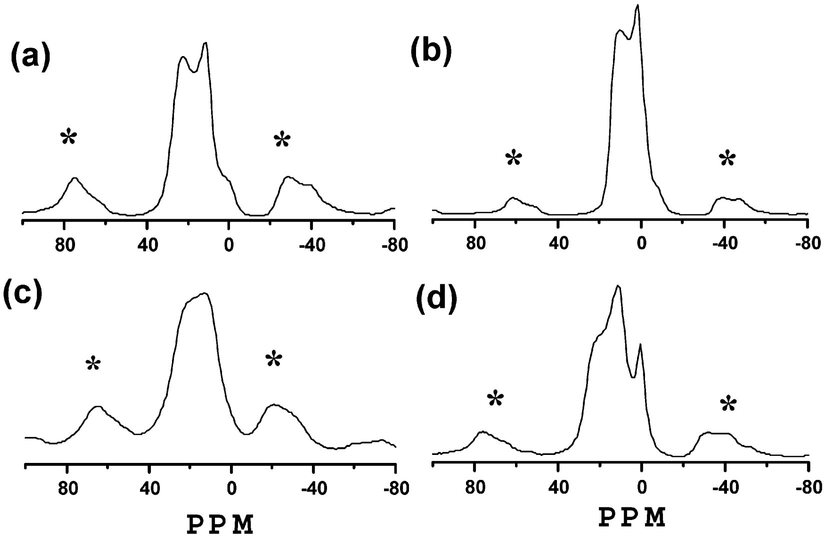

Figure 4. ^{11}B MAS NMR profiles of BN measured at 9.4 T, hBN after deoxidization, B_2O_3, aBN treated in dry N_2 atmosphere, and aBN affected by humidity in the air. The MAS speed was about 6 kHz. Asterisks (*) indicate spinning sidebands.

above process is free from oxygen and water. The levels of oxygen and water in the glovebox were kept below 0.5 ppm throughout the procedures. Once aBN powders are affected by water and oxygen, elimination of these component is extremely difficult. Because the aBN will be recrystallized at high temperature, any heat treatment to eliminate water cannot be carried out.

There was no discernible difference in the XRD profiles of milled powders affected by humidity and those free from humidity. However, the oxygen content of the former was measured to be more than 1 wt % by chemical analysis (LECO), whereas the latter showed an oxygen concentration of less than 100 ppm. A solid-state nuclear magnetic resonance (NMR) study revealed a clear difference between the two types of milled BN powder. The ^{11}B magic-angle spinning (MAS) NMR spectra of the hBN and B_2O_3 powders are shown in Figure 4a and b, respectively. A sharp peak near the 0 ppm region with a shoulder corresponds to the B−O bonding feature, while the double peaks near 20 ppm with a shoulder in the 0 ppm region represent the $B-N_3$ sp^2 bonding state.[21,22] The spectrum of aBN powder without H_2O and O_2 indicates only the $B-N_3$ sp^2 bonding state, similarly to the spectrum of high-purity hBN, as shown in Figure 4 c. On the other hand, the B−O bonding feature is represented by a sharp peak near the 0 ppm region in the spectrum obtained from aBN powder affected by humidity (Figure 4d).

Consequently, we prepared two types of milled BN powder. One was treated in dry nitrogen atmosphere free from water and oxygen. The other was treated in air with atmospheric humidity and oxygen as impurities. These two types of powder were used to study the phase transformation under high pressure and high temperature.

HP Treatment. The aBN powders obtained by milling were encapsulated in a Ta capsule and treated at 5.5−7.7 GPa and 800−2500 °C for 15 min, using a modified belt-type HP apparatus with a bore diameter of 32 mm. The temperature was estimated up to 2200 °C from the predetermined relationship between input electric power and temperature by using a (W−5 wt % Re)/(W−26 wt % Re) thermocouple, with no correction for the effect of pressure on the emf. The experimental procedures have already been described elsewhere.[4,5] After HP treatment, the Ta foil was mechanically removed. The recovered specimens were then characterized by XRD, SEM, and HRTEM analyses.

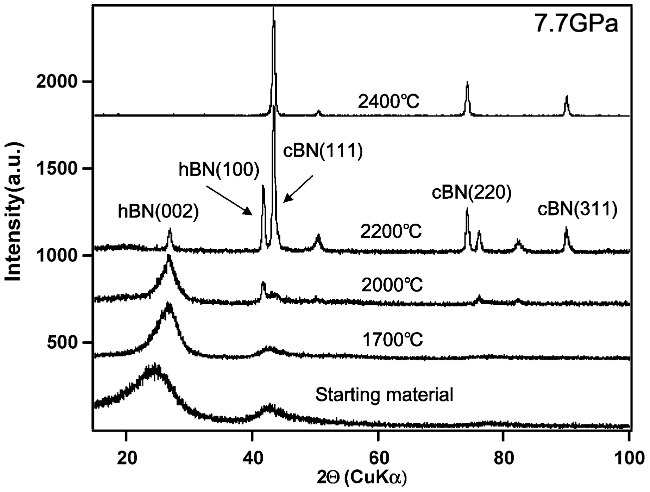

Figure 5. XRD profiles of HP/HT treated products obtained from aBN without H_2O and O_2 as the starting material.

Results

HP Treatment of aBN Powder under Air- and Humidity-Free Conditions. Figure 5 shows typical XRD profiles of HP-treated aBN that had been prepared under an atmosphere free from air and humidity. The initial broad peak became sharp with increasing temperature. At 2000 °C, some transformation to hBN was observed. Transformation to the cBN phase clearly appeared above 2200 °C and was completed above 2400 °C at 7.7 GPa. This transformation behavior of aBN was significantly different from the behaviors reported previously for samples obtained using aBN, tBN, and hBN as starting materials. The phase transformation from hBN to cBN is known to take place with the formation of wurtzite BN (wBN) in the 7.7 GPa and 1500 °C region.[6,7] For comparison, starting hBN powders were treated at HP before being milled in this study. Consequently, the formation of cBN was found above 1500 °C at 7.7 GPa. The formation boundary from aBN to cBN shifted to a higher temperature at 7.7 GPa compared with that from crystalline phases of BN. Note that we did not observe the formation of wBN or compressed hBN in this study.

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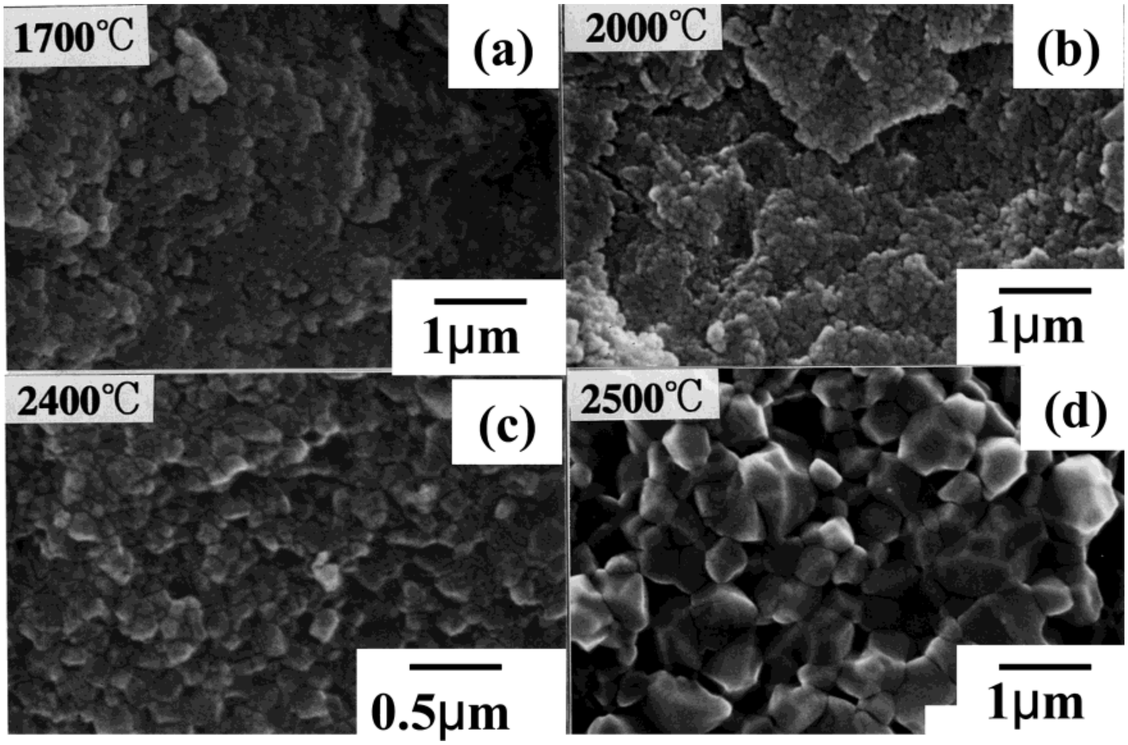

Figure 6. SEM images of HP/HT treated products obtained from aBN without H_2O and O_2 as the starting material: (a) 7.7 GPa and 1700 °C, (b) 7.7 GPa and 2000 °C, (c) 7.7 GPa and 2400 °C, (d) 7.7 GPa and 2500 °C. Duration = 15 min.

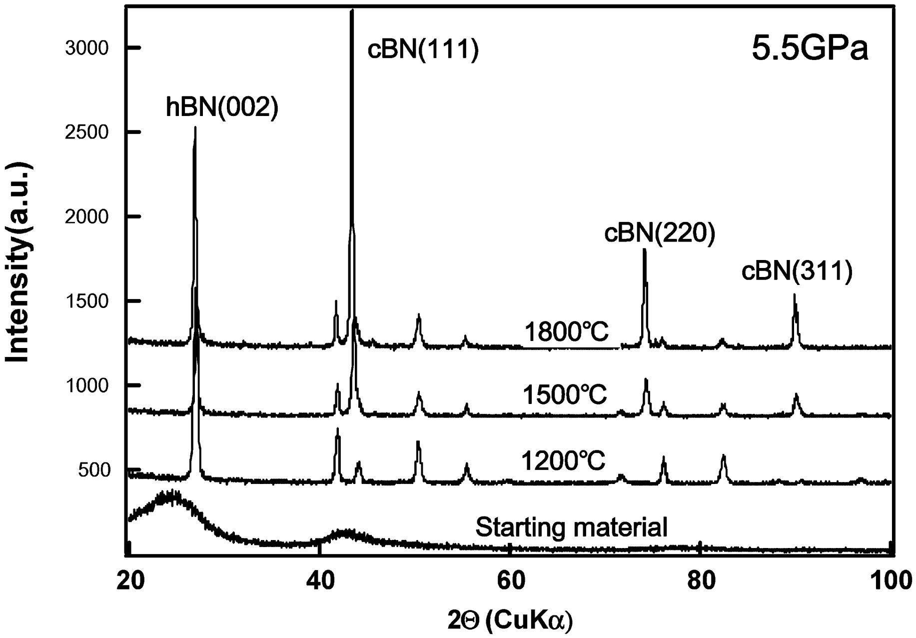

Figure 7. XRD profiles of HP/HT treated products obtained from aBN affected by H_2O and O_2 as the starting material.

Figure 6 shows an SEM image of the recovered products. Fine-grained powder (less than 500 nm) was observed in the recovered product up to 2400 °C. At 2400 °C, a fracture surface of the sintered body of the cBN single phase showed a homogeneous texture with a fine-grained structure. Obvious grain growth took place above 2500 °C, as shown in Figure 5d.

HP Treatment of aBN Affected by Air and Humidity. Figure 7 shows XRD profiles of HP-treated products starting from aBN affected by air and humidity. It should be noted that the cBN phase was detected at 1500 °C and 5.5 GPa. The formation boundary from aBN to cBN was, therefore, observed to be at a much lower pressure and temperature than when using aBN free from air and humidity. The reaction boundary of aBN to cBN is summarized in Figure 8, where the starting powder was treated in air. It can be seen that the reaction boundaries from aBN to cBN were similar to those obtained in previous studies, where the starting BN materials were affected by H_2O.[12,14,18,19]

An HRTEM image of the recovered sample shows nanocrystalline cBN grains (Figure 9). This fine-grained powder contained no catalytic component and was not damaged by the crushing process. Typical impurities in

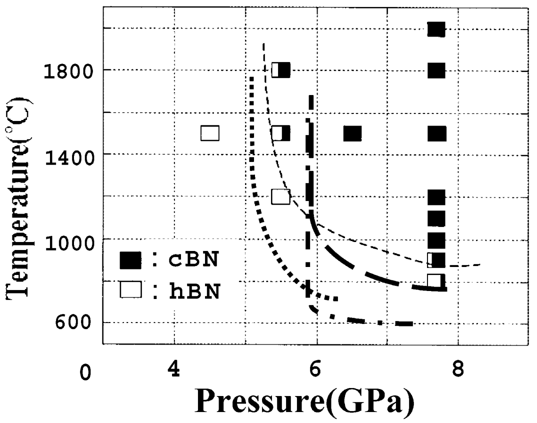

Figure 8. Boundary of cBN formation from aBN affected by H_2O and O_2. - - -, present study; —, H. Sumiya et al.;[12] — — —, K. Ichinose et al,[15] • • •, T. Kobayashi et al.;[19,20] — • — • —, I. S. Gladkaya et al.[13]

the recovered cBN fine powder, commercial cBN, and cBN fabricated using alkali-earth metal/BN solvent system were characterized by ICP chemical analysis; the results are summarized in Table 1. It can be seen that the levels of residual catalytic components in the present product, cBN(1), were very small compared with those detected in the samples obtained via the conventional processes, cBN(2) and cBN(3).

Discussion

Phase Transformation of aBN to cBN. It is clear that aBN affected by humidity shows behavior similar to that previously reported for aBN and hBN affected by water.[12,15,19,20] For aBN powder maintained in a dry nitrogen atmosphere, achievement of the phase transformation from aBN to cBN is more difficult, compared to transformations starting from other crystalline states of BN. Complete transformation from aBN to cBN requires a very high temperature.

It should be noted that the broad XRD profile of aBN powder essentially did not change from the initial state up to 7.7 GPa and 1700 °C under dry nitrogen, as shown in Figure 5. The hBN phase appeared even in the $P-T$ region of 7.7 GPa and 2000 °C. In this $P-T$ region, the energy state of cBN should be lower and that of aBN higher, with the energy state of hBN intermediate between them. A metastable hBN phase might appear on the way from the aBN state to the cBN phase via unknown kinetic effects at HP and HT. The observed hBN phases of (100) and (002) in Figure 5 exhibit comparable diffraction intensities, suggesting that nucleation for hBN occurred with random orientation in the

Table 1. Summary of Impurities in cBN Powders (wt %)

element	cBN(1)[a]	cBN(2)[b]	cBN(3)[c]
Li	<0.0001	0.0002	ND[d]
Ca	<0.025	0.078	0.098
Ba	<0.0001	0.002	0.0086
Mo	0.002	0.002	ND
W	ND	ND	ND

[a] cBN(1) was prepared in this study using aBN as the starting material. [b] cBN(2) was a commercial product. [c] cBN(3) was prepared at 5.5 GPa and 1600 °C using hBN as the source and Li–Ca–Ba–BN as the solvent. [d] ND = not detectable.

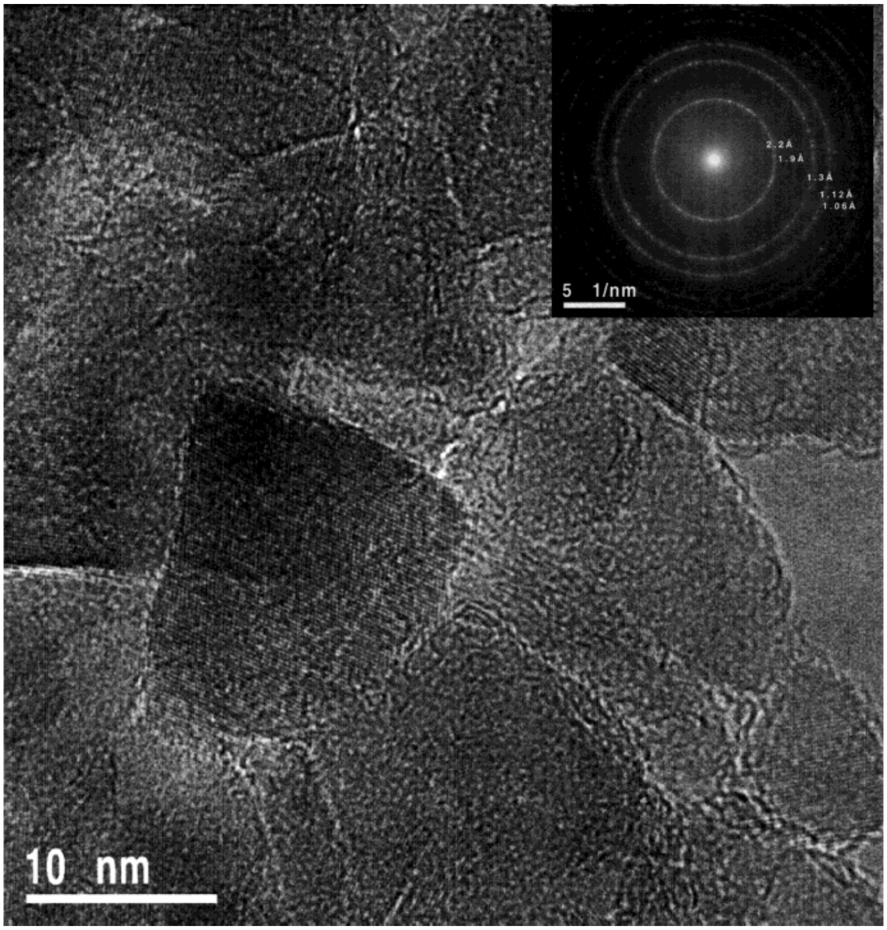

Figure 9. HRTEM image of recovered fine-grained cBN: aBN affected by H_2O and O_2 was treated at 7.7 GPa and 1500 °C.

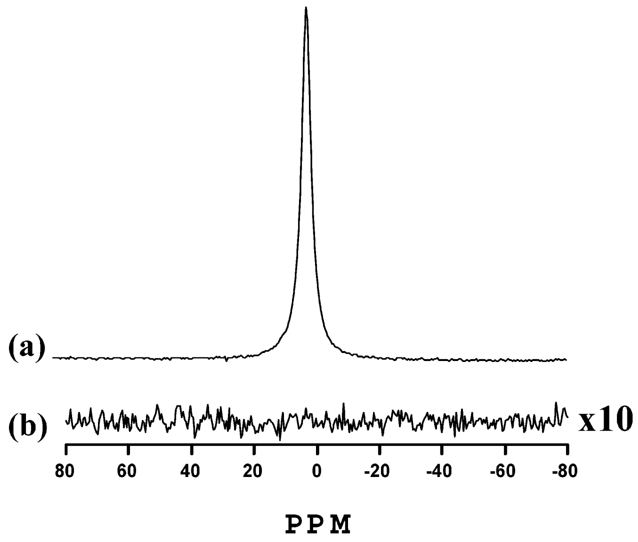

Figure 10. ^{10}B MAS NMR profiles of BN measured at 9.4 T: (a) cBN standard crystal, (b) aBN affected by humidity in the air.

aBN matrix. Because the milled aBN sample did not have a homogeneous structure (it consisted of nanocrystalline and amorphous features, as shown in Figure 2), these variations in the starting structure might affect the kinetic effect on their phase stability.

Above 2400 °C, the transformation to cBN phase was completed. Taking account of the sintering behavior of cBN grains, 2400 °C is the typical temperature for the occurrence of grain growth at 7.7 GPa.[5] The transformation from aBN to cBN might also require such a high temperature to enhance the lattice diffusion process.

It was speculated[18] that the cBN phase nucleates directly from the sp^3-hybridized amorphous matrix, which is originally induced by the ball-milling process. Considering the phase transformation behavior of aBN discussed above, however, aBN powder produced by the ball-milling process had no advantage in terms of nucleation of cBN under HP without water as a catalytic component. The approach to an analysis of an EELS spectrum used in ref 18 was used in the literature to estimate the sp^2/sp^3 fraction in CVD diamond-like carbon films, while the existence of sp^3 hybridization was already known in these films.[23,24] To clarify the existence of the sp^3 hybridization fraction, a MAS NMR analysis of milled aBN was also carried out. The ^{10}B MAS NMR spectra of cBN and aBN powders are shown in Figure 10a and b, respectively. The spectrum of cBN exhibits a symmetrical resonance in the 0 ppm region, representing B$-$N$_4$ sp^3 bonding state, as shown in Figure 10a.[20,25] No trace of signals related to the B$-$N bonding state with sp^3 hybridization was found in the spectrum of milled aBN, as shown in Figure 10 b. Although the change of the EELS spectrum of aBN[18] could exhibit some unknown unique properties ofthe B$-$N bonding state, the present experimental study does not provide any practical evidence for the formation of sp^3 hybridization in milled aBN in view of its phase transformation behavior and MAS NMR analysis.

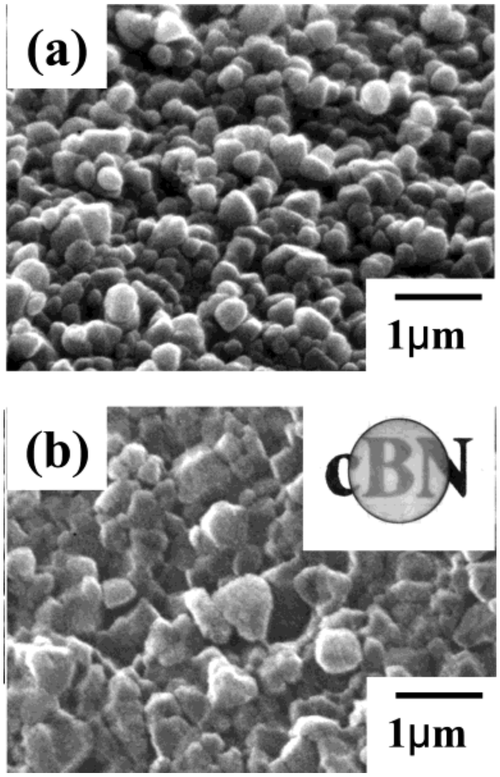

Figure 11. SEM images of recovered products: (a) recovered fine-grained cBN obtained from aBN affected by by H_2O and O_2 as the starting material treated at 6.5 GPa and 1500 °C for 20 min, (b) fracture surface of sintered cBN body obtained by sintering purified recovered cBN powder (Figure 11a) at 7.7 GPa and 2200 °C. A complete view of the translucent feature is also shown in the inset of Figure 11b.

Some previous studies on the synthesis of cBN using catalysts of water, urea, and boric acid have been conducted.[19,20] Although the preparation of the starting powder in the present study is different from the approached used in those studies, the reaction mechanism of cBN formation seems to be essentially the same. In the water catalyst method, it was understood that ammonium borate, made by water reacting with the starting hBN and/or aBN material, acted as a solvent, dissolving the hBN and/or aBN so that it crystallized into cBN.[20] In the present study, the smaller amount of water in the reaction system might be more effective than that in ref 20, where 40 wt % water was added to hBN. This difference can be attributed to the smaller grain size and higher activity of aBN powder, which facilitates reaction with water. In this study, the threshold $P-T$ boundary of cBN formation from aBN with humidity was located at 5.5 GPa and 1500 °C. To shift the boundary to lower $P-T$ regions, we should optimize the detailed kinetic factors of cBN nucleation. More precise characterization of the reaction system in terms of its transformation behavior is an important topic for future work.

Characteristics of Synthesized Fine-Grained cBN Powders. Ball-milling might provide some advantage for synthesizing fine-grained cBN crystal. By preparing aBN powder in air, one can easily synthesize fine-grained cBN powder at HP/HT using the prepared aBN powder as a starting material. From the industrial

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viewpoint, a finer-grained structure of the sintered body should lead to the fabrication of sharp cutting edges having superior cutting performance. Preparation of high-quality fine powders suitable for the sintering process is, therefore, particularly important.

The fine-grained cBN powders we recovered contained no impurities from the conventional catalytic component and were not damaged by the crushing process, although some B−O compounds could have been mixed in the recovered product. It should be emphasized that sintered products obtained from aBN affected by humidity exhibited poor mechanical properties, with Vickers hardness values of less than 20 GPa (indentation load of 4.8 N), probably because of residual B−O in the grain boundaries. To achieve the expected superior properties of synthesized fine-grained cBN powders, one must apply an appropriate cleanup process to the powders, such as acid treatment. Figure 11a shows an SEM image of synthesized fine-grained cBN powder treated at 6.5 GPa and 1800 °C. The powder was treated by acid to eliminate the expected residual B−O component and capsule materials. Although the fine-grained powder was not completely recovered because of technical difficulties in recovering it after acid treatment, the recovered grains were still very small, less than 300 nm. The fracture surface of the sintered body obtained by sintering the recovered powder, shown in Figure 11a, at 7.7 GPa and 2200 °C is also shown in Figure 11b. Without typical grain growth, the body seems to be well sintered, so it appears translucent. The entire view of the sintered body is shown in the inset of Figure 11b. This product exhibited higher translucency than those obtained from commercial cBN powders,[5] suggesting that it had superior properties with fewer impurities such as residual components of the catalyst. According to preliminary characterization, the Vickers hardness of the body was about 40 GPa (indentation load of 4.8 N). Further study to clarify the detailed sintering behavior and mechanical properties of the resultant sintered body is important for future work.

Conclusion

By controlling the atmosphere for reactive aBN powder, we were able to clarify its intrinsic phase transformation behavior. Amorphous BN powder prepared by ball milling was extremely reactive, so it was easily affected by humidity from air. Once exposed to air, the system changed to aBN/H_2O instead of pure aBN. In this study, we clarified a significant difference in the phase transformation behaviors of two types of aBN powder. The phase transformation to cBN from aBN powder free from humidity and air took place above 2200 °C and 7.7 GPa. Amorphous BN free from humidity is rather difficult to transform into cBN compared to transformations starting from other crystalline states of BN. Freshly fired hBN (oxygen content of less than 100 ppm) before being mechanically milled to aBN state was transformed into cBN from 1500 °C at 7.7 GPa, suggesting that amorphization inhibits nucleation of cBN under high pressure. A temperature high enough to enhance lattice diffusion in the amorphous matrix is required for the phase transformation. This temperature corresponds to the temperature causing grain growth in the solid-state sintering process of cBN.

On the other hand, aBN powder affected by humidity transformed to cBN at 1500 °C and 5.5 GPa. Because it has been pointed out that water has the catalytic effect of converting cBN from hBN,[19,20] a similar catalytic effect seems to be present in the aBN/H_2O system. The boundary for forming cBN from aBN/H_2O was close to the boundaries reported in previous studies.[12−14,19,20] On the other hand, fine-grained cBN powder suitable for sintering can be obtained using ball-milled aBN powder affected by humidity. The powder has promising potential for fabricating sintered bodies with a finer structure.

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