Influence of Water Agent on High-Pressure/ High-Temperature Transformation of Graphitic BC_2N

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Graphitic BC_2N has been exposed to high pressure (7.7 GPa) and high temperature (800−2200 °C) in the presence of water as a fluid agent to explore the reactivity of the graphitic BC_2N and crystallization behavior to cubic compounds in a B−C−N ternary system. The graphitic BC_2N reacted with water above 1200 °C, which describes that the graphitic BC_2N is similar to graphite in reactivity rather than hexagonal boron nitride (hBN). The dissolved BC_2N was not recrystallized as a cubic B−C−N compound but was disproportionated into graphite and cubic boron nitride (cBN) in the temperature range of 1200−1800 °C. Then, the precipitated graphite was transformed into diamond above 2000 °C. The precipitation behavior of the cubic compounds in the BC_2N−H_2O system can be explained by the simple sum of the formation of cBN in hBN−H_2O and that of diamond in graphite−H_2O.

Introduction

Carbon and boron nitride, a group IV material and a III−V compound in the same row of the periodic table, have the same structural polymorphism, which leads to some similarities. Their hexagonal forms (graphite and hBN) are transformed into cubic ones (diamond and cBN) at high-pressure and high-temperature (HP/HT) conditions. Diamond and cBN have useful characteristics such as high hardness (large bulk moduli), high thermal conductivities, wide band gaps, and low dielectric constants.

However, carbon and boron nitride show some differences as well. For instance, graphite behaves as a semimetal but hBN as an insulator. Diamond is reactive with Fe but cBN is not. Interestingly, most of the catalytic solvents for graphite/diamond transformation are not effective in hBN/cBN transformation.

The similarities and differences of carbon and boron nitride make their hybrid, B−C−N ternary compounds, an attractive object to be studied. Graphitic BC_2N is one of the B−C−N compounds that has been relatively well-characterized. Graphitic BC_2N is metastable and prepared by a low-temperature chemical-vapor-deposition (CVD) method.[1,2] Measurement of its physical properties indicates that graphitic BC_2N is a semiconductor with a band gap of 2 eV, which is intermediate between graphite and hBN.[3] Graphitic BC_2N is directly transformed into a diamond-like cubic form at 7.7 GPa and 2150−2300 °C but it tends to decompose into diamond and cBN at higher temperatures, which suggests that the cubic B−C−N compound is not thermodynamically stable.[4−6]

Catalytic behavior of Co and Mg_3BN_3 onto graphitic/cubic transformation of BC_2N has been previously reported.[2] The molten Co promotes segregative transformation to diamond and cBN in a 1:1 ratio at 5.5 GPa and 1400−1600 °C. This reaction scheme suggests that the graphitic BC_2N was dissolved into the molten Co and thermodynamically stable diamond and cBN were precipitated from it. It is interesting that cBN was crystallized via the molten Co, which is a catalytic solvent for diamond synthesis.[7] On the other hand, the graphitic BC_2N did not react with Mg_3BN_3, which is a catalytic solvent for cBN synthesis,[8] up to 6 GPa and 1600 °C. Such a study for the solvent reaction of the graphitic BC_2N should be advanced to elucidate two points: the chemical reactivity of the B−C−N hybrid and the crystallization mechanism of diamond-like compounds in the B−C−N system with solvents.

In the present study, we examined the reaction of the graphitic BC_2N with H_2O (distilled water) because it is a rare agent effective for the formation of both cBN and diamond. Previously, Susa et al.[9] and Kobayashi[10] have described HP/HT transition of hBN to cBN in the presence of H_2O at 6 GPa and above 600 °C. Yamaoka

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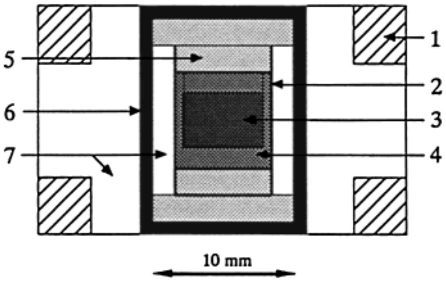

Figure 1. Sample assembly for the HP/HT treatments. 1, steel ring; 2, Mo foil; 3, sample (ground BC_2N); 4, Mo capsule; 5, NaCl + ZrO_2 (20 wt %) as a pressure medium; 6, graphite heater; 7, NaCl + ZrO_2 (10 wt %) as a pressure medium.

et al.[11] have demonstrated diamond crystallization in the system of graphite and H_2O at 7.7 GPa and above 2000 °C.

The states of H_2O at HP/HT conditions have attracted considerable interest in the fields of geophysics, particularly from the viewpoint of the natural diamond because it often contains some C−O−H species (CO_2, CH_4, and H_2O) as inclusions.[12] H_2O under HP/HT conditions has been thought to be a supercritical fluid phase, which is reactive with graphite or organic compounds to produce so-called C−O−H fluids.[13] Recently, some HP/HT fluids have been experimentally confirmed to be effective for diamond formation from graphite.[14−17] In this context, it is extremely interesting to examine the interaction between graphitic BC_2N and H_2O, which will shed light on the behavior of a supercritical fluid in the B−C−N system.

Experimental Section

Preparation of the Graphitic BC_2N and HP/HT Treatments. Graphitic BC_2N was prepared by the CVD method between BCl_3 and CH_3CN, which has been described elsewhere,[2] and then annealed in a nitrogen gas flow at 1800 °C for 2 h to remove any volatile components.

The pulverized graphitic BC_2N (150 mg) was loaded in a Mo capsule at 600 MPa and then distilled water (10 μL) was dripped in by a microinjector. The water added corresponds to 6 wt % of the total system. The capsule was capped with Mo foil and disk and then put into a pressure cell, as shown in Figure 1. HP/HT treatments were carried out at 7.7 GPa and 800−2200 °C for 5−30 min using a modified belt-type high-pressure apparatus with a bore diameter of 32 mm.[18] The pressure and the temperature were calibrated as described elsewhere.[4] No reaction between the sample and the Mo capsule was observed under the conditions above.

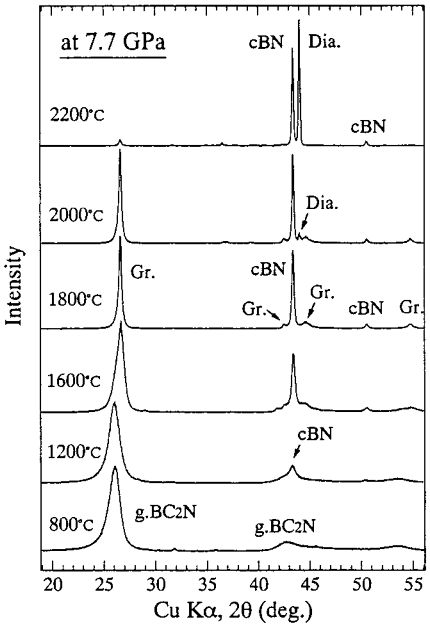

Figure 2. Powder XRD patterns of the products obtained from BC_2N-6 wt %H_2O at 7.7 GPa and various temperatures for 30 min.

Characterization. The recovered samples were identified by powder X-ray diffraction (XRD) with a Phillips PW-1800 type X-ray diffractometer with Cu Kα radiation.

The microscopic texture was examined using a Hitachi S-900 type scanning electron microscope (SEM) and a JEOL JEM-3000F type analytical transmission electron microscope (ATEM). The microanalysis for small specimens was performed by the combination of electron diffraction (ED) and electron energy loss spectroscopy (EELS).

Results

Dissolution of Graphitic BC_2N and Crystallization of Graphite and cBN. Figure 2 shows powder XRD patterns of the samples that were treated at 7.7 GPa and 800−2200 °C for 30 min. No change was observed below 800 °C but new diffraction peaks appeared above 1200 °C accompanied by a decline of the 001 reflection of graphitic BC_2N, suggesting that graphitic BC_2N reacted with H_2O. Note that without H_2O the graphitic BC_2N was not transformed up to 2000 °C at the same pressure.[4]

Above 1200 °C the new products were clearly identified as graphite and cBN (Figure 2). SEM and TEM images of the products at 1800 °C are shown in Figures 3 and 4, respectively. The product was a mixture of thin film-like crystals (“a” in Figure 4) and fine crystals (<100 nm) of triangular shape (“b”). ED patterns and EELS spectra (Figure 5) indicate that the crystal “a” is graphite on the basis of sp^2 carbon and a hexagonal structure. On the other hand, the crystal “b” reveals the composition of boron nitride with sp^3 bonding and has a diamond-like cubic structure, which is diagnostic of cBN.

The obtained graphite was undoubtedly crystallized from fluid because it was highly crystalline and the morphology was significantly different from that for the starting BC_2N. Its basal spacing (d_{002}) of $a = 0.3355$ nm is very close to that for well-crystallized graphite ($d_{002} = 0.3354$ nm).[19] Moreover, the crystallite size of the graphite, La > 60 nm and Lc > 40 nm, which was

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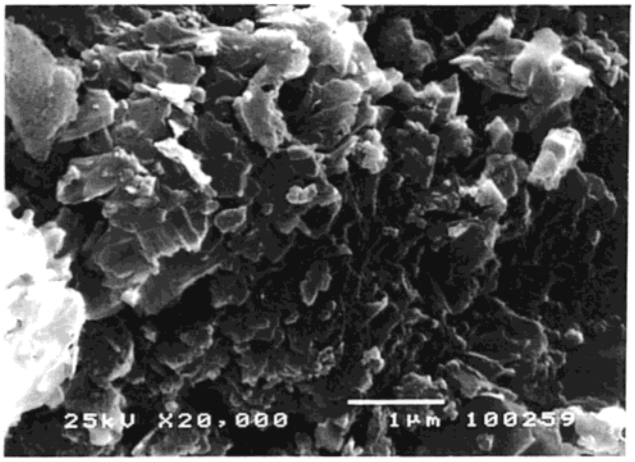

Figure 3. SEM image of the products obtained at 7.7 GPa and 1800 °C for 30 min.

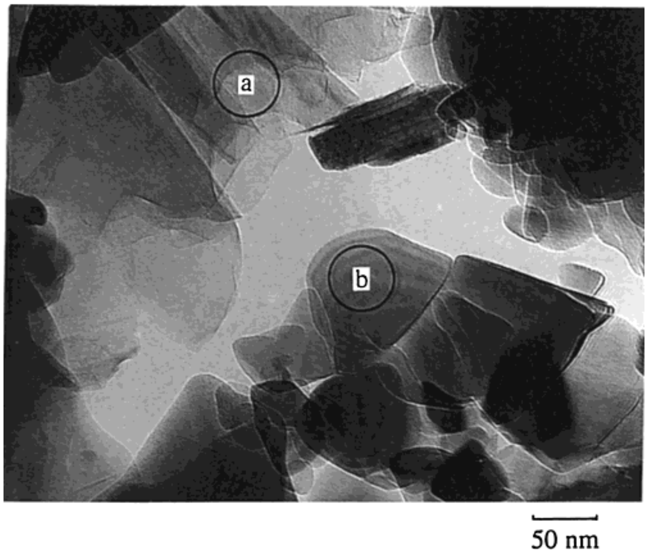

Figure 4. TEM image of the products obtained at 7.7 GPa and 1800 °C for 30 min.

calculated from a full width at half-maximum (fwhm) of XRD peaks, was comparable to that of graphite in spectroscopic grade. This high quality is in sharp contrast to the poor crystalline graphite ($d_{002} = 0.3440$ nm) formed by the solid-state decomposition of graphitic BC_4N at 6.6 GPa and 1400 K,[20] which is strong evidence for its formation from fluid.

The cBN crystal shape was similar to that synthesized from the hBN−H_2O system by Kobayashi,[10] which suggests the similar mechanism of cBN crystallization from the fluid produced by H_2O in both BC_2N−H_2O and hBN−H_2O systems.

Crystallization of Diamond. Above 2000 °C, diamond started to crystallize and its yield increased with increasing temperature (see Figure 2).

SEM and TEM micrographs of the products at 2200 °C (Figures 6 and 7) demonstrate that the products consist of large crystals with octahedral facets (>1 μm) and fine crystals of triangular shape (<300 nm). A diamond-like cubic structure was confirmed for both crystals by ED patterns (Figure 8). The larger crystals

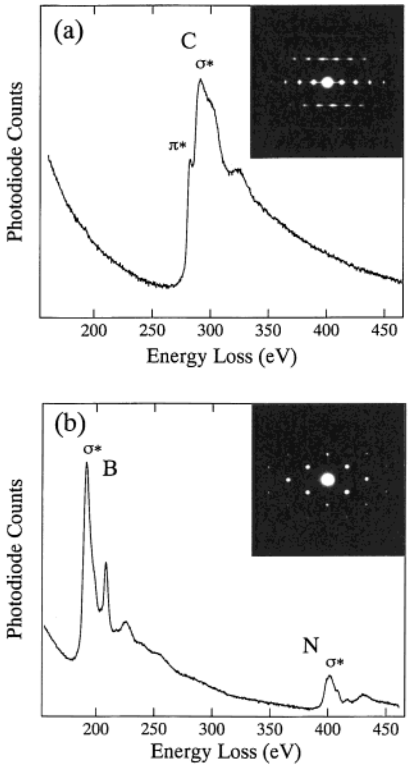

Figure 5. ED patterns and EELS spectra of the crystals obtained at 7.7 GPa and 1800 °C for 30 min. Figure (a) and (b) correspond to thin crystal (a) and triangle one (b) in Figure 4, respectively.

were identified as diamond and the fine ones as cBN by EELS spectra as shown in Figure 8a,b.

There are two possible reaction routes for the crystallization of diamond in the BC_2N−H_2O system at 7.7 GPa as described below: diamond was transformed from graphite, which has been already crystallized (eq 1), or diamond was crystallized directly in the decomposition of graphitic BC_2N (eq 2). To examine which is true, time

$$\text{graphitic } BC_2N \xrightarrow[(T \geq 1200\ °C)]{H_2O} \text{cBN} + \text{graphite} \xrightarrow[(T \geq 2000\ °C)]{H_2O} \text{cBN} + \text{diamond} \quad (1)$$

$$\left.\begin{array}{l} \text{graphitic } BC_2N \xrightarrow[(1200 \leq T \leq 1800\ °C)]{H_2O} \text{cBN} + \text{graphite} \\ \text{graphitic } BC_2N \xrightarrow[(T \geq 2000\ °C)]{H_2O} \text{cBN} + \text{diamond} \end{array}\right\} \quad (2)$$

dependence of the diamond formation was followed at 2200 °C. Figure 9 compares the products obtained at 7.7 GPa and 2200 °C for 5 and 30 min. This result clearly indicates that graphite was first crystallized in the decomposition of the BC_2N and then it was transformed to diamond, according to the reaction scheme in eq 1.

Discussion

Reactivity of Graphitic BC_2N with H_2O. The graphitic BC_2N was decomposed into graphite and cBN

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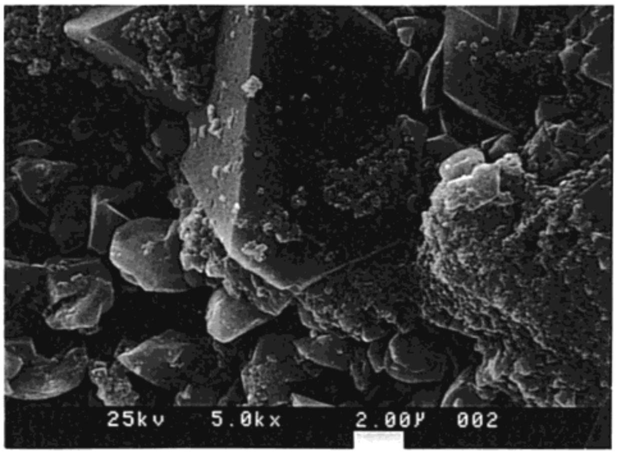

Figure 6. SEM image of the sample obtained at 7.7 GPa and 2200 °C for 30 min.

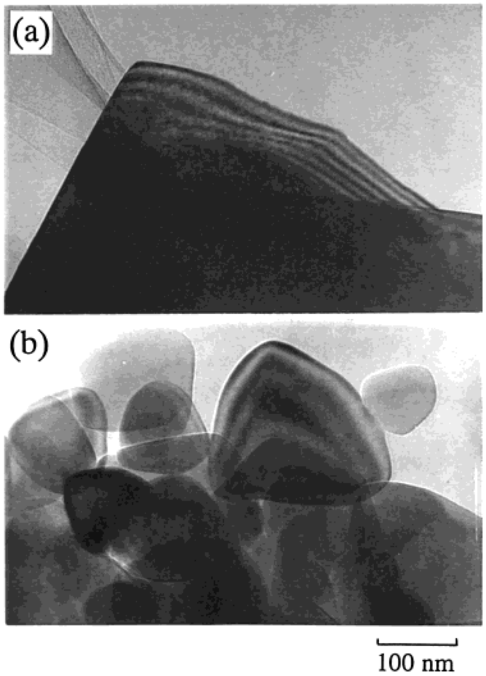

Figure 7. TEM images of the crystals obtained at 7.7 GPa and 2200 °C for 30 min. Figure (a) and (b) correspond to a larger crystal and a fine one in Figure 6, respectively.

at 1200 °C. The graphite was evidently crystallized from a fluid as mentioned above.

Considering recent reports on diamond formation from the C−O−H fluid,[15−17] it seems reasonable to assume that graphitic BC_2N reacted with H_2O to produce B−C−N−O−H supercritical fluid and graphite and cBN were precipitated from the fluid. However, we have no detailed information about the fluid component. To discuss the reaction mechanism in detail, an analysis of volatile components quenched in the capsule should be performed in the future.

The temperature of 1200 °C at which graphitic BC_2N started to react with H_2O is comparable to the reaction temperature of graphite with H_2O, which is estimated from the recrystallization behavior of graphite.[17] On the basis of previous work,[9] the reaction temperature of hBN with H_2O at 7.7 GPa should be lower than 600 °C, where hBN/cBN conversion temperatures were 1500 °C at 5 GPa and 600−700 °C at 6 GPa. Ultimately, the reactivity of graphitic BC_2N toward H_2O is similar to that of graphite rather than that of hBN.[21] This agrees with previously reported data on catalytic action of Co and Mg_3BN_3 solvents.[2]

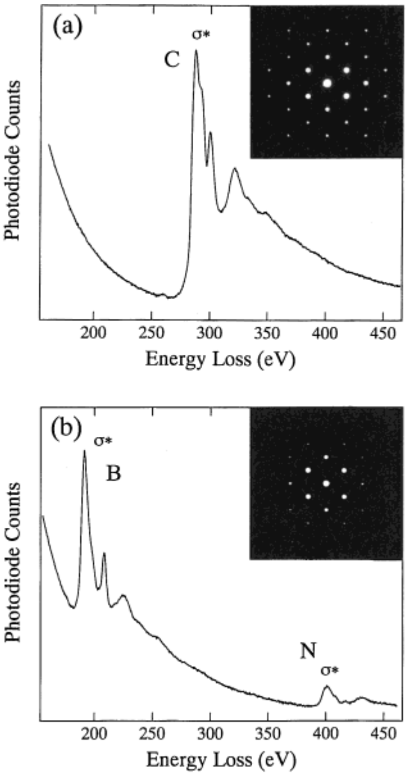

Figure 8. ED patterns and EELS spectra of the crystals obtained at 7.7 GPa and 2200 °C for 30 min. Figure (a) and (b) correspond to a larger crystal (a) and a fine one (b) in Figure 7, respectively.

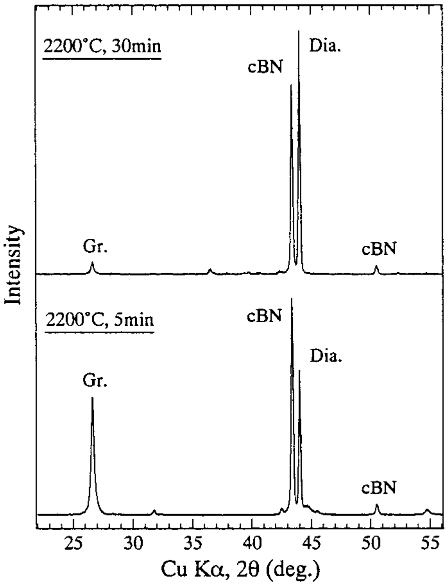

Figure 9. Powder XRD patterns of the products obtained from BC_2N-6 wt %H_2O at 7.7 GPa and 2200 °C for 5 and 30 min.

Crystallization of Graphite in the Diamond Stable Region. It is not clear why graphite was synthesized at the HP/HT conditions where diamond is thermodynamically stable. Previously, similar phenomena have been reported in C−H_2O and C−Cu systems.[17,22] The results suggest that graphite could be precipitated from the solutions at relatively low temperatures, even in the diamond stable region. The crystallization of graphite from the BC_2N-H_2O system in the present study is parallel to these data.

These results that graphite is crystallized even at the diamond stable conditions may be explained by a kinetic cause. Akaishi and Yamaoka[15] have reported that diamond formation temperature from C−O−H fluid at 7.7 GPa became lower with increasing duration time of HP/HT conditions. They found diamond formation as low as 1400 °C for the long duration time of 360 h while a much higher temperature of >2000 °C was needed when the duration was limited to 30 min. This implies an unexpectedly high energy barrier for diamond crystallization, even at the diamond stable conditions, which might suppress diamond formation kinetically from fluids or solvents particularly in the low-temperature region.

Crystallization Mechanism of Cubic Products in the BC_2N-H_2O System. As mentioned above, it is most likely that cBN crystals were crystallized from the BC_2N-H_2O system in the manner similar to that of the $hBN-H_2O$ system. Then, diamond was crystallized from graphite, which had been formed with cBN in advance (see eq 1). Another interesting question is the influence of cBN crystals on the crystallization of diamond: whether the diamond was spontaneously crystallized from the graphite in the fluid or heterogeneously grown on the cBN crystals.

If the diamond was grown on cBN crystals, boron and nitrogen should be detected in the EELS spectrum. However, the confirmation was difficult in the present observations because analyses could be performed only in thin edge parts of the large diamond crystals.

It is noteworthy that, at the same pressure (7.7 GPa) for the same duration (30 min), diamond has been crystallized spontaneously from the C−O−H fluid[14−17] without cBN above 2000 °C, which agrees with the present temperature where diamond was obtained from the BC_2N-H_2O system. It strongly suggests that diamond formation from BC_2N-H_2O could take place in the same manner as that from $C-H_2O$, and that, in other words, diamond could be crystallized spontaneously in the BC_2N-H_2O system regardless of cBN crystals.

Conclusions

Water was found to be an effective agent for transformation of graphitic BC_2N into diamond-like cubic forms. The reactivity is similar to that of graphite rather than hBN. BC_2N was dissolved above 1200 °C into HP/HT fluid and precipitated as carbon and boron nitride separately. In the temperature range of 1200−1800 °C, graphite was formed with cBN, even at the diamond stable conditions. Above 2000 °C, graphite was transformed into diamond. These precipitation behaviors of the cubic forms in the BC_2N-H_2O system can be understood as the simple sum of the precipitation behavior in graphite$-H_2O$ and that in $hBN-H_2O$.

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(21) Susa et al.[9] and Kobayashi[10] have added maximum 40 wt % water to hBN and loaded them directly into a cylindrical graphite heater without a capsule (this assembly might lose the water easily during HP/HT treatment). Hong et al.[14] have added 10 wt % water to graphite in the Mo capsule for diamond synthesis. Their water contents are higher than that of the present experiment. Strictly speaking, it is difficult to compare the present reaction temperature with others because the reactivity possibly depends on the content of water and sealing ability of the capsule used. Nevertheless, the reaction temperature of hBN with H_2O by Susa et al. and Kobayashi is obviously lower than that of graphitic BC_2N. On the other hand, the reaction temperature of graphite with H_2O by Hong et al. is identical to the present.

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