Synthesis of Cubic Boron Nitride by Al-Mg Solvents

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The aluminum-magnesium (Al-Mg) alloys have been proved to be an effective solvent for synthesis of cubic-phase boron nitride (cBN) from hexagonal-phase boron nitride (hBN) at the conditions of high pressures and high temperatures (HP/HT). Various kinds of hBN powders having different crystallinity have been tested for cBN synthesis with Al-Mg solvents. The conversion ratio from hBN to cBN and the shape of synthesized cBN crystals appeared to be affected strongly by chemical composition and added amount of Al-Mg solvents as well as crystallinity of BN powders. As the magnesium content increased in the Al-Mg solvents, the conversion ratio increased and the size of cBN crystals became larger. The crystal facets developed well in the specimens with solvents having high Mg content. It was observed that a hBN→cBN transformation occurred more easily in the specimens having well crystallized hBN powders. Amorphous BN having much B_2O_3 impurity exhibited a low threshold temperature for transformation to cBN, which was attributed to crystallization of amorphous BN to well crystallized hBN prior to transformation into cBN with help of B_2O_3.

Key words : Cubic borom nitride, High pressure & high temperature, Solvent, Al-Mg

I. Introduction

Cubic boron nitride (cBN) is an excellent superabrasive material next to diamond in hardness and superior to diamond in machining the various iron group metals such as hardened steels, cast irons and Ni-/Co-base superalloys. The cBN is synthesized from hBN at HP/HT conditions either directly without any solvent (catalyst) or indirectly with various kinds of solvents selected from alkali or alkaline earth metals or their nitrides such as Li_3N, Mg_3N_2 and Ca_3N_2.[1-5] The effects of solvent materials as well as crystallinity of raw hBN materials on the transformation kinetics and on the synthesized crystal quality have been studied.[6-9] In most of solvents, their strong chemical affinity to moisture and oxygen is a crucial issue to have to be overcome in developing a new solvent material.

Various metallic solvents having relatively low chemical affinity to moisture and oxygen have been developed but they had another problem of reduced catalytic effectiveness.[1,10-12] Therefore the metallic solvents have not been applied to the cBN synthesis yet. Recently Al-Mg alloy solvents were developed, which were proved to have several advantages such as strong catalytic effectiveness, high chemical inertness against moisture and oxygen, and easily controllable catalytic effectiveness.[13,14]

The cBN synthesis process is known to depend closely on the crystallinity of BN materials. The purposes of present study are to synthesize various cBN crystals with Al-Mg solvents and to investigate an effect of hBN crystallinity on cBN synthesis in the presence of Al-Mg solvent at the conditions of high pressures and high temperatures.

II. Experimental Method

Three kinds of Al-Mg alloy compounds were used as the solvents for cBN synthesis, of which preparation method was introduced in Refs. 13 and 14, and their respective compositions were 66Al-34Mg, 50Al-50Mg, and 40Al-60Mg by weight fraction. Three kinds of hBN powders were used as raw materials for cBN synthesis: well crystallized hBN powder with little B_2O_3 (GP-1 grade, Denki Kagaku Kogyo company) (hereafter called as 'GP' powder) and amorphous BN powder with much B_2O_3 (hereafter called as 'ABO' powder) or amorphous BN powder with little B_2O_3 (hereafter called as 'AB' powder). The amorphous BN powders were made by heat-treating a mixture of boric acid and urea by a ratio of $1:2$ at 850°C for 3 h under flowing nitrogen and subsequently by washing in distilled water several times and finally in ethanol for removing residual B_2O_3. The crystallinities of the BN powders were investigated by X-ray diffraction method (XRD).

The hBN powder was mixed homogeneously with Al-Mg solvent powder and the solvent content in the mixture was fixed to 5% by weight for determining an effect of hBN crystallinity on cBN synthesis. The amorphous

BN powders were degassed in a vacuum furnace at 1000°C for 10 h. The powder mixture was compacted into the cylindrical disks of 7 mm in diameter and about 4 mm in height and two compacts were charged into a high pressure reaction cell. The reaction cell was subjected to high pressures above 40 kb and high temperatures for less than 30 minutes. The morphology of cBN crystals was observed after removing untransformed hBN in the specimens.

III. Results and Discussion

1. Effect of BN powders on the threshold P-T conditions for hBN → cBN transformation

Figure 1 shows the XRD patterns of three kinds of BN powders. Fig. 1(a) is a XRD pattern from as-received ABO powder synthesized from the mixture of urea and boric acid by the ratio of 2:1. Many extra-peaks indicated by asterisks in Fig. 1(a) show that it contains much B_2O_3 impurity. Fig. 1(b) shows a XRD pattern from AB powder, which is obtained by washing the ABO powder several times in the distilled water and degassed in vacuum at 1000°C for 10 h. B_2O_3 impurity was removed almost completely. The amorphous BN was slightly crystallized during degassing. Fig. 1(c) is a XRD pattern from GP powder.

Figure 2 shows a cBN synthesis region obtained from the mixture of AB powder and 5 wt.% (40Al-60Mg) solvent, when the specimens were subjected to each HP/HT condition for 10 minutes. The threshold temperature and pressure for hBN → cBN transformation were 1300°C and 42 kb, respectively. The AB powder exhibited a slightly higher threshold temperature than a well crystallized GP powder.[14] The threshold temperature and pressure for transformation of GP powder into cBN were reported as 1260°C and 42 kb, respectively.[14] This is well agreed that
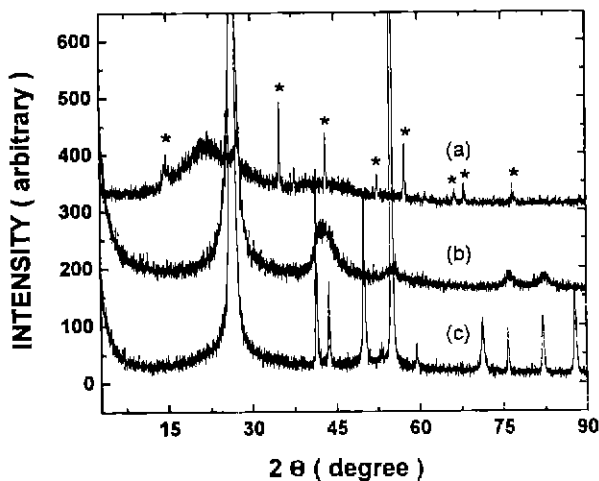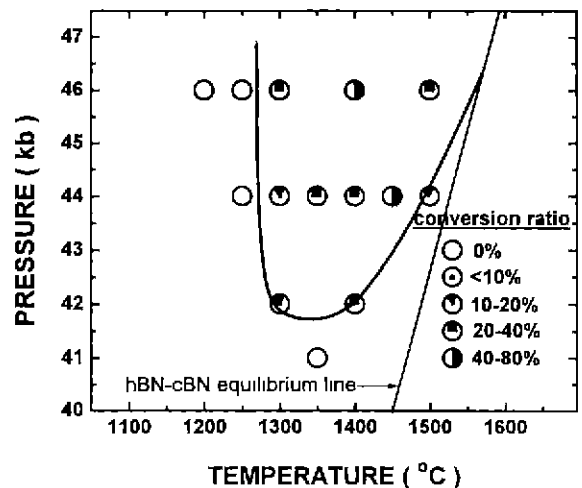

Fig. 2. The P-T diagram showing dBN synthesis region from AB powder with 5% (40Al-60Mg) solvent (Holding time at each synthesis condition was fixed to minutes)
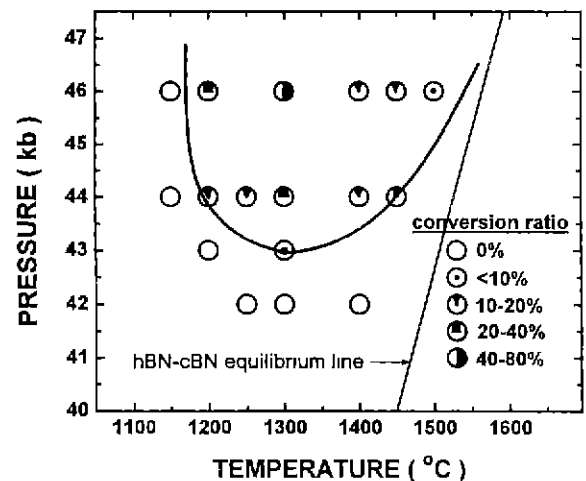

Fig. 3. The P-T diagram showing cBN synthesis region from ABO powder with 5% (40Al-60Mg) solvent (Holding time at each synthesis condition was fixed to 10 minutes).

a hBN powder having relatively high crystallinity shows a lower transformation temperature than the hBN powder with poor crystallinity in the absence of B_2O_3.

A cBN synthesis region obtained from the APO powder at the same condition with Fig. 2, is shown in Fig. 3. The threshold temperature and pressure required for cBN synthesis were 1200°C and about 43 kb, respectively. Compared with a threshold temperature obtained from the AB powder, the threshold temperature for cBN synthesis from ABO powder was lowered considerably by about 100°C. Contrary to threshold temperature for cBN synthesis, threshold pressure increased slightly by B_2O_3. The B_2O_3 impurity in the ABO powder appears to assist crystallization of amorphous BN prior to transformation to cBN at HP/HT conditions.

2. Effect of solvent compositions on the cBN synthesis

Fig. 1. The XRD patterns of BN powders used for dBN synthesis: (a) amorphous BN powder with much B_2O_3 (ABO powder), (b) amorphous BN powder without B_2O_3 (AB powder), and (c) well crystallized BN powder (GP powder).
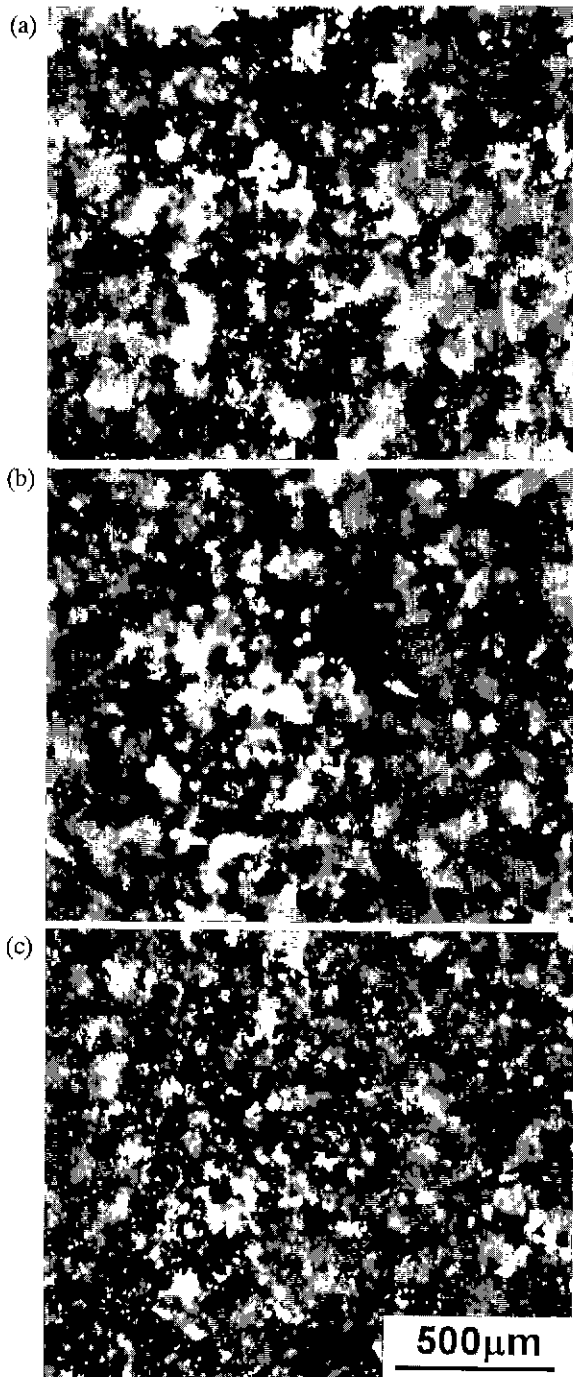
Fig. 4. Optical micrographs of fracture surfaces of the specimens treated at 50 kb and 1300°C for 30 minutes with 5% solvent: (a) 66Al-34Mg, (b) 50Al-50Mg and (c) 40Al-60Mg.

Fig. 5. Morphologies of cBN crystals synthesized with Al-Mg solvents: (a) 66Al-34Mg, (b) 50Al-50Mg and (c) 40Al-60Mg.

As the Mg content in Al-Mg solvents varied from 34% to 60%, the transformed amount of hBN into cBN increased considerably but it was not estimated quantitatively. Figure 4 shows the fracture surfaces of the specimens treated at 50 kb and 1380°C for 30 minutes, respectively. The black and gray phase is a cBN phase and the white area is a residual hBN phase.

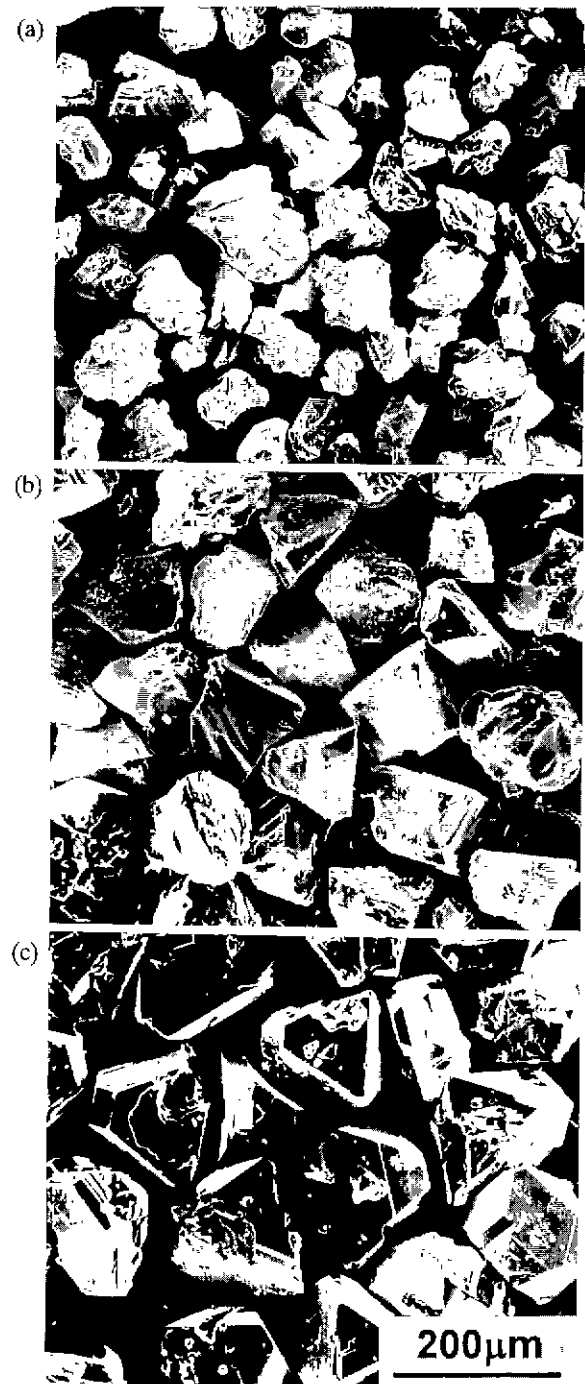The Mg content in the solvents affected strongly the morphology of cBN crystals. The shape of cBN crystals

obtained with 66Al-34Mg solvent are very irregular while the cBN crystals have a faceted shape in the specimens having 40Al-60Mg solvent. In addition to crystal shape, the Mg content affected the cBN crystal size (Fig. 5). As the Mg content increases from 34% to 60% in the Al-Mg solvent, the synthesized cBN crystal size increases several times.

Magnesium is well known as a strong solvent material for cBN synthesis. Aluminum is not a solvent in a pure

state but it can have a catalytic effect, because the cBN tools react catalytically with aluminum alloys and transform to cBN during machining. Here, it appears that aluminum does not deteriorate much the catalytic effect of Mg. A role of aluminum in the Al-Mg solvents should be investigated further, whether it acts as a solvent or as a simple diluent.

IV. Conclusions

The effects of crystallinity of hBN materials to B_2O_3 content in the amorphous BN powders on the cBN synthesis region were determined with 40Al-60Mg solvent. The hBN powder with high crystallinity (GP powder) exhibited a lower threshold temperature than the amorphous BN powder with little B_2O_3 (AB powder). The amorphous BN powder with much B_2O_3 (ABO powder) showed a threshold temperature much lower than the amorphous BN powder with little B_2O_3 (AB powder). The B_2O_3 impurity in the amorphous BN powder appeared to enhance a crystallization of amorphous BN into well crystallized BN (hBN) prior to transformation to cBN at HP/HT conditions.

The conversion ratio from hBN to cBN and the morphology of cBN crystals depended strongly on the Mg content in the Al-Mg solvents. As the Mg content in the Al-Mg solvents increased, the conversion ratio increased and the crystal facets developed well. A role of aluminum in the Al-Mg solvents on the cBN synthesis could not be elucidated in the present study.

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