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Effect of oxygen on the growth of cubic boron nitride using Mg_3N_2 as catalyst

TADAO SATO, HIDEO HIRAOKA,* TADASHI ENDO,
OSAMU FUKUNAGA, MINORU IWATA
National Institute for Researches in Inorganic Materials, 1-1 Namiki, Sakura, Niihari, Ibaraki 305, Japan

Cubic boron nitride (cBN) was synthesized from hexagonal boron nitride (hBN) under high pressure and high temperature using Mg_3N_2 as catalyst. The yield and morphology of cBN were investigated in relation to the oxygen impurity of the BN–Mg_3N_2 system. Magnesium oxide precipitated as a by-product in this system and the amount of the precipitate increased with an increase in the oxygen content of the starting materials. The morphology and surface patterns of cBN crystals synthesized using an hBN which contained oxygen showed unusual features. It was confirmed that the precipitation of MgO interfered with the free growth of cBN crystals. Purification of starting materials and addition of zirconium powder to the catalyst as an oxygen getter increased the yield of cBN crystals showing smooth surfaces.

1. Introduction

Cubic boron nitride (cBN) is a super-hard material which is an excellent abrasive for steels. It is synthesized under high pressures (P) and high temperatures (T) in the presence of a catalytic solvent. Graphite-like hexagonal boron nitride (hBN) is generally used as a starting material to obtain cBN. Common catalytic solvents for the synthesis of cBN are alkalis and alkaline earth metals and their nitrides such as Li, Mg, Ca, Li_3N, Mg_3N_2 and Ca_3N_2.

Wentorf [1] has pointed out that the activity of some of these catalysts is greatly reduced by the presence of a few per cent of boric oxide in the starting materials. This suggests that the catalyst reacts with oxygen in the formation process of cBN. Hexagonal BN is produced by reduction of boric oxide or borax followed by reaction with nitrogen. This process tends to leave a boric oxide residue in the product because the reaction of boric oxide is hindered by the formation of glassy layers of boric oxide which covers the surface of the reactant in the heating process.

For this reason, commercial powders or hot-pressed samples of hBN contain oxygen. Alkaline earth metals or their nitrides are reactive with atmospheric moisture and easily form alkaline earth hydroxides. It is considered that the oxygen impurity affects the growth of cBN.

This study was carried out to clarify the effect that oxygen has on the formation of cBN in the BN–Mg_3N_2 system.

The result of the study enables us to estimate the amount of oxygen in the starting materials by observing the cBN crystals under optical and scanning electron microscopes.

2. Experimental procedure

2.1. Starting materials

Hexagonal BN samples used in the experiments are listed in Table I. Their graphitization indices [2] were measured by analysis of the peak profile of their X-ray diffraction patterns. The oxygen content of these hBN were determined by fast neutron radio activation analysis. Magnesium nitride was synthesized by heating magnesium metal under a nitrogen stream at 800° C for 3 h and was stored in glass ampoules to prevent reaction with moisture in the air.

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*Present address: Central Research Laboratory, Denka Ltd, Machida, Tokyo.

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TABLE I hBN used for the synthesis of cBN

hBN	Form*	GI†	Oxygen	Remarks
DAP	P	(T)	24.1 wt%	–
DAP-1800	P	(P)	0.3	DAP baked at 1800° C
DGP	P	1.5	0.5	–
DGP-1800	P	1.5	0.2	DGP baked at 1800° C
DGP-Mg	P	1.5	–	DGP treated with Mg
SHPL	P	–	–	–
SS-Mg	P	–	–	SS treated with Mg
DNI	H	1.7	7.9	–
DR	H	1.6	1.9	–
DHC	H	1.6	8.8	Containing CaO
SS	H	8.5	4.0	–

*P: powder, H: hot-pressed.

†GI: graphitization index for hBN [2] which increased with degree of disordering. (T): turbostratic, (P): partial three-dimensional ordering.

2.2. High pressure and high temperature experiment

The experiments were carried out using a belt apparatus [3]. The reaction chamber assembly is shown in Fig. 1. At the centre of the reaction chamber, Mg_3N_2 powder was compacted in an hBN sleeve. Discs of hBN were packed in at both ends of the catalyst. The sleeve and discs of hBN were the starting material for the synthesis of cBN.

Fig. 2 shows the pressure–temperature region for the synthesis of cBN in the BN–Mg_3N_2 system [4]. Synthesis of cBN in the study was mainly carried out at about 57 kbar and 1340° C for 30 min.

Calibration of the temperature and pressure in the cell were carried out using hBN dummy cells.

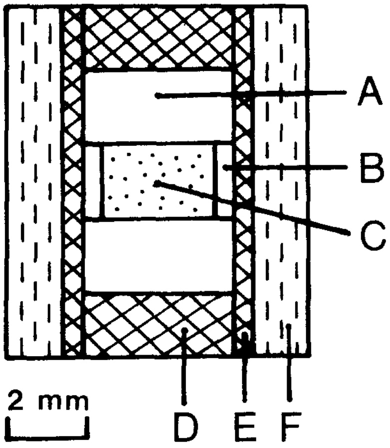

Figure 1 The reaction chamber, A: hBN disc or powder, B: hBN cylinder, C: Mg_3N_2 catalyst, D: graphite disc, E: graphite heater and F: pyrophylite sleeve.

The pressure calibration was made at room temperature by detection of changes in electrical resistance of Bi, Ba and Sn placed in the cell. Points of sharp change in the resistance with pressure (25.5 and 77 kbar in Bi, 55 and 120 kbar in Ba and 90 kbar in Sn) were adopted as fixed points in the pressure calibration.

The temperature in the reaction cell was estimated from the relation between temperature and electrical power supplied to the heater. The temperature was kept within ± 30° C up to 1500° C at a given pressure. The pressure effect of emf of the thermocouple was ignored. After high pressure and high temperature treatment, the samples were quenched and examined by X-ray diffraction to identify the products. Residual catalyst and hBN were removed by treating first with hydrochloric acid, followed by a mixture of sodium fluoride and sulphuric acid.

Cubic BN so obtained was observed by scanning electron microscopy and optical microscopy.

3. Results and discussion

3.1. Yield of cBN

Details of the results are listed in Table II where the oxygen content of hBN, pressure–temperature conditions and yield of cBN are shown. When hBN with a low oxygen content was used as the starting material, the cBN yield was high. Fig. 3a shows typical features of a sample prepared from hBN with a high oxygen content (SS, oxygen 4.0%). Yellow coloured crystals of cBN were seen along the margin of the sample. Magnesium oxide was precipitated at the centre of the sample where catalyst had been placed. The yield of cBN was poor in this case.

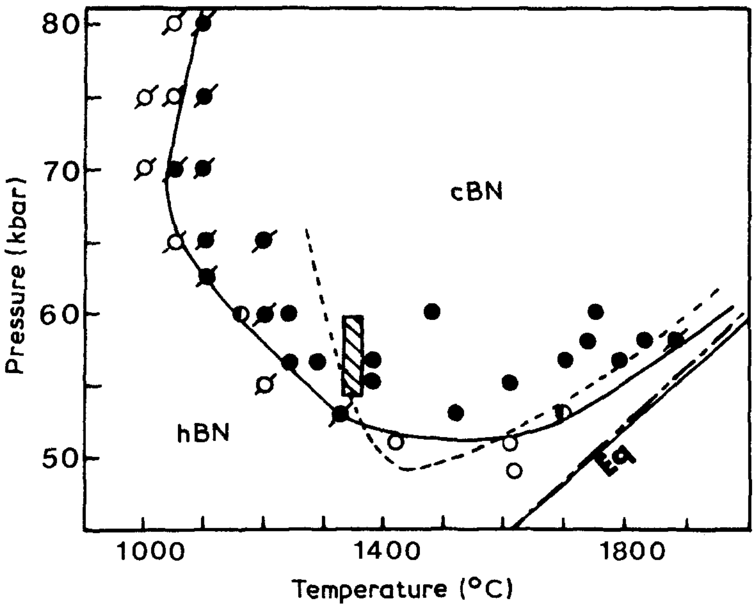

Figure 2 Pressure–temperature conditions for the synthesis of cBN in the $BN–Mg_3N_2$ system. o: SS was used as the starting material, ø: DNI was used as the starting material, closed circle: cBN was produced, open circle: no cBN was produced. —·— Wentorf [1], – – – – DeVries and Fleischer [6], $\overline{\text{Eq}}$ equilibrium line between hBN and cBN, ▨ main region for this experiment.

Endo *et al.* [5] reported that the lower temperature limit for the synthesis of cBN was markedly raised from 1400 to 1700° C with an increase of oxygen content of hBN when magnesium metal was used as the catalyst. On the other hand, in the $BN–Mg_3N_2$ system, the oxygen had little influence on the lower limit of the pressure and temperature values. Fig. 2 shows the $P–T$ region in the $BN–Mg_3N_2$ system using hBN with different oxygen contents (SS, oxygen 4.0%, and DNI, 7.9%). As shown in Fig. 2, synthesis of cBN was carried out effectively in the central region of the $P–T$ limit; so the effect of oxygen on the yield of cBN was not attributed to the shift of the lower limit of synthesis.

It was considered that the yield of cBN may increase on heating hBN to remove the oxygen impurity. Two simple treatments were carried out on the hBN starting material to decrease the oxygen content. An hBN powder (DAP) was heated at 1800° C in a nitrogen gas stream for 2 h. This material was designated DAP-1800. The results using DAP-1800 shows an increase in the intensity of the X-ray diffraction lines in cBN. The sample SS–Mg (designated in Table I) was prepared by the following process; hBN (SS) rods

TABLE II Yield of cBN from various starting materials and the pressure–temperature conditions

Sample number	hBN starting material	Oxygen content of the hBN (wt %)	P (kbar)	T (° C)	Yield*	Remarks
48	DAP	24.1	60	1890	+	–
19	DGP	0.5	57	1340	++	–
45	DGP	0.5	58	1340	++	–
46	DGP	0.5	60	1890	++++	Encapsulated with Zr foil
32	DGP	0.5	60	1330	++++	Mixed with Zr powder
42	DAP-1800	0.3	60	1340	++	–
43	DGP-1800	0.2	60	1340	++	–
41	DGP-Mg		60	1340	++++	–
47	SHPL		60	1340	++	–
23	SS-Mg		57	1340	++++	–
17	DNI	7.9	53	1330	++	–
24	DHC	8.8	57	1340	++	–
12	SS	4.0	57	1300	++	–
14	SS	4.0	57	1390	++	–
25	SS	4.0	60	1240	++	–
10	SS	4.0	57	1700	++	–

*+: trace of cBN; ++: ~ 30% cBN; and ++++: > 80% cBN.

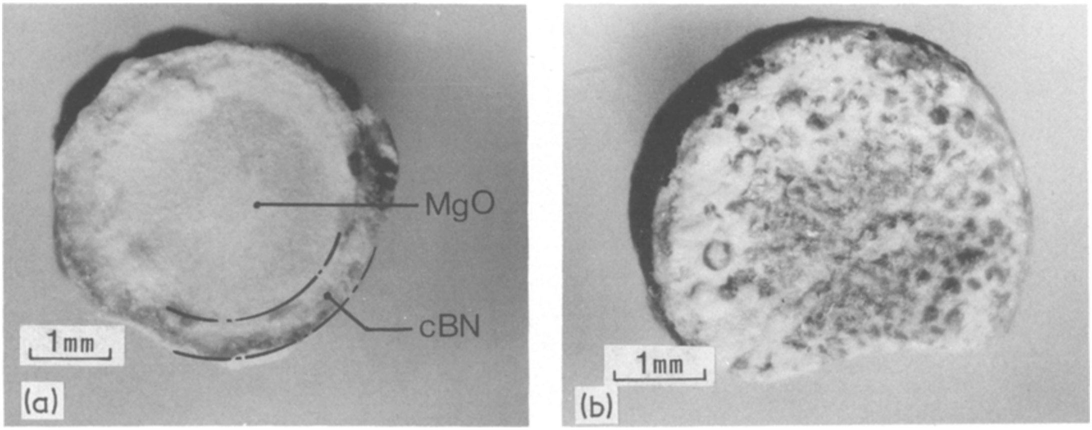

Figure 3 Cross-sections of the reacted samples: (a) No. 10 (SS, 57 kbar, 1700° C). cBN crystals are seen at the margin, and (b) No. 23 (SS-Mg, 57 kbar, 1340° C). cBN crystals are seen all over the lump.

were crushed and mixed with pieces of magnesium metal, the mixture was heated at 800° C in a nitrogen gas stream for 2 h, the product was leached in hydrochloric acid and hBN powder SS–Mg was obtained by filtration. The following reaction probably occurred during this process,

$$B_2O_3 + 3Mg + N_2 = 3MgO + 2BN. \quad (1)$$

The magnesium oxide was dissolved in the hydrochloric acid.

X-ray diffraction patterns in Fig. 4 show the existence of MgO and cBN in the samples prepared from hBN, SS (Fig. 4a) and SS–Mg (Fig. 4b). The ratio of the intensity of the X-ray diffraction peak of cBN to that of MgO was increased by the pretreatment of hBN. The pretreatment for reducing the oxygen content of hBN was effective in increasing the yield of cBN and decreasing the amount of MgO precipitated.

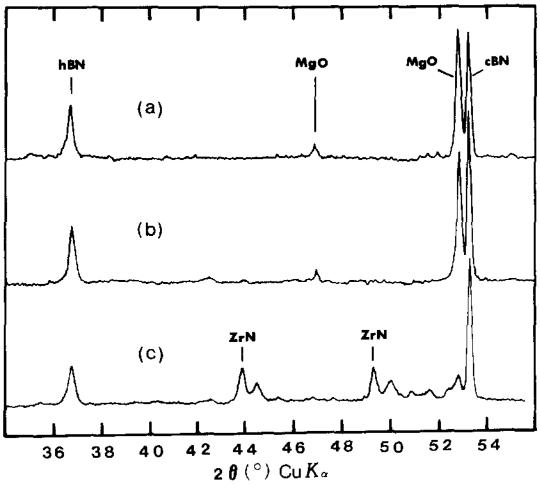

Figure 4 X-ray diffraction patterns of the products: (a): No. 25 (SS, 60 kbar, 1240° C), (b): No. 23 (SS–Mg, 57 kbar, 1340° C) and (c): No. 32 (DGP mixed with Zr powder, 60 kbar, 1330° C).

The best result was obtained by mixing zirconium metal powder with magnesium nitride catalyst, 30 to 50 wt %. Fig. 3b shows the sample prepared using the catalyst $Mg_3N_2 + Zr$. Cubic BN was precipitated over all the sample, and a remarkable decrease in the intensity of MgO was obvious, as seen in Fig. 4c.

The summarized results in Table II shows a strong relation between the yield of cBN and the amount of oxygen contained in the hBN starting material.

3.2. Morphology and surface patterns

In this study it was noted that many unusual cBN crystal morphologies appeared, especially, in the samples made from hBN with a high oxygen content. Some of them were modified tetrahedrons (or octahedrons) which were composed of a set of circular smooth faces belonging to a tetrahedral form $\{1\,1\,1\}$ or $\{\bar{1}\,\bar{1}\,\bar{1}\}$ surrounded by rough surfaces composed of small facets of tetrahedral forms often with round edges (Fig. 5a). In extraordinary cases, these smooth circular faces formed a large spiral-like shape as shown in Fig. 5b.

These abnormal morphologies were rarely observed in the sample obtained from hBN with a low oxygen content (Fig. 5c). Fig. 5d shows cBN crystals synthesized in a BN–Li_3N system, using hBN with a high oxygen content (SS, oxygen 4.0%), in which tetrahedrons and octahedrons with acute corners and sharp edges are seen. The abnormal

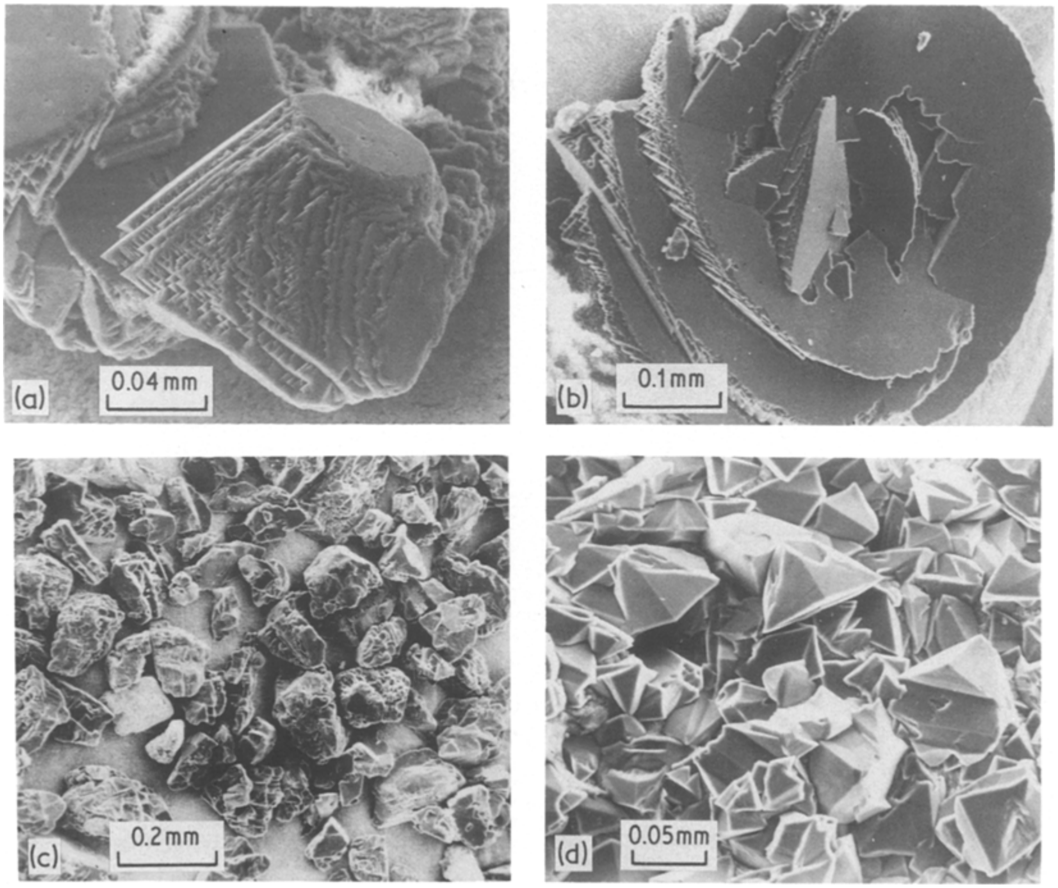

Figure 5 Morphologies of cBN crystals obtained from various starting materials (SEM photograph): (a) No. 17 (DNI, 53 kbar, 1330° C), (b) No. 16 (DNI, 57 kbar, 1340° C), (c) No. 46 (DGP encapsulated with Zr foil, 60 kbar, 1890° C) and (d) prepared in a BN–Li_3N system.

morphologies in the BN–Mg_3N_2 system was caused by the co-existence of magnesium and oxygen.

It is considered that cBN crystals precipitated from a liquid phase saturated with BN in the BN–Mg_3N_2 system. The most probable component of the liquid is $Mg_3B_2N_4$ [6]. The liquid easily reacts with boric oxide

$$Mg_3B_2N_4 + B_2O_3 = 3MgO + 4BN.$$

The growth of cBN in the BN–Mg_3N_2 system begins with the precipitation of MgO; hBN is dissolved in liquid $Mg_3B_2N_4$; and the cBN precipitates from the solution saturated by BN. As the cBN crystals grow, magnesium oxide is pushed out from the growth front of the cBN and accumulates around the surface. As a result of the surrounding MgO, the growth rate of the cBN crystal may become isotropic. Thus, the acute corners and sharp edges of the tetrahedron (or octahedron) may be replaced by rough surfaces and the triangular flat faces become circular faces.

Many tetragonal pits were observed on the surface of the cBN crystals under a scanning electron microscope and an optical microscope as shown in Fig. 6a. No relation between the orientation of the pits and the crystal direction of cBN was found. These pits remarkably decreased in number and size on reducing the oxygen content of the starting hBN material (Fig. 6b). The size of the pits ranged from 1.5 (run No. 17) to 0.3 μm (run No. 23) in diameter. No such pits were found on the cBN crystals in run No. 32 in which zirconium was used as an oxygen getter. The tetragonal pits were not observed on the cBN crystals synthesized in the BN–Li_3N system. The tetragonal pits were also related to the formation of MgO during the growth of cBN crystals. It is probable that the tetragonal pits were the marks of MgO crystals which were precipitated during

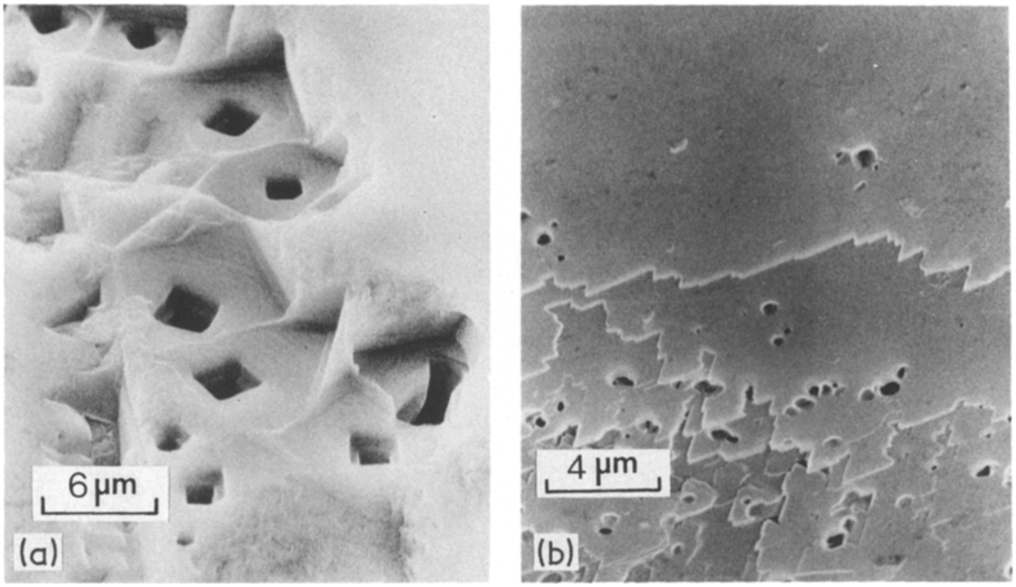

Figure 6 Pits on the surface of the cBN crystals (SEM photographs): (a) No. 17 (DNI, 53 kbar, 1330° C) and (b) No. 32 (DGP mixed with Zr powder, 60 kbar, 1330° C).

the process and were trapped on the surface of the cBN crystal.

4. Conclusions

In this experiment cBN was prepared in the BN–Mg_3N_2 system with hBN starting material containing various amounts of oxygen. Magnesium oxide was precipitated in the process. Reducing the oxygen content of hBN by heating it in a nitrogen gas stream or heating it with magnesium metal, resulted in an increase in the yield of cBN. Mixing of metal zirconium powder into Mg_3N_2 was another effective technique for increasing the yield of cBN.

Abnormal morphologies of the cBN crystals and small tetragonal pits on the crystal surface appeared in the BN–Mg_3N_2 system, when hBN with a high oxygen content was used. From observations of crystal morphology and the size of the pits on the surface, the oxygen content of the hBN starting material can be estimated.

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