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Effects of added c-BN seed crystals on the reaction sintering of c-BN accompanied by a conversion from h-BN to c-BN

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Reaction sintering behaviour of c-BN which is accompanied by a conversion from h-BN to c-BN was investigated under high pressure (7 GPa) and temperature (1700° C) conditions for 30 to 60 min. A high conversion yield of c-BN in the sintered compact was attained by adding fine-grained c-BN seed crystals (particle size 0.5 to 8 μm) to h-BN powder in the presence of 1 wt% NH_4NO_3 as a catalyst. An induced transformation from h-BN to c-BN occurs over a large surface area of c-BN seed crystals, which results in the formation of direct interparticle bonding between c-BN grains in the sintered compact. A fully dense sintered compact of c-BN (bulk density 98% theoretical) was obtained from the specimen of 70 wt% h-BN with 30 wt% added c-BN crystals having a particle size of 0.5 μm. This c-BN compact had an average microhardness of 5100 kg mm^{-2} and a specific dielectric constant of 10.0 at a frequency of 1 MHz.

1. Introduction

Cubic BN (c-BN) was synthesized by Hirano *et al.* [1–4] from hexagonal BN (h-BN) in the presence of AlN as a catalyst at temperatures above 1000° C and pressures above 5.5 GPa. A fully dense sintered compact of the c-BN (80 mol %)–AlN (20 mol %) system was prepared with a complete conversion from h-BN or amorphous BN (a-BN) to c-BN and an accompanied sintering under 6.5 GPa at temperatures higher than 1400° C [2–4]. AlN was found to serve as a catalyst-substrate for the solid state epitaxial growth of c-BN [4].

On the other hand, an analogous epitaxial growth of c-BN on to c-BN seed crystals was observed by treating h-BN powder in the presence of 30 wt % c-BN powder at 7 GPa and 1700° C for 30 min [5]. An induced transformation from h-BN to c-BN was greatly affected by an ambient pretreatment of the starting powder in a hydrogen and nitrogen stream. In the present work, the effects of the added c-BN seed crystals with various surface areas on the epitaxial growth and reaction sintering behaviour of c-BN was investigated and correlated to the evaluation of the microhardness and dielectric properties of the sintered compact.

2. Experimental procedure

Fig. 1 shows the experimental procedure for high pressure reaction sintering of c-BN. Commercially available h-BN powder (Denki Kagaku Kogyo Co.; purity > 99.9%, grain size 1 to 5 μm) and c-BN powder (General Electric Co.; purity > 99%, average grain size 0.5, 8, 25 and 42 μm) were used as starting powders. These mixed powders of various compositions were vacuum-treated at 600° C for 60 min. Subsequently, they were pretreated at 1000° C for 60 min in a stream of H_2 + N_2 (1 : 1) under a pressure of 1 atm [5]. 1 wt % ammonium nitrate (NH_4NO_3) was added as a volatile catalyst to the pretreated powder. This assorted powder was packed into a specimen cell and treated at 7 GPa and 1700° C for 30 to 60 min in a girdle-type high-pressure apparatus. Fig. 2 shows a typical cell assembly of the girdle-type high-pressure apparatus. The pressure and temperature calibrations were carried out in the same manner as in previous papers [1, 4, 5].

The sintered compact was identified by X-ray diffraction from which the c-BN content in the sintered compact (defined as weight % added c-BN and converted c-BN) was determined by using an established calibration curve. X-ray microanalysis (XMA) was also carried out for detection of boron, nitrogen and oxygen. The bulk density of the sintered compact was measured by Archimedes' method. The Vickers microhardness (Hv) was measured under 1000 g load. The as-grown surface as well as the polished or fractured surface of the sintered compact was observed under an optical microscope or scanning electron microscope (SEM). The specific dielectric constant and dielectric loss of the sintered compact were measured by an LCR meter (frequency < 10 kHz) and an impedance analyser (frequency > 1 MHz).

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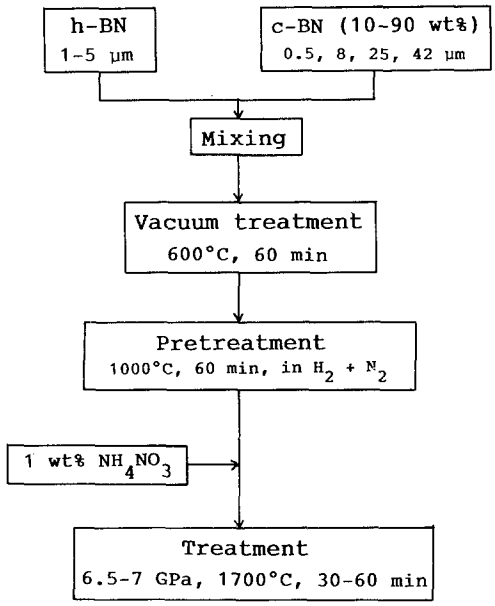


Figure 1 Experimental procedure for high-pressure reaction sintering of c-BN.

3. Results and discussion

3.1. Effects of particle size and amount of added c-BN on reaction sintering behaviour

Fig. 3 shows the c-BN content in the specimen treated at 7 GPa and 1700° C for 30 min, when 30 or 70 wt % c-BN seed crystals with various particle sizes were added to h-BN. Completely converted sintered compacts having 100% c-BN content were obtained by adding both 30 and 70 wt % c-BN grains with an average particle size of 0.5 μm. When 30 wt % c-BN with particle sizes greater than 8 μm were added, however, the c-BN content decreased to less than 80 wt %, when the recovered specimen remained unsintered. At the increased content of c-BN, i.e. 70 wt % addition of c-BN seed crystals, sintered compacts were obtained with average particle sizes of 8 and 25 μm, while the specimen with the addition of 42 μm c-BN seed crystals remained unsintered, mainly due to the weak bonding between c-BN grains, as will be discussed in section 3.2.

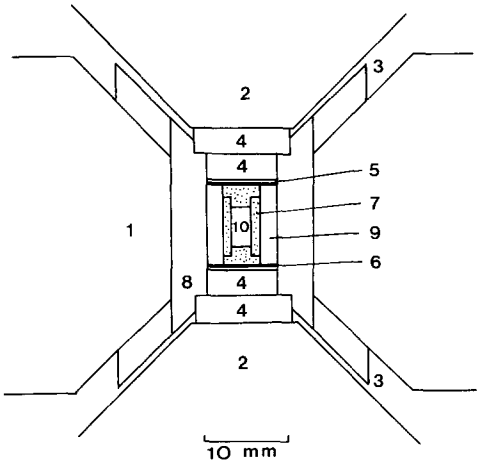


Figure 2 Cell assembly of the girdle-type high-pressure apparatus: 1, cylinder; 2, anvil; 3, composite gasket; 4, cemented carbide disc; 5, molybdenum plate; 6, graphite plate; 7, graphite heater; 8, pyrophillite holder; 9, fired pyrophillite sleeve; 10, specimen room.

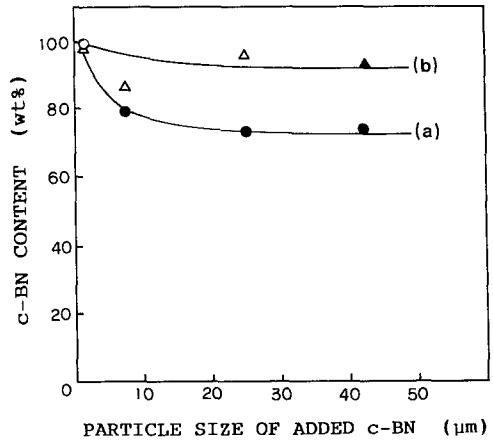


Figure 3 Relationship between c-BN content in the treated specimen and the average particle size of added c-BN: (a) 70 wt % h-BN–30 wt % c-BN; (b) 30 wt % h-BN–70 wt % c-BN; (△, ○) sintered, (▲, ●) unsintered.

Fig. 4 shows the relation between c-BN content in the treated specimen and the amount of added c-BN seed crystals with various particle sizes. A net conversion yield from h-BN to c-BN at a given added c-BN amount is shown in the figure by the ratio of [the separation from the symbol to the diagonal line]/[the separation from the 100% c-BN content to the diagonal line]. Conversion ratio over 95% from h-BN to c-BN is attained by adding only 10 wt % c-BN when using seed crystals with an average particle size of 0.5 μm. When using seed crystals with particle sizes above 8 μm, however, the conversion ratio is considerably lower at the added c-BN content of 30 wt %. Sintered compacts could not be obtained from these specimens in spite of the increased conversion ratios in the range 50 to 70 wt % added c-BN. Higher contents of added c-BN were required in order to obtain a single sintered compact.

3.2. Microhardness and microstructure of c-BN sintered compacts

Table I shows the influence of particle size and added amount of c-BN seed crystals on the average microhardness of c-BN sintered compact treated at 7 GPa and 1700° C for 30 min. The microhardness of the compact obtained by adding 30 wt % c-BN with a

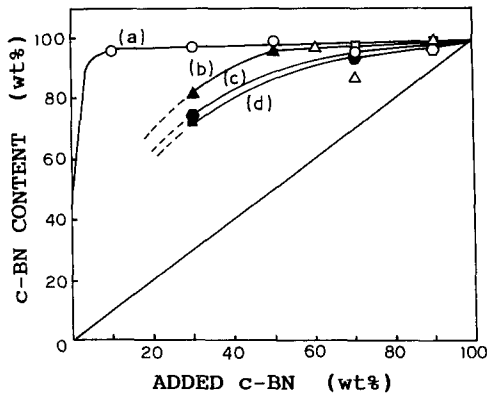


Figure 4 Relationship between c-BN content in the treated specimen and the amount of added c-BN seed crystals. Average particle size: (a) 0.5 μm, (b) 8 μm, (c) 25 μm, (d) 42 μm; (○, △, □, ⬡) sintered, (▲, ■, ⬢) unsintered.

TABLE I Influence of particle size and added amount of c-BN seed crystals on the microhardness of c-BN sintered compact at 7 GPa, 1700° C for 30 min.

Particle size (μm)	Added amount (wt %)	Microhardness, Hv (kg mm^{-2})
0.5	30	5100
8	60	4090
8	70	3600
25	70	3030
25	90	1690
42	90	1860

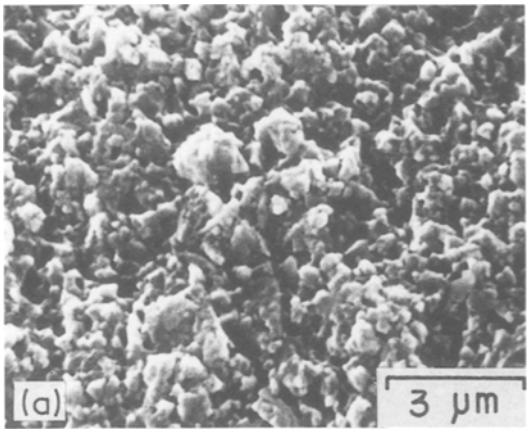
particle size of 0.5 μm, reached 5100 kg mm^{-2}, which is comparable with that of polycrystalline c-BN sintered compacts [6, 7]. This high value verifies the extensive presence of direct interparticle bonding between c-BN grains. It is seen from Table I that the average microhardness decreases as the particle size and the added amount of c-BN seed crystals increase. This tendency corresponds to the variation of microstructure of the sintered compacts.

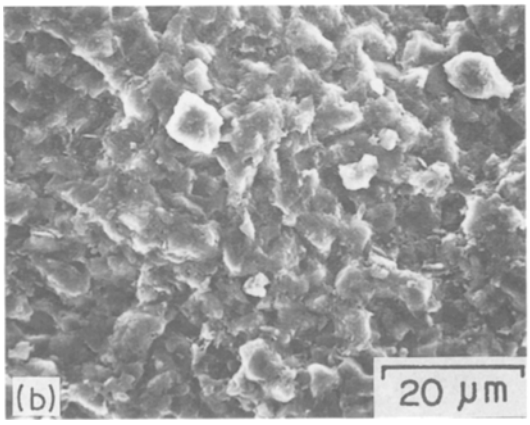
Fig. 5 shows the fractured surface of c-BN sintered compacts which were treated at 7 GPa and 1700° C for 30 min using different types and amounts of c-BN seed crystals. Unconverted h-BN was removed by treating the specimen in boiled 2N NaOH aqueous solution. On adding 30 wt % c-BN seed crystals with a particle size of 0.5 μm, a homogeneous fine-grained microstructure of c-BN sintered compact is obtained as can be seen in Fig. 5a. The grain size in the sintered compact is as low as 0.5 to 1 μm, which is a little larger than that of the added c-BN seed crystals. Direct bonding can be observed among c-BN grains in a whole compact. An analogous microstructure to Fig. 5a, is observed when using 60 wt % c-BN with a particle size of 8 μm (see Fig. 5b), although the grain size increases up to that magnitude of seed crystals (5 to 10 μm). With increased particle sizes and added amounts of c-BN seed crystals (e.g. see Fig. 5c), however, the bonding between c-BN grains in the sintered compact looks rather weak, which can also be verified by the decreased microhardness of this specimen in Table I. The microstructure remained unchanged even after high pressure and temperature treatment for as long as 60 min.

Because the formation of direct bonding between c-BN grains is required to improve the mechanical properties (hardness and toughness) of the sintered compact, it is important to control the nucleation and particle joining which occurs and spreads on the surface of the seed crystal. When the particle size of the seed crystals is small enough to give a large reaction surface area required for the induced transformation and epitaxial growth, a sintered compact of fully dense microstructure having direct interparticle bonding can be obtained even at a small content of c-BN seed crystals.

3.3. Analysis and dielectric properties of a single phase of c-BN sintered compact

A typical c-BN sintered compact was prepared by treatment at 7 GPa and 1700° C for 30 min from the starting powder composition of 70 wt % h-BN–30 wt % c-BN with the addition of 1 wt % NH_4NO_3. The as-treated specimen had dimensions of 8 mm diameter and 1.5 mm thickness. The bulk density of the sintered compact was 3.41 g cm^{-3}, i.e. 98% theoretical. It was confirmed by X-ray diffraction of the polished surface of the specimen [5] that the sintered compact is a single phase of c-BN with 100% conversion ratio from h-BN to c-BN and no crystalline catalytic component detected. Fig. 6 shows XMA images of the polished surface of this c-BN sintered compact, which indicates the two-dimensional analysis of boron and nitrogen. A homogeneous distribution of both elements can be confirmed, which reflects a uniform composition and texture of the sintered compact. Oxygen content was only 1 wt %, while no carbon was detected.





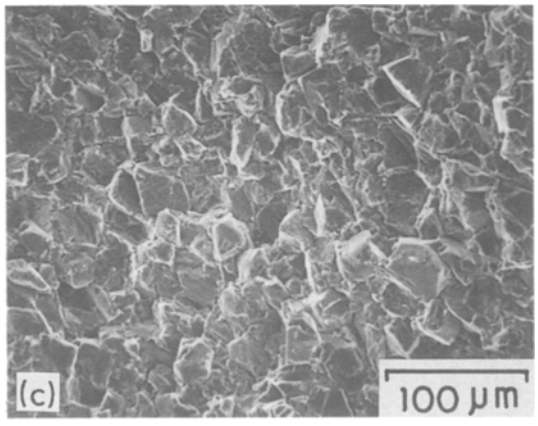


Figure 5 Scanning electron micrographs of the fractured surface of c-BN sintered compacts treated at 7 GPa and 1700° C for 30 min. Average particle size and added c-BN content: (a) 0.5 μm, 30 wt %, (b) 8 μm, 60 wt %, (c) 25 μm, 70 wt %.

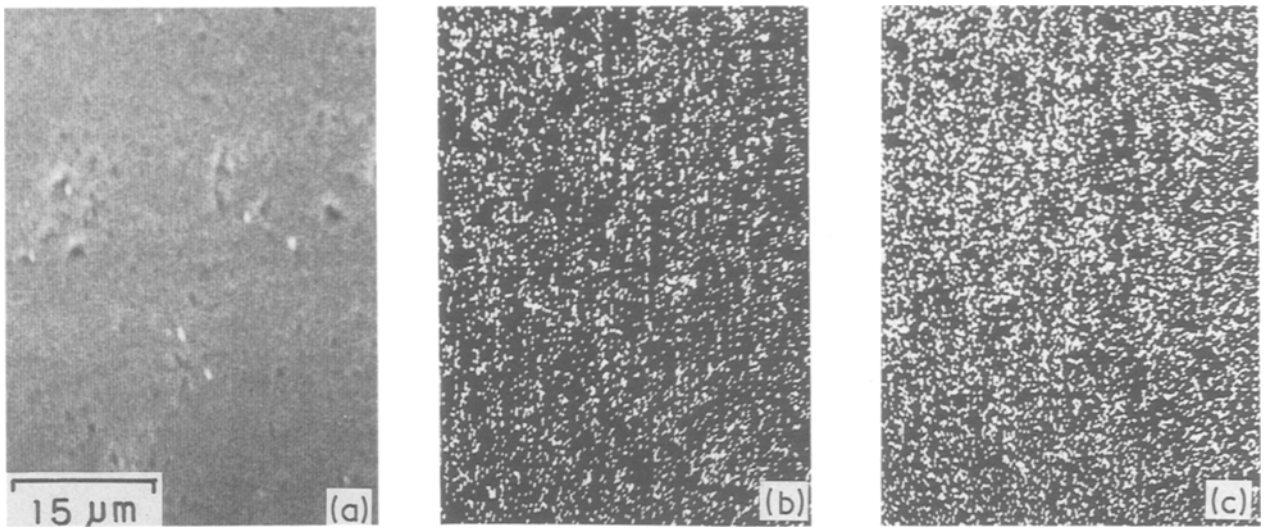


Figure 6 XMA images of c-BN sintered compact prepared at 7 GPa and 1700° C for 30 min from the starting powder composition of 70 wt % h-BN–30 wt % c-BN in the presence of 1 wt % NH_4NO_3: (a) SEM image; (b) B*K*α image, (c) N*K*α image.

Fig. 7 shows the plots of specific dielectric constant (ε_0) and dielectric loss (tan δ) of the same sintered compact as in Fig. 6 as a function of frequency applied. A gradual decrease in ε_0 value is observed in the frequency range 10^3 to 10^9 Hz, which is analogous to the frequency dependence obtained by Shipilo *et al.* [8]. A constant value of 10.0 was attained at frequencies above 1 MHz. The measured tan δ also decreased monotonically with an increase in frequency and had a constant value of 0.1 above 10 MHz.

4. Conclusions

The following conclusions were obtained in relation to the reaction sintering behaviour of c-BN and the effects of added c-BN seed crystals on the microstructure, hardness and dielectric properties of the sintered compacts.

1. The conversion ratio from h-BN to c-BN was increased by adding c-BN seed crystals with a particle size as small as 0.5 μm. A large amount of added c-BN seed crystals was necessary in order to gain a high conversion yield of c-BN when using a coarse c-BN powder (particle size > 8 μm) as seed crystals.

2. Microhardness of the sintered compact increased with decreasing particle size and added amount of c-BN crystals, which reflects the tendency to form direct interparticle bonding of c-BN by reaction sintering. When the particle size of the seed crystals was small enough to give a large reaction surface required for the induced transformation and epitaxial growth, a directly bonded c-BN sintered compact could be prepared even at a small content (about 10 wt %) of added crystals.

3. A typical sintered compact of c-BN was prepared at 7 GPa and 1700° C for 30 min from the specimen of the 70 wt % h-BN with 30 wt % added c-BN crystals (particle size 0.5 μm) using a volatile catalyst, NH_4NO_3. This compact contains no inclusions and has a fully dense microstructure (density 98% theoretical) and microhardness of 5100 kg mm^{-2}. The specific dielectric constant and dielectric loss of the sintered compact were 10.0 and 0.1 at a frequency above 1 MHz, respectively.

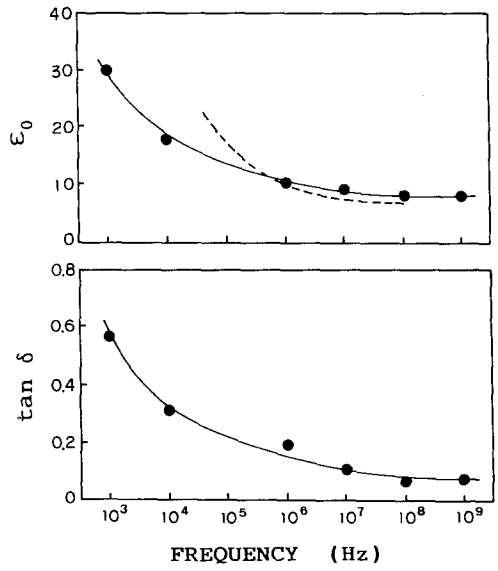


Figure 7 Specific dielectric constant (ε_0) and dielectric loss (tan δ) as a function of frequency: (——) present work, (– – –) Shipilo *et al.* [8].

References

1. S. HIRANO, T. YAMAGUCHI and S. NAKA, *J. Amer. Ceram. Soc.* **64** (1981) 734.
2. S. HIRANO, S. HON and S. NAKA, in "High Pressure in Research and Industry", Proceedings of the 8th AIRAPT Conference, edited by C. M. Backman, T. Johannisson and L. Tegner, Vol. 1 (1982) p. 376.
3. *Idem, Zairyo (J. Soc. Mater. Sci. Jpn)* **33** (1984) 1355.
4. S. HIRANO, N. FUJII, A. FUJII and S. NAKA, *Adv. Ceram.*, in press.
5. H. ITOH, T. MATSUDAIRA, H. ASANO, K. INOUE and S. NAKA, *Funtai Oyobi Funmatsu-Yakin (J. Jpn. Soc. Powder Powder Metall.)* **35** (1988) 125.
6. M. WAKATSUKI, K. ICHINOSE and T. AOKI, *Mater. Res. Bull.* **7** (1972) 999.
7. T. AKASHI and A. B. SAWAOKA, *J. Mater. Sci.* **22** (1987) 1127.
8. V. B. SHIPILO, E. M. SHISHONOK, A. I. AKIMOV and N. A. SHISHONOK, *Dokl. Akad. Nauk. SSSR* **29** (1985) 604.

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