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Microstructure of cBN–diamond sintered compact prepared by reaction sintering

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cBN–diamond composite sintered compacts (diamond content 15–70 wt %) were prepared by reaction sintering at 7–7.5 GPa and 1400–1700 °C for 10–30 min from the starting powder of the hBN–diamond system in the presence of 1 wt % NH_4NO_3 as a volatile catalyst. A fully dense sintered compact with 99% conversion from hBN to cBN was obtained at 7 GPa and 1700 °C after 30 min. An induced transformation from hBN to cBN seemed to occur on the surface of the added diamond seed crystals. Diamond seed crystals (about 30 wt %, grain size 0.2–1.5 μm) were found to be well-dispersed in the reaction-bonded cBN matrix. The Vickers microhardness of the sintered compact was 5100 kg mm^{-2}. The contacts between diamond grains were observed in the sintered compacts containing diamond seed grains of more than 70 wt %. The toughness of the sintered compact tended to increase with decreasing diamond content and the grain size of seed crystals.

1. Introduction

A single-phase sintered compact of cBN was prepared by Itoh *et al.* [1, 2] by reaction sintering in which an induced transformation from hBN to cBN occurs effectively on the surface of added fine-grained cBN seed crystals. Direct interparticle bonding between cBN grains was observed in the sintered compact with the result of a relative density of 98% and a measured Vickers microhardness of 5100 kg mm^{-2}. An analogous induced transformation from hBN to cBN occurs on the diamond seed crystals when a composite sintered compact is prepared in the cBN–diamond system [3, 4]. An alternative reaction sintering for preparation of the cBN–diamond composite compact was reported using the starting powder in the cBN and graphite system [5].

In the present work, we investigated the effects of the starting powder composition in the hBN–diamond system and the grain size of diamond seed crystals on the microstructure of the sintered compact. The relationship between microstructure, density and microhardness is also studied in relation to the sintering conditions.

2. Experimental procedure

hBN powder (grain size: 2–8 μm) and diamond powder (average grain size 0.2, 1.5, 7.0, 22 and 42 μm) were mixed with various compositions. The mixed powder was treated in vacuum (1×10^{-5} torr) at 600 °C for 60 min in order to eliminate the adsorbed gases. The vacuum-treated powder was subsequently pretreated in a stream of nitrogen and hydrogen (1:1) at 1000 °C for 60 min under 1 atm pressure. Then, the pretreated powder was added by 1 wt % ammonium nitrate (NH_4NO_3) as a volatile catalyst. A preliminary experiment showed that the pretreatment and catalyst described above were necessary to enhance the conversion from hBN to cBN, so that these procedures were employed in all the experiments. Detailed study on the catalytic action of these procedures will be reported elsewhere [6]. Thus assorted powder was packed into the specimen cell which was arranged as shown in Fig. 1, and then treated under high pressure and temperature conditions (6–7.5 GPa, 1300–1700 °C) using the girdle-type high-pressure apparatus. The generated pressure was calibrated at room temperature at the fixed points of the phase transition of Bi (2.55 and 7.7 GPa), Tl (3.67 GPa) and Ba (5.5 GPa). The temperature was determined from the calibrated curve of the melting points of Ag, Au and Ni, plotted against the applied electric power.

The specimen before and after the treatment was identified by X-ray diffraction. The conversion ratio from hBN to cBN was determined by the peak–height ratio of 1 1 1 of cBN to 0 0 2 of hBN using an established calibration curve. The microstructure of the sintered compact was examined by scanning electron microscopy (SEM). The bulk density of the sintered compact was measured by Archimedes' method, and the relative density was calculated supposing that the theoretical density is given by the weighted average of inherent densities of unconverted hBN, converted cBN and added diamond in the composite sintered compact. The Vickers microhardness was measured under a 2000 g load.

3. Results and discussion

3.1. Reaction sintering conditions of cBN coexistent with diamond seed crystals

Fig. 2 shows the relation between the conversion ratio from hBN to cBN and the treatment temperature at various pressures (6–7.5 GPa), where the composition

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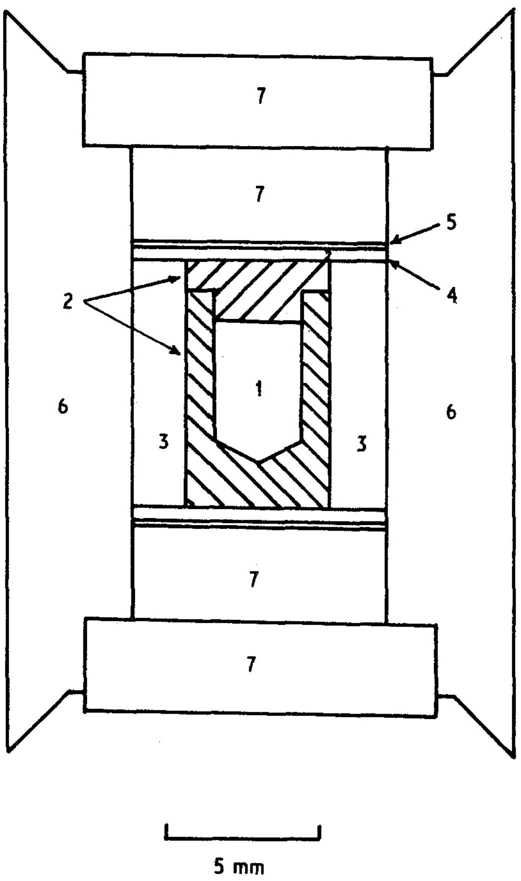

Figure 1 Cell arrangement for girdle-type high-pressure apparatus. (1) Specimen, (2) graphite heater, (3) fired pyrophyllite tube, (4) graphite plate, (5) molybdenum plate, (6) pyrophyllite holder, (7) WC disc.

of starting powder was kept constant at 70 wt % hBN–30 wt % diamond (DIA). The conversion ratio tended to decrease with treatment temperature below a pressure of 6.5 GPa, when the specimen was not sintered because of the lubricant hBN which remained on the grain boundaries of converted cBN or added diamond. On the other hand, the conversion apparently increased with increasing temperature at a given pressure of 7 GPa, attaining a conversion of over 85% at temperatures above 1500 °C with the result of the formation of sintered compacts. At the elevated pressure of 7.5 GPa, the specimen was sintered even at 1400 °C. The influence of treatment time over the range 10–30 min on the microstructure of sintered compacts was minor at 7 GPa and 1700 °C, with no observation of exaggerated grain growth. A typical sintered compact with a conversion ratio of 99% was prepared at 7 GPa and 1700 °C for 30 min. Under these conditions the control of microstructure of the sintered compact was investigated using 1 wt % NH_4NO_3 as a catalyst.

3.2. Effects of starting powder composition on the microstructure

Fig. 3 shows the relation between the conversion ratio and the added diamond content, where the specimens were treated at 7 GPa and 1700 °C for 30 min, and the average grain size of added diamond was 1.5 μm. When no diamond was added to hBN starting powder, the conversion ratio was only 40 wt % and the specimen was not sintered. This low yield of cBN could be attributed to the lack of catalytic action by a small content of NH_4NO_3 catalyst (1 wt %) [6]. However, the conversion ratio increased considerably on adding more than 15 wt % diamond seed crystals, and a fully dense composite sintered compact was prepared. Conversion ratios higher than 99% were maintained up to an added diamond content of 70 wt %. The sintered compact containing 70 wt % diamond was easily broken because of its weak toughness.

Fig. 4 shows the X-ray diffraction patterns of the specimens, which have starting powder compositions of (a) 100 wt % hBN, and (b, c) 70 wt % hBN–30 wt % DIA. After high pressure and temperature treatment (7 GPa, 1700 °C, 30 min) of the specimen without the addition of diamond seed crystals, a small amount of

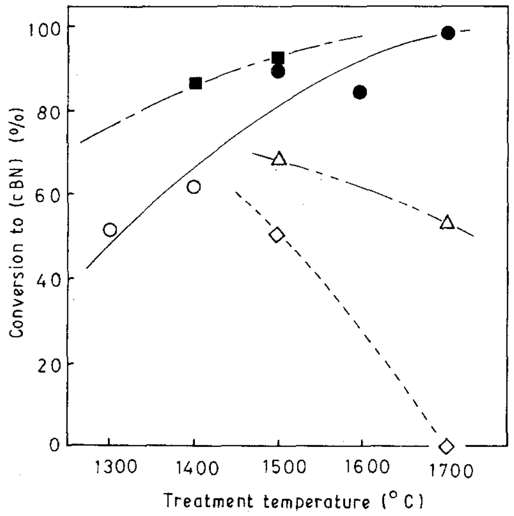

Figure 2 Conversion ratio from hBN to cBN at various pressures and treatment temperatures. Starting powder composition 70 wt % hBN–30 wt % DIA; catalyst 1 wt % NH_4NO_3; treatment time 30 min; pressure: (◇) 6 GPa, (△) 6.5 GPa, (●, ○) 7 GPa, (■) 7.5 GPa; (●, ■) sintered; (○, ◇, △) unsintered.

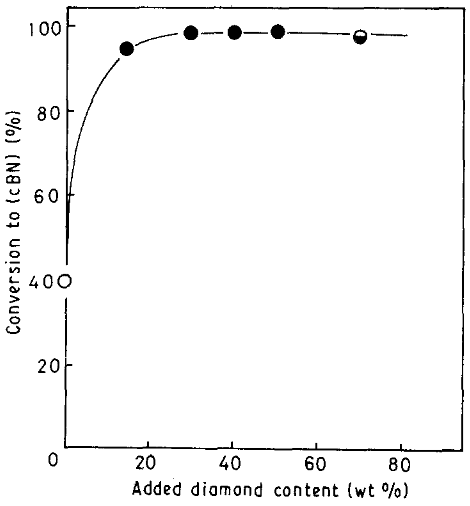

Figure 3 Conversion ratio from hBN to cBN plotted against added diamond content. Treatment conditions: 7 GPa, 1700 °C, 30 min; catalyst 1 wt % NH_4NO_3; grain size of added diamond 1.5 μm; (●) sintered; (◒), partially sintered; (○) unsintered.

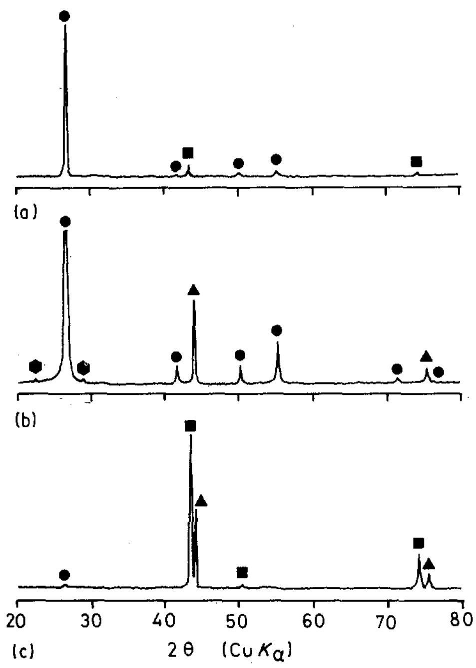

Figure 4 X-ray diffraction patterns of the specimens (b) before and (a, c) after the high pressure and temperature treatment (7 GPa, 1700 °C, 30 min). Catalyst 1 wt % NH_4NO_3; grain size of added diamond 1.5 μm; (●) hBN, (■) cBN, (▲) diamond, (⬢) NH_4NO_3; added diamond content: (a) none, (b) 30 wt %, (c) 30 wt %.

cBN can be identified together with residual hBN. When using the composition 70 wt % hBN–30 wt % DIA, however, the diffraction lines (see Fig. 4b) of the starting hBN powder and NH_4NO_3 catalyst disappeared after the treatment, and lines corresponding to the converted cBN and diamond were observed, as shown in Fig. 4c. The sintered compact is found to comprise crystalline cBN and diamond.

Fig. 5 shows scanning electron micrographs of the fractured surface of the sintered compacts with different amounts of added diamond (grain size 1.5 μm), which were prepared at 7 GPa and 1700 °C for 30 min. Unreacted hBN was removed from the surface by post-treating in alkaline solution (2N NaOH) at 100 °C. When adding 30 wt % diamond, fine-grained cBN were found to be sintered together. The well-dispersed diamond grains can be seen as crystals with steep edges in Fig. 5a, and they are embedded and cemented in the cBN matrix. A direct bonding between cBN grains would form this strong matrix phase of cBN [2]. On the other hand, contacts between diamond grains without neck growth are observed in the specimen containing 70 wt % added diamond. The bonding between cBN and diamond does not seem so strong that this sintered compact was brittle because of a low content of cBN.

3.3. Effects of grain size of diamond seed crystals on the microstructure

Fig. 6 shows the relation between the conversion ratio from hBN to cBN and the grain size of diamond seed crystals which were added by 30 wt %. Nearly 100% conversion ratio was obtained when using a grain size of 0.2 μm. The conversion ratio decreased progressively with increasing grain size from 0.2–7.0 μm, when the specimens sintered in every case. However, the conversion ratio was about 80% when using larger diamond grains with diameters of 22 and 42 μm. These specimens were not sintered due to the lower conversion ratio. The yield of cBN would decrease because of the low surface area of diamond seed crystals. This result shows that an induced conversion

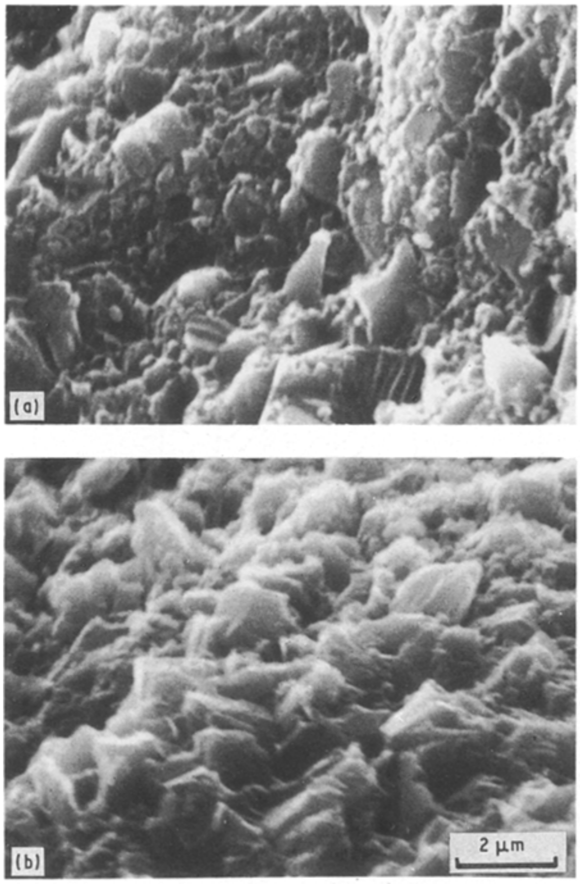

Figure 5 Scanning electron micrographs of the fractured surface of the composite sintered compacts. Treatment conditions: 7 GPa, 1700 °C, 30 min; catalyst 1 wt % NH_4NO_3; grain size of added diamond 1.5 μm; added diamond content: (a) 30 wt %, (b) 70 wt %.

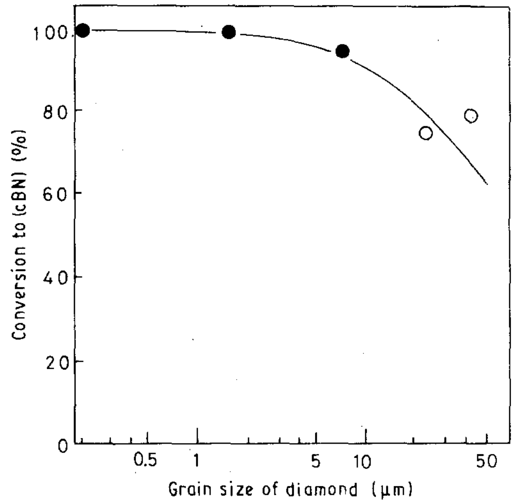

Figure 6 Conversion ratio from hBN to cBN plotted against grain size of diamond. Treatment conditions: 7 GPa, 1700 °C, 30 min; catalyst 1 wt % NH_4NO_3; starting powder composition 70 wt % hBN–30 wt % DIA; (●) sintered; (○) unsintered.

TABLE I Density and Vickers microhardness of composite sintered compacts (7 GPa, 1700 °C, 30 min)

Added diamond content (wt %)	Grain size of added diamond (μm)	Conversion ratio from hBN to cBN (%)	Bulk density (g cm^{-3})	Relative density (%)	Microhardness (kg mm^{-2})
70	1.5	98	–	–	6000
50	1.5	99	3.49	98	5400
40	1.5	99	3.49	99	5200
30	1.5	99	3.48	99	5100
30	0.2	99	3.49	99	5100

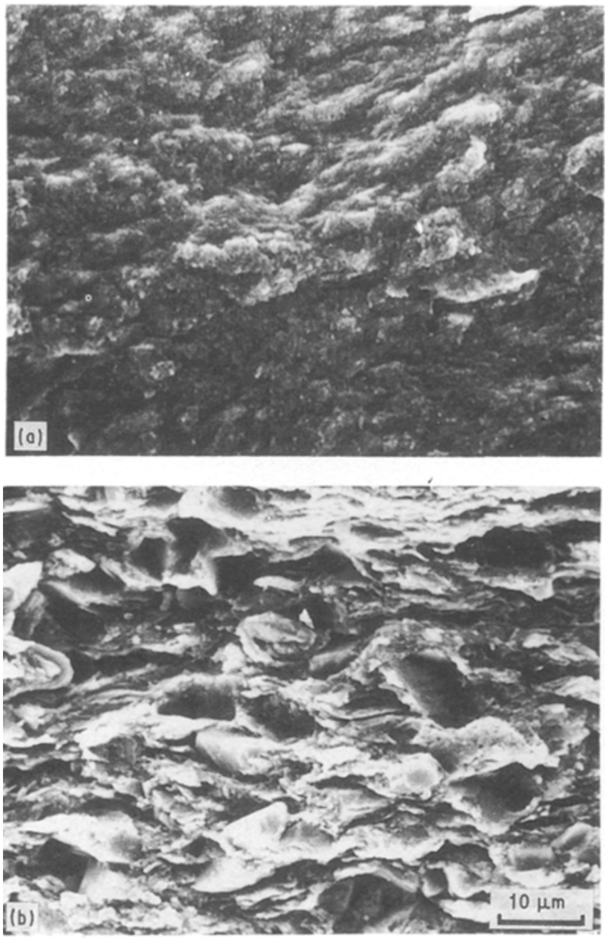

Figure 7 Scanning electron micrographs of the fractured surface of the composite sintered compacts. Treatment conditions: 7 GPa, 1700 °C, 30 min; catalyst 1 wt % NH_4NO_3; starting powder composition 70 wt % hBN–30 wt % DIA; grain size of added diamond: (a) 0.2 μm, (b) 7.0 μm.

would occur preferentially on the surface of diamond grains.

Scanning electron micrographs of the fractured surface of the composite sintered compacts are shown in Fig. 7, where the specimens contain 30 wt % diamond seed crystals with diameters of (a) 0.2 μm and (b) 7.0 μm. It is difficult to distinguish the fine diamond seed crystals from the cBN grains, when using diamond seed crystals of 0.2 μm diameter. A smooth and dense surface can be observed in Fig. 7a, in which the diamond grains appear to be well dispersed in the directly reaction-bonded cBN matrix. In the specimen containing relatively large diamond seed crystals (diameter 7.0 μm), however, some voids which would be formed by chipping-out of diamond from the cBN matrix, can be seen in the rough texture of the sintered compact. This verifies that the fracture occurs mainly through the grain boundary between the diamond grains and the cementing cBN matrix.

3.4. Density and microhardness of the cBN-diamond composite sintered compacts

Table I shows the bulk and relative densities as well as the Vickers microhardness of the cBN-diamond composite sintered compacts. The specimens were obtained at 7 GPa and 1700 °C for 30 min using the various contents of diamond seed crystals (30–70 wt %) having diameters of 1.5 and 0.2 μm. The conversion ratio was mostly 98%–99% in every specimen. The density could not be measured precisely for 70 wt % added diamond because the specimen was easily broken into small pieces, although the microhardness exceeded 6000 kg mm^{-2}. The microhardness decreased with decreasing diamond content, while the relative density was nearly constant at 98%–99%. The microhardness of the specimen containing 30 wt % diamond seed grains, was 5100 kg mm^{-2} in both cases of grain sizes of 1.5 and 0.2 μm.

4. Conclusions

A composite sintered compact in the cBN-diamond system was prepared by reaction sintering of the starting powder composed of hBN and diamond seed crystals in the presence of 1 wt % NH_4NO_3 as a volatile catalyst. The following conclusions were obtained.

1. A fully dense sintered compact in the cBN–diamond system was prepared with 99% conversion ratio from hBN to cBN under the conditions of 7 GPa and 1700 °C.

2. A composite compact having Vickers microhardness of 5100 kg mm^{-2} was obtained with the starting powder composition of 70 wt % hBN–30 wt % DIA. Diamond seed crystals were found to be well dispersed and cemented with the reaction-bonded cBN matrix. The contacts between the diamond grains themselves were observed in the sintered compact, containing 70 wt % diamond seed crystals, which was brittle although the microhardness exceeded 6000 kg mm^{-2}.

3. The toughness of the composite sintered compact increased with decreasing diamond content and grain size of the diamond seed crystals.

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