

# Use of a Ti/C/N ceramic to promote sintering of nanoparticles of shock-synthesized superhard B/C/N with a diamond-like structure

Tamikuni Komatsu,<sup>\*a</sup> Satoru Hosomi<sup>b</sup> and Shuzo Fujiwara<sup>c</sup>

<sup>a</sup>clo National Institute of Materials and Chemical Research-High Density Energy Laboratory, Asahi Kasei Corporation, 1-1 Higashi, Tsukuba-shi, Ibaraki, 305, Japan.

E-mail: BRA01367@nifty.ne.jp

<sup>b</sup>Tomei Diamond Co. Ltd., 4-5-1 Jyoto, Oyama-shi, Tochigi, 323, Japan

<sup>c</sup>National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba-shi, Ibaraki, 305, Japan

Received 4th April 2001, Accepted 24th April 2001

First published as an Advance Article on the web 15th May 2001

Novel superhard sinters of shock-synthesized B/C/N heterodiamond that have both the high hardness of diamond and the excellent steel-cutting capability of cubic BN have been investigated. The addition of special Ti/C/N ceramics unexpectedly made sintering possible. Surprisingly, the heterodiamond particles in the sinters showed a very unique nanoscale dispersion, meaning perfect sintering had occurred. The nanostructure-controlled sintering of the heterodiamond will open a new field of all-purpose cutting and zero-friction materials in the near future.

Diamond is one of the most valuable materials for scientific and technological progress because of its outstanding potential with regard to hardness, heat conduction, *etc.*, mainly through industrial use of sintered diamond. A weak point of diamond is that it is exceptionally labile for steel cutting and air-oxidation over 600 °C. In comparison, sintered cubic boron nitride (c-BN) is strong for steel cutting and inert up to 1100 °C in air, but c-BN has only half the hardness of diamond. A few progressive experts, Wedlake *et al.*<sup>1</sup> and Badzian,<sup>2</sup> tried to produce B/C/N hard materials and prepared cubic BN–C mixed crystals with a face-centered cubic form but not a diamond structure, using a high pressure and high temperature apparatus. In 1992, the diamond-like B/C/N material (heterodiamond) was prepared for the first time by our invention of the industrially-designed explosive shock-synthesis method.<sup>3</sup> Several important matters were found: the heterodiamond consists of nanoparticles,<sup>4</sup> is very stable to thermal oxidation in the air<sup>5</sup> and is capable of scratching the (100) plane of diamond; that is, the material possesses all of the ideal properties for cutting tools.

Sintering of the cubic B/C/N material had not been achieved for the following reasons. Sintering aids such as cobalt induced phase separation of the material under the sintering conditions of diamond.<sup>6</sup> With no sintering aid, the sintering was insufficient even at the upper limit in the stable *P–T* area. However, we found at last several ceramic sintering aids to overcome this difficulty. A mixture of shock-synthesized BC<sub>2.5</sub>N heterodiamond powders<sup>4</sup> (50–95 vol.%), chemical-vapor-deposited Ti/C/N ceramic fine powders (50–5 vol.%) and appropriate amounts of additives was placed into a cylindrical tantalum capsule, covered with a tungsten carbide disk and pressed at 6 GPa and 1500 °C for 5–20 min. The sintered sample was polished on the surface and cut into tips for cutting tools. Field-emission SEM observation showed a

dense texture in which all grains of *ca.* 20–400 nm in size (mainly 50–100 nm) are solidified all over the sample surface (Fig. 1). The grain size observed was no less than the secondary particle size of heterodiamond. From EPMA–EDX measurements, it was found that the B, C, N and Ti elements are almost homogeneously dispersed below 1 μm<sup>3</sup> in spatial resolution (Fig. 2). The XPS B1s measurement showed an unsymmetrical signal that is fitted with two curves (Fig. 3). The binding energies of 189.2 and 190.9 eV were close to the values of 190.5 and 192.7 eV for the unsymmetrical signal of heterodiamond, but differed significantly from the value of 194.5 eV for the symmetrical signal of c-BN. The lower energy shifts were due to a matrix effect of the Ti/C/N ceramic. Since the boron originates from only the added heterodiamond, the B1s signal shows that the diamond-like structure is retained. The values of 287.0 eV for C1s and 400.4 eV for N1s signals, when taken separately from the signals due to Ti/C/N, were close to the values of 288.0 and 400.8 eV for heterodiamond, but the N1s energy was different from the value of 402.3 eV for c-BN. These results show the successful sintering of the heterodiamond on the nanometer scale. It was confirmed that the heterodiamond itself is stable at 6 GPa and 1500 °C and that the Ti/C/N ceramic solidifies but neither melts nor dissolves the heterodiamond under these conditions. So, the

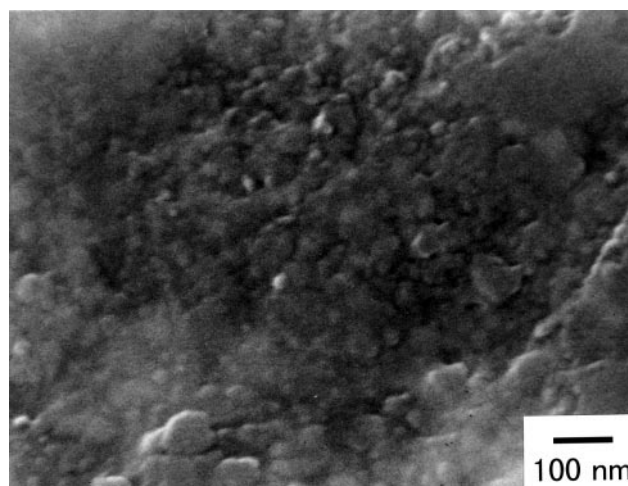
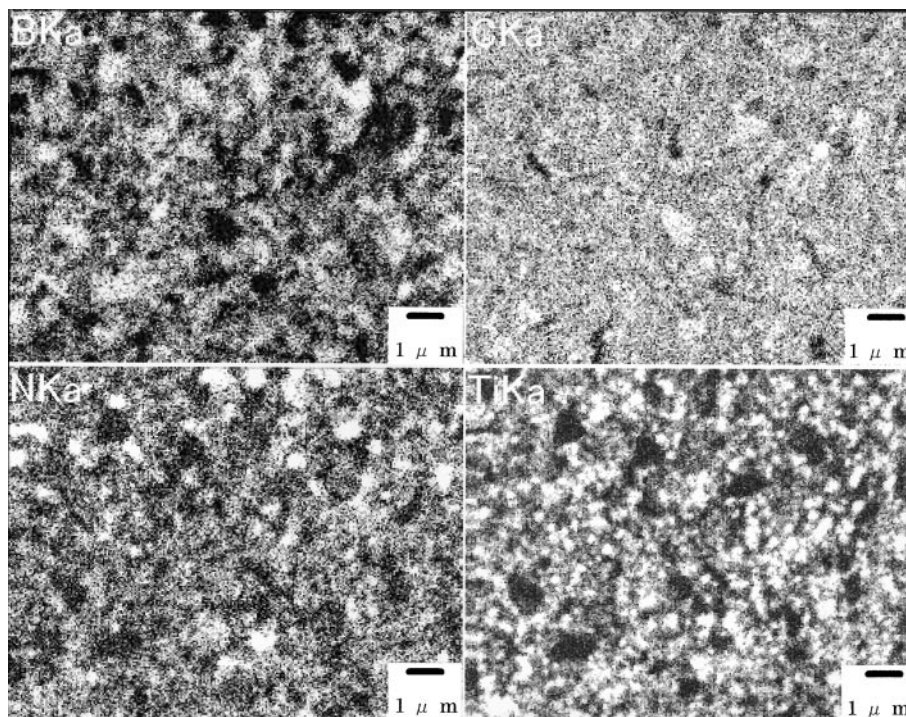
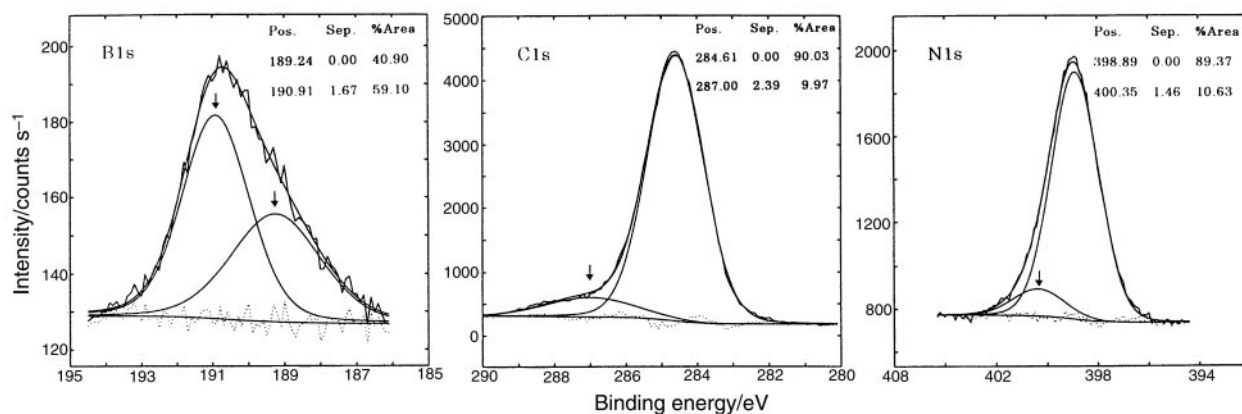


Fig. 1 FE-SEM image of the sintered sample surface observed at a magnification of 10<sup>5</sup>. The image shows a dense texture in which all grains of *ca.* 20–400 nm in size are solidified.



**Fig. 2** EPMA-EDX mapping images of the B, C, N and Ti elements for the sintered sample. They show that the heterodiamond particles and Ti/C/N ceramic are almost homogeneously dispersed below  $1 \mu\text{m}^3$  in spatial resolution.



**Fig. 3** X-Ray photoelectron B1s, C1s and N1s spectra of the sintered sample. Each spectrum is curve-fitted. The binding energies at the arrows are closer to those of heterodiamond than c-BN.

Ti/C/N ceramic is dispersed in the intergranular regions of the heterodiamond particles and promotes sintering. For a 60 vol.% heterodiamond sinter, the steel cutting capability is four times as large as that of sintered diamond and the Knoop hardness is 1.3 times as high as that of sintered c-BN.

Fracture mechanics<sup>7</sup> teaches that the strength and toughness of composites are ruled by microcracks. The present nanoscale dispersion which is free from such cracks produces mechanically the strongest sinters. The smooth, hard surface leads to the possibility of zero friction.<sup>8</sup> There is no precedent for this unique dispersion, since the conventional sinters of diamond and c-BN show micron-sized aggregation of the particles. Possibly, the Ti/C/N ceramic selected as a sintering aid has a good affinity for the heterodiamond. The heterodiamond has good affinity for diamond and c-BN, due to their common elements. Perfect co-sintering of the three materials will open a new field in materials science.

## Notes and references

- 1 De Beers Industrial Diamond Division Ltd., *US Patent* 4187083, 1980; R. J. Wedlake and A. L. Penny, *Chem. Abstr.*, 1979, **90**, 428665Z.
- 2 A. R. Badzian, *Mater. Res. Bull.*, 1981, **16**, 1385.
- 3 Central Glass Co. Ltd., Agency of Industrial Science and Technology and Asahi Chemical Industry Co. Ltd., *Jpn. Patent* 316411, 1994; S. Fujiwara, M. Yoshida, Y. Kakudate, S. Usuba, H. Yokoi, K. Aoki, M. Kawaguchi, T. Kawashima, K. Kasami and T. Komatsu, *Chem. Abstr.*, 1995, **122**, 20920r.
- 4 T. Komatsu, M. Nomura, Y. Kakudate and S. Fujiwara, *J. Mater. Chem.*, 1996, **6**, 1799.
- 5 T. Komatsu, Y. Kakudate and S. Fujiwara, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 5067.
- 6 T. Sasaki, M. Akaishi, S. Yamaoka, Y. Fujiki and T. Oikawa, *Chem. Mater.*, 1993, **5**, 695.
- 7 G. R. Irwin, *J. Appl. Mech.*, 1957, **24**, 361.
- 8 Diamond films excellent in wear and friction resistance have the potential for use as zero-friction tribo-materials. K. Miyoshi and D. H. Buckley, *Appl. Surf. Sci.*, 1980, **6**, 161.