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The effect of copper on the crystallization of hexagonal boron nitride

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The crystallization process of hexagonal boron nitride in the presence of copper has been investigated. The positive effect of copper on the crystallinity of boron nitride was observed in the three studied systems of: nitrided boron, nitrided boron–carbon, and previously prepared turbostratic boron nitride. However, the presence of copper hindered the formation of boron carbonitride and produced graphite and boron nitride phases separately. Poor crystallinity was found as a *conditio sine qua non* for the existence of such a compound. Well-crystallized boron nitride had a very low spacing parameter 0.3328 nm and a regular hexagonal shape.

1. Introduction

Carbon and also boron nitride when it has a disordered structure can be categorized into soft and hard forms with respect to the ease of crystallization. The soft form can be easily crystallized by heat treatments whereas the hard form is resistant to heat treatments and remains disordered. The disordered phase is called turbostratic, a partially ordered phase is called mezographitic, and finally, the completely ordered phase is called "hexagonal" or "graphitic" [1, 2]. Many metals, especially those of the IVb-IVa, groups of the periodic table, have however been found to produce the graphitization of hard carbons [3]. In the case of boron nitride, oxygen-containing impurity phases present in the starting material promote the crystallization into the regular hexagonal form (hBN) [4, 5].

The analogous chemical and structural properties possessed by carbon and boron nitride led us to examine for the possible effects of metals on the crystallization of boron nitride. The inertness, i.e., stability of the prospective metal was a key selection requirement since with boron and its compounds the majority of metals easily form borides or nitrides at high temperatures [6, 7].

For this reason, copper was chosen as the model metal to be investigated in this work. Elemental boron and also mixtures of boron with carbon were nitrided and previously synthesized turbostratic boron nitride powder was also heat treated. All the experiments were performed both with and without copper.

2. Experimental procedure

The materials used in this work were amorphous boron with an average particle size of 0.05 μm (Callery Co. Ltd., USA), graphite (spectroscopic grade HGS-P2, Hitachi Chemicals Co. Ltd., Japan), and copper (grade No. 90210, Rare Metals Co. Ltd., Japan). Turbostratic boron nitride (tBN) with a maximum oxygen content of 2.5 wt % was prepared by a process derived from that first reported by O'Connor [8], which is based on the reductive nitriding of a pre-treated mixture of boric acid and urea in ammonia at 1100 °C. To obtain a chemical mixture of tBN with copper, crystalline cupric nitrate was added to a mixture of urea and boric acid. The final product contained 15 wt % copper with a grain size smaller than 0.1 μm. The method has been described in detail elsewhere [9].

Mechanical powder mixtures consisting of either pure boron or its mixtures with carbon were prepared by milling in a vibration agate mill with 60 wt % copper for 1 h. Pellets 12 mm in diameter, were formed by dry pressing in a hard-metal die at 10 MPa. The pellets were placed in boron nitride crucibles with their lids on and were inserted into a graphite susceptor and heated in nitrogen for 3 h at 1950 °C.

The crystallinity and phase composition of the final products were evaluated from the X-ray diffraction (XRD) patterns of powders, produced by pulverizing the products, using a Philips 1130 diffractometer producing CuK_α radiation. In addition infrared spectra were obtained using an FTS-65 IR spectrometer Bio-Rad, Japan, KBr technique. Scanning electron Microscopy (SEM) was performed using an Akashi DS130 microscope.

3. Results and discussion

3.1. Nitriding of elemental boron

XRD patterns of boron nitride prepared by direct synthesis of boron with nitrogen at 1950 °C are

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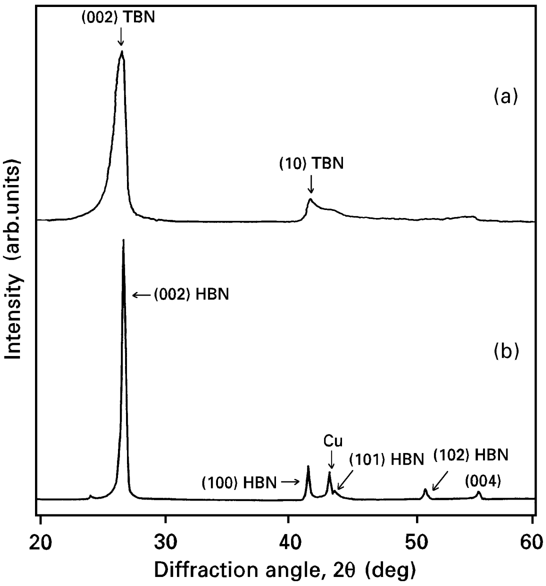

Figure 1 XRD patterns of boron nitride prepared by direct fusion of elemental boron with nitrogen at 1950 °C ((a) pure boron, (b) boron mixed with 30 wt % copper).

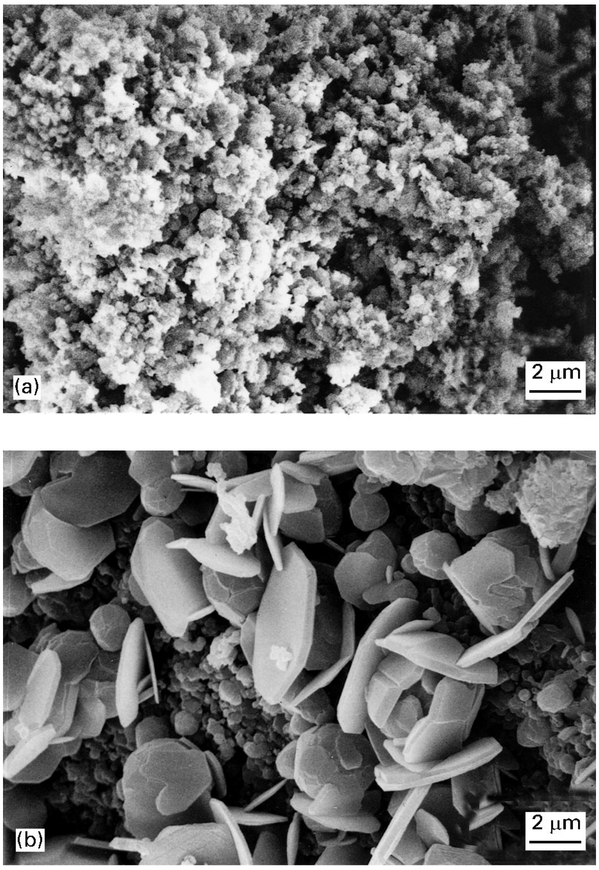

Figure 2 SEM micrographs of boron nitride prepared by direct fusion of elemental boron with nitrogen at 1950 °C ((a) pure boron, (b) boron mixed with 30 wt % copper).

shown in Fig. 1. The boron nitride produced in the copper-free system had a turbostratic structure characterized by a broad (002) diffraction peak and another broad peak attributed to the (10) two-dimensional diffraction (pattern A). This is the usual observed behaviour in systems without any oxide catalyst. The addition of copper had a positive effect on the crystallinity of the final product which is shown in pattern B on Fig. 1 by the complete separation of the (10) peak into (100) and (101) peaks. In addition the d_{002} values i.e., the d value associated with the 002 reflection, which is related to interlayer spacing reached a value 0.3328 nm, which is typical for well-crystallized hexagonal boron nitride [10].

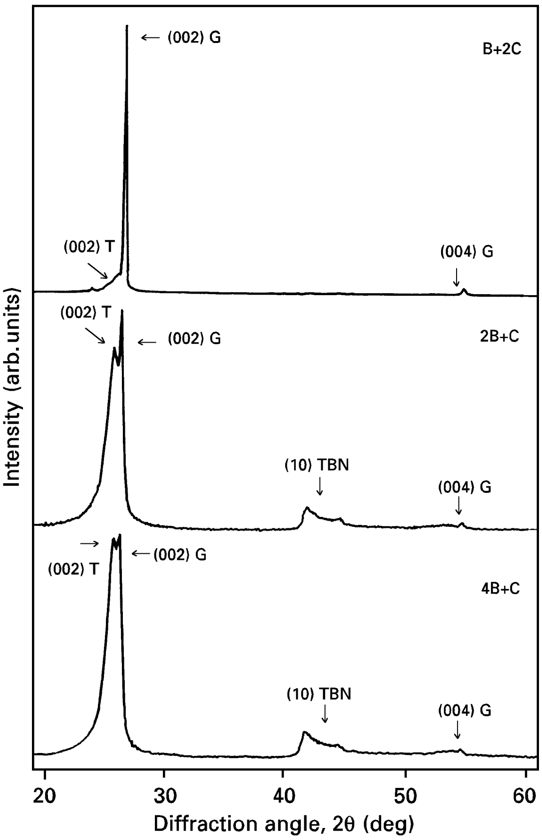

Figure 3 XRD patterns of boron–graphite mixtures after heating in nitrogen at 1950 °C.

In the copper-free specimen, the size of the final boron nitride grains, shown in Fig. 2a, reflected the size of the starting ultrafine boron powder. The boron nitride synthesized in the presence of copper possessed large and angular grains with a hexagonal shape, shown in Fig. 2b which is due to the intrinsic crystal structure of hBN.

3.2. Nitriding of boron–graphite mixtures

In the presence of carbon, boron nitride rearranges its layers to produce an ordered lattice, which is probably driven by the reducing effect of the boric oxide catalyst. It is therefore of interest to determine if copper can act even in such severe conditions. For this purpose, mixtures with varying boron-to-carbon ratios were prepared, both with and without copper.

The XRD patterns of the nitrided products obtained in the copper-free system are shown in Fig. 3. In addition to graphite, a turbostratic phase with a diffraction peak at a lower diffraction angle (marked as a T-phase) was detected, pattern (a). The T-phase content was proportional to the boron fraction in the

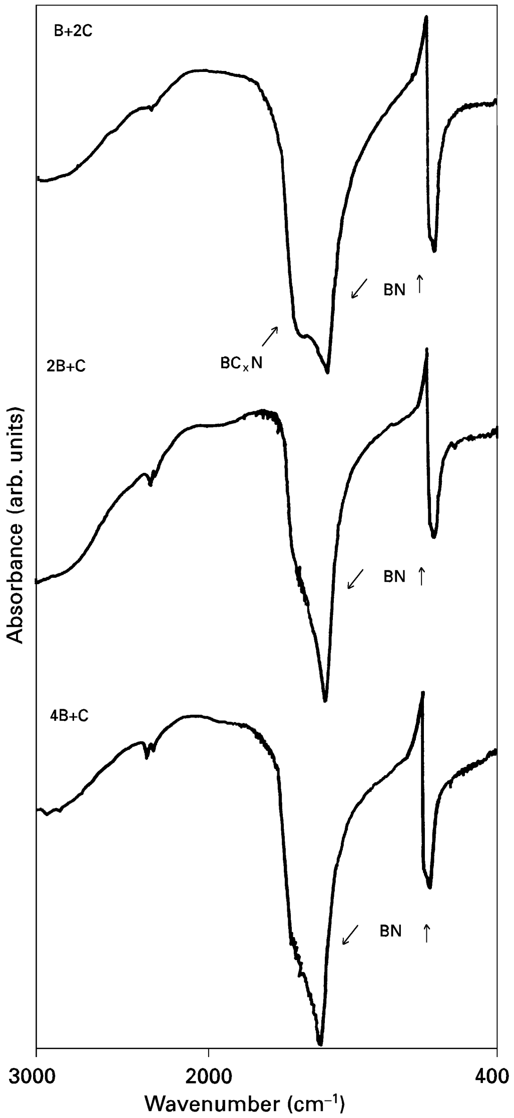

Figure 4 Infrared spectra of boron–graphite mixtures after heating in nitrogen at 1950°C.

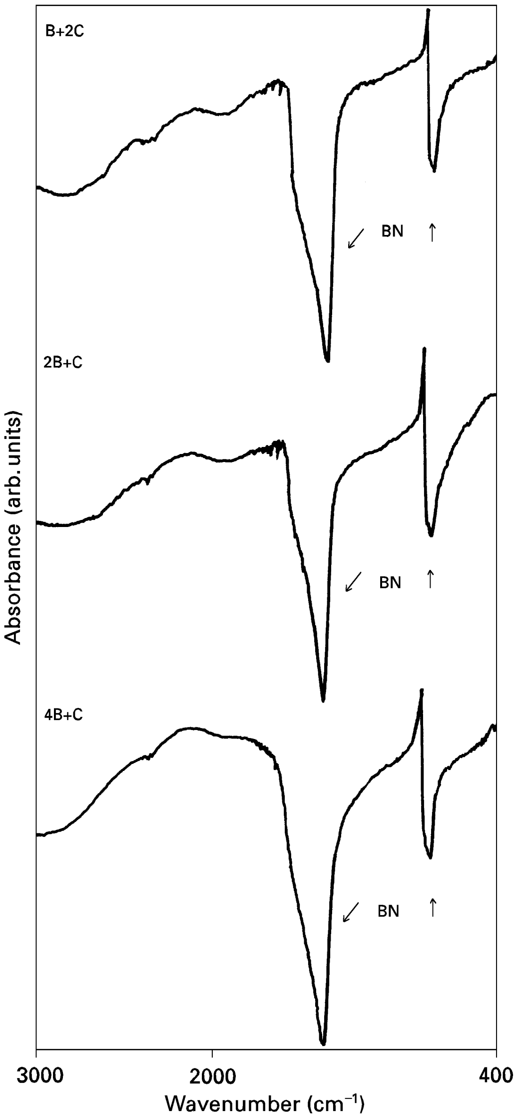

Figure 5 Infrared spectra of boron–graphite–copper (30 wt %) mixtures after heating in nitrogen at 1950 °C.

starting mixture. This T-phase could be assigned as tBN on the basis of the infrared spectrum (wavenumber $\approx 1380\ \text{cm}^{-1}$) shown in Fig. 4. Furthermore, another signal is apparent in the spectrum (wavenumber $\approx 1500\ \text{cm}^{-1}$), the intensity of which was proportional to the carbon content in the starting mixture. This additional signal could be explained by the presence of a ternary compound in the B–C–N system, and the formation of such a B–C–N compound under these conditions has been previously reported [11].

After nitriding of the copper containing mixtures, only boron nitride was observed in the infrared spectra shown in Fig. 5. It is clear from the XRD patterns shown in Fig. 6 that the boron–carbon system was monophasic after nitriding since the diffraction patterns only contain a single peak at the position corresponding to the graphite (002) peak. However, a broadening on the low 2Θ side of the (002) peak and also an increase in the intensity of the peak assigned as the (100) peak of mezographitic BN (MBN) were noticed at increasing boron fractions.

The broadening can be explained by the presence of mezographitic BN which has a slight but detectable difference in the d_{002} spacing compared to graphite. It was thus shown that the crystallization of BN proceeds even in a carbonaceous environment. However, the crystallinity of the boron nitride formed with the aid of copper is still considerably poorer than that in the carbon-free system.

3.3. Crystallization of turbostratic boron nitride

Mechanical and chemical mixtures of tBN with copper were annealed in nitrogen to examine the influence of copper on the crystallization of previously synthesized boron nitride. The temperature dependence of the d_{002} spacing is shown in Fig. 7. As can be seen from curve a it was found that rather coarse grains of commercially available copper were not able to completely convert tBN into crystallized hBN. At the highest investigated temperature of 1950 °C, a small fraction of the tBN was converted to highly-crystallized hBN as is shown in Fig. 8. Ultra-dispersed copper, on the other hand, was very effective and only

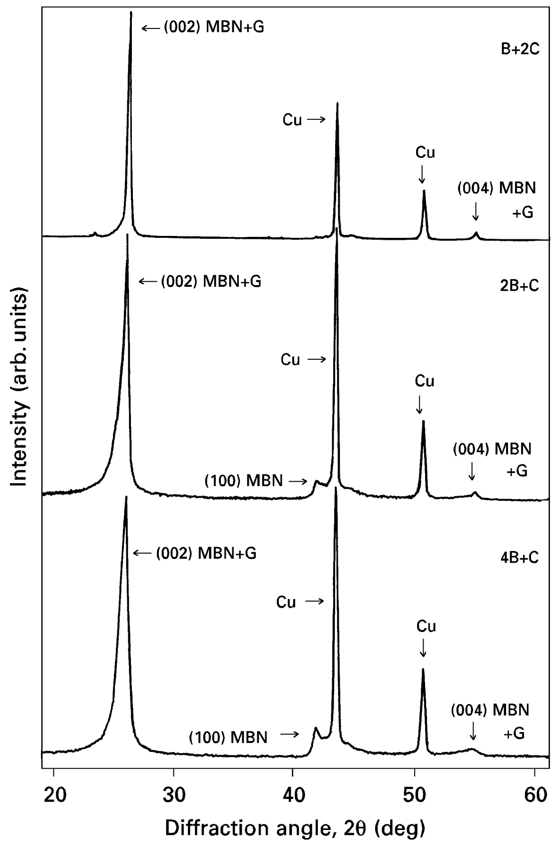

Figure 6 XRD patterns of boron–graphite–copper (30 wt %) mixtures after heating in nitrogen at 1950 °C.

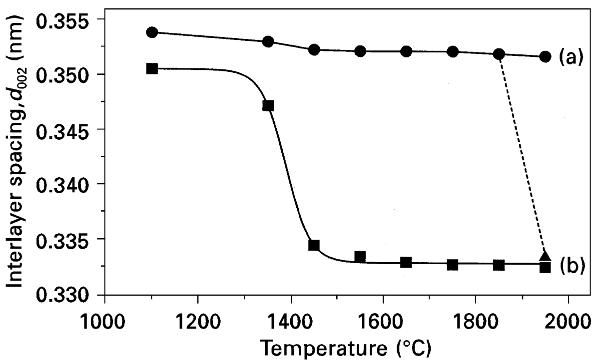

Figure 7 Temperature dependence of the d_{002} spacing parameter of (a) mechanical and (b) chemical Cu–BN mixtures.

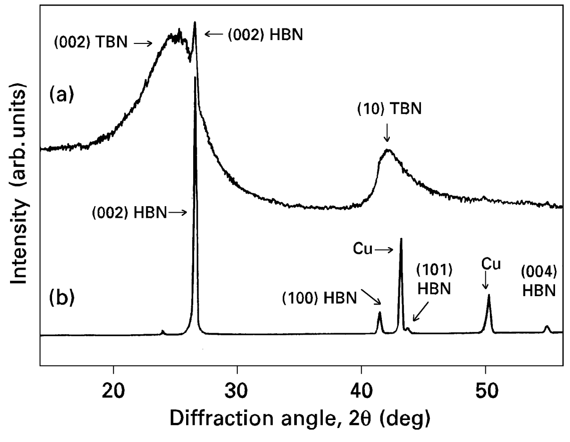

Figure 8 XRD patterns of (a) mechanical and (b) chemical Cu–BN mixtures after heating at 1950 °C.

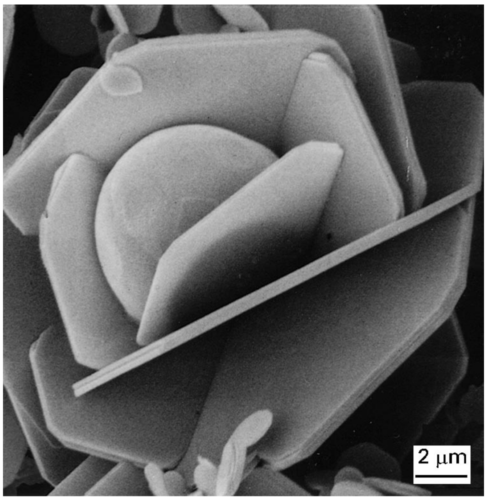

Figure 9 SEM micrograph of a Cu–BN chemical mixture after annealing at 2150 °C.

crystalline hBN was observed in the XRD patterns even at the low temperature of 1650 °C, as can be seen from curve b in Fig. 7. After heating at a temperature, of 2150 °C, the hBN grains became highly regular in shape, and in fact formed bizzare aggregates resembling flowers. In some cases, the size of the "petals" exceeded 7 μm, as is shown in Fig. 9. The dispersion of copper is thus an important factor in determining the catalytic efficiency for the crystallization.

4. Conclusions

The catalytic effect of copper on the crystallization of hexagonal boron nitride was observed. When elemental boron was nitrided, the addition of copper caused the creation of a perfect crystal lattice with a d_{002} spacing as low as 0.3328 nm. The formation of angular grains with a regular hexagonal shape and with a size that exceeded that of the copper-free system by approximately one hundred times was found. Copper thus significantly contributed to the mass transport during the nitriding of elemental boron.

The copper even catalysed the crystallization of previously synthesized tBN. The grain size of the copper was the dominant factor in determining the effectiveness of the process. For carbon, the metals can act effectively, even when in the form of coarse grains, to graphitize hard carbons. This is in striking contrast to the case of BN [3] where the metal has to be in a finely dispersed form. It is suggested that finely dispersed metallic copper accelerates mass transportation for the crystal growth of boron nitride rather than through dissolution and precipitation of BN from the molten metal.

When carbon was mixed with boron, a turbostratic B–C–N phase was formed. The addition of copper to a boron–carbon mixture, resulted in the synthesis of mezographitic boron nitride with no B–C–N impurities phase being produced. It is suggested that for the three element compounds layered structures with regular hexagonal symmetry cannot be formed, most probably due to differences in the C–C and B–N bond lengths and therefore the planar networks are deformed and also their stacking must be irregular. If the layered system is forced to crystallize, then the formation of a ternary B–C–N compound cannot be expected.

Copper as a chemically inert metal towards BN and also carbon has been demonstrated as a novel type of catalyst promoting the crystallization of boron nitride.

The findings reported here need to be supported with a theoretical model that explains the observed phenomena. The examination of other groups of elements as potential catalysts should be undertaken.

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References

1. B. E. WARREN, *Phys. Rev.* **59** (1941) 693.
2. T. E. O'CONNOR, *J. Amer. Chem. Soc.* **84** (1962) 1753.
3. A. OYA and H. MARSH, *J. Mater. Sci.* **17** (1982) 309.
4. T. A. INGLES and P. POPPER, in "Special ceramics", edited by P. Popper (Heywood & Co. London, 1960) pp. 114–167.
5. V. V. VIKULIN, *Poroshk. Metallurgiya* **9** (1978) 64.
6. K.-A. SCHWETZ and A. LIPP, *Ber. Dt. Keram. Ges.* **56** (1979) 1.
7. V. I. MATKOWICH, (ed) "Boron and refractory borides", (Springer Verlag, Berlin, 1977).
8. T. E. O'CONNOR, US Patent 3 241 919 (1966).
9. M. HUBÁČEK, T. SATÓ and T. ISHII, in Proc. of the Intl. Symposium on Material Chemistry in Nuclear Environment, Tsukuba, Japan 1992, edited by N. Okamoto (Mitsubishi Research Institute, Tokyo, Japan, 1992) pp. 81–91.
10. "Hexagonal boron nitride", *Nat. Bur. Stand.* (*US*) *Monogr.* **20** (1983) 22
11. T. YA. KOSOLAPOVA, G. N. MAKARENKO, T. I. SEREBRYAKOVA, E. V. PRILUTSKIJ, O. T. KHORPYAKOV and O. I. CHERNYSHEVA, *Poroshk. Metallurgiya* **1** (1971) 27.

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