Layer-structured BC$_x$N compounds produced from mixed melt of C and BN

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Abstract. Melting method for synthesizing BC$_x$N compounds has been improved, where the starting material is a mixture containing C and BN and wholly melted without reacting the container wall. Product is composed of two phases of BC$_x$N compounds. Their structures are cleared to be of the hBN-type and of the graphite-type, respectively. Variation of lattice parameters of the both phases and their formation ratio are investigated in relation to the composition of the starting mixture. Existence of ordered arrangement of B, C and N atoms is suggested, too. A structure model is given for the phase of the hBN-type.

1. Introduction
Compounds having composition of BC$_x$N have been usually produced by the CVD method and considered to be intermediate compounds between C and BN having the structure of stacked hexagonal network planes, like graphite or hBN [1, 2]. Some trials have been carried out to use them as the starting material for synthesizing hard solid solutions between diamond and cBN using very high pressure [3]. Some models are proposed for the atom arrangement of B, C and N within the network plane for the BC$_x$N materials synthesized by CVD [2]. However, those materials are very poorly crystallized and discussion about the atom arrangement in the plane is very difficult on the basis of diffraction. The stacking structure of the planes is considered as being turbostratic.

In the preliminary work of our study [4], we synthesized similar materials from graphite and hBN by melting them together at very high temperature. In the present study, we have refined the synthesis method, and carried out more detailed characterization of the product. We synthesize the materials by melting graphite in an hBN case, or powder mixture containing C and BN in an hBN case, the sample being confined in a high pressure space of a cubic anvil apparatus. The products are composed of very well-crystallized particles of two phases, each showing very sharp, almost ideal x-ray diffraction patterns. We are trying to characterize structural features of the products, including the atom arrangements in the hexagonal network planes.

2. Synthesis
Synthesis can be performed by two types of experiments. In the one, a rod of graphite was located in a container (hollow cylinder) of hBN, as shown in Fig.1, and strong electric current (ac of 50 Hz) was passed through the sample for a short period (a few seconds) at a confining pressure of 1.5 - 2 GPa. The heating was stopped when the sample resistance showed a steep and large rise. The inner part of the hBN container was reacted and a black-colored lump was recovered as the product.
In the other, powder mixture of graphite and hBN was filled in the hBN container. The mixing composition was changed from (2C+BN) to (6C+BN). A mixture of (C+BN) (corresponding to BCN) could not be heated because the mixture showed insulating nature. Fortunately, however, powdered product from the mixture of (2C+BN) is well conductive and we used this product instead of graphite, and decreased the mixing ratio of insulating hBN. In order to melt graphite, a rod was charged together with diamond layer. On the other hand, pure hBN cannot be melted with our method at present. The sample arrangement was the same as that in Fig.1. The injected energy can be controlled by the “switch-on period” of a switching system using thyristers. It was actually adjusted so that the melted region extended just to the inner surface of the hBN case. Switch-on periods were typically 0.1 to 1.6 seconds depending on the inner diameter of the case (2.0 to 5.0 mm) and the mixture composition. Voltage and current through the sample were recorded as functions of time. The sample resistance, electric power and integrated energy injected into the sample were calculated afterwards.

3. Products

A product lump from graphite rod melted and reacted by hBN until the sample resistance rose showed a diameter a little larger than that of the initial rod. The resistance increase, though its mechanism has not been analyzed in details, may be a sign of the extension of the reaction. On the other hand, the melted sample with adjusted injection energy keeps the cylindrical shape of the initial charge in the container because reaction is carefully adjusted as stopping just at the inner surface of the container. It is considered that the averaged composition of the product is changed only little from that of the initial mixture. The maximum quantity of recovered product is about 200 mg from the mixture of (2C+BN) filled in a sample space of 5 mm in diameter and 10 mm in length.

Every product is colored black for all starting composition and clearly shows radial freezing texture on the sectioned surface. Powdered sample is composed of very well-crystallized particles like crystalline graphite, ranging from several to several hundreds in micrometers (Fig.2).

4. Characterization

Results of x-ray diffraction analysis, on the powdered samples using Cu-\(K\alpha\) radiation, are summarized as follows.

(1) Two similar phases are contained. Each can be indexed very well with hexagonal network layers stacked with a repeating period of two sheets, like graphite or hBN. The one (tentatively named M) has a set of lattice parameters \((a_0\) and \(c_0\)) rather near to those of hBN compared to the other, and in the other (tentatively named m) they are near to those of graphite. However, the parameters are clearly shifted from those of hBN and graphite and positioned intermediate between the both. In Fig.3 are shown diffraction peaks for several samples. Symbols C1 to C6 correspond to averaged compositions of starting mixtures of (1C+BN) to (6C+BN). “Graphite” means pure graphite melted in the diamond layer. A well-crystallized pure hBN (Denka-Grade GP) is contained for comparison though it is not melted. Peaks of 100, 101 and 102 are located from left to right. Peaks of the both phase are clearly separated at each index. It is well known that very sharp and clearly separated peaks of 100, 101 and 102 show the three-dimensionally perfect state of the graphite-like crystal [5].
(2) Based on intensities of the non-fundamental peaks (101 and 102), we can assign the stacking structure of the phase M and m to the hBN-type and the graphite-type, respectively.

(3) On the other hand, intensities of fundamental peaks (110 and 112) offer the produced ratio of the both phases. The phase ratios evaluated by the two peaks reasonably agreed with each other. The evaluated ratio, [M]/([M]+[m]), were around 0.1, 0.3 and 0.5 for relative BN-concentration of 0.25(C6), 0.5(C2) and 0.33(C1) in the starting mixture, respectively.

(4) Lattice parameters also change continuously depending on the composition of the starting mixture, as shown in Fig.4. It should be noted that compositions of particles might be different between the two phases even though they are produced in a single bath. However, composition looks essentially uniform among particles of the same phase, because every peak is very sharp and lattice parameters can be defined with a narrow width.

(5) As for composition of each particle, microprobe AES analyses on particles show that each of B, C and N is contained as a main component. B and N are nearly equally contained but relative concentration of carbon seems ranging wider.

(6) A weak signs of existence of a super-lattice is suggested. That is, a very weak peak has been observed at 13.588 degree corresponding to 0.6511 nm, agreeing with three times the spacing of 100 lattice planes of the phase M.

5. Discussion
Existence of two different product phases (M and m) is easily understood because graphite and hBN are stacked in different manner. Most of the results of characterization tempt us to suppose that we may have merely realized a simple binary eutectic reaction between graphite and hBN from melted mixture. However, each phase is clearly not a pure phase of graphite or hBN but is composed of B, C and N. Each component is not a small quantity impurity but plays a role of main component. This is suggested by AES analyses as described. Furthermore, an EELS-mode observation using TEM shows uniform distribution of each of B, C and N throughout within a particle [6].

It is reasonably supposed, though tentatively, that concentration of C in the phase M is smaller than that in the phase m because a smaller concentration of C will make the hBN-type stacking more stable than the graphite-type stacking. In order to confirm this we need to correlate AES analysis to
diffraction on each of single particle, because we have not yet succeeded in synthesizing single-phase compounds.

As for the ordering of B, C and N atoms, B-C-N materials prepared by the CVD method often shows stoichiometric compositions such as BCN and BC$_2$N, suggesting some ordered arrangement in the plane. Some models of the ordered arrangements have been proposed from a view point of nature of chemical bonds observed by ESCA [2]. While, highly crystallized product in our study should be favorable for discussion on the basis of diffraction. The observed lattice spacing was 0.6511 nm as described above. At the same time this particular sample showed a 100 spacing of 0.2169 nm for the phase M, and three times 0.2169 (0.6507) excellently agreed with 0.6511. This fact suggests existence, in the phase M, of a super-lattice with lattice spacing three times larger as the 100 spacing. If we assume an ideal phase of M in which the composition is accurately BCN, an atom of B (N) would prefer an atom N (B) as its neighbor, or -B-N- chains are preferably formed within the network plain. Similarly would be formed -C-C- chains, too. Furthermore, we consider the three times period in the a-axis direction. Then, one -C-C- chain and two -B-N- chains must be repeated in the network plane. As for the stacking, an N (B) atom must be positioned on a B (N) atom in the neighboring plane, a C atom being on another C atom. This structure, if limited within a single sheet, agrees with one of those proposed by other authors [2]. The composition of particles may not be ideal, which will make diffraction peaks of the super-lattice very weak actually.

As another example showing existence of super-lattices, spots having four times period in the direction of a-axis were clearly observed in a pattern of electron diffraction carried out on a small particle [6]. The period is different from that in the phase M, and we consider it may be attributed to the phase m, though some confirming works are needed before we conclude it.

6. Conclusions
A mixture containing carbon and BN in their low-pressure phases is charged in an hBN case and strong electric ac current was passed for a short period with injected heating energy adjusted. The mixture was melted and recovered as compounds between C and BN.

(1) The recovered product is composed of well crystallized particles, looking like graphite. Particle size ranges from several to several hundred micrometers.

(2) The product consists of two phases. One (M) has a crystal structure of the hBN-type and the other (m) of the graphite-type. Lattice parameters vary between those of graphite and hBN, according to the relative composition of C in the starting mixture.

(3) Formation ratio of the two phases also varies depending on the starting mixture composition.

(4) Every particle of the both phases contains all of B, C and N. Relative concentrations of B and N are essentially the same in any particle with small deviations, while the carbon concentration differs depending on the sample.

(5) There is suggested existence of an ordered arrangement of B, C and N atoms. A super-lattice with a lattice spacing three times that of 100 spacing in the phase M is observed by x-ray diffraction. This super-lattice can be reasonably explained if an ideal M-phase with composition of BCN is assumed. A model of three-dimensional ordered arrangement of atoms is proposed for the phase M.

References
[1] J. Kouvetakis, T. Sasaki, C. Shen, R. Hagiwara, M. Lernaer, K. M. Krishnan and N. Bartlett, Synth. Met., 34 618 (1989)
[2] M. Kawaguchi, T. Kawashima and T. Nakajima, Chem. Mat., 8, 1197 (1996)
[3] Y. Kakudate, Trans. Mat. Res. Soc. Japan., Vol. 14B, Elsevier, Amsterdam, 1994, 1447
[4] M. Wakatsuki, K. J. Takano and H. Kagi, in New Functionality Materials, Vol. C, ed. by T. Tsuruta, M. Doyama and M. Senoo, Elsevier, Amsterdam, 1993, 91
[5] J. Thomas, J., N. E. Weston and T. E. O’Conner, J. Am. Chem. Soc., 84, 4619 (1963)
[6] M. Wakatsuki, et. al., to be reported elsewhere.