## *Crystallinity of Boron Nitride Fabricated in Various Ways*

By Hiroaki TAGAWA and Kikuo ISHII

(Received May 7, 1962)

Crystallinity of boron nitride fabricated in variety of ways has been investigated by means of X-ray diffraction. The structure of boron nitride is very similar to that of graphite[1]. As is shown in graphitizing nature of carbon, the physical and chemical properties of boron nitride may vary considerably according to the nature of starting materials and the conditions of preparation. This communication describes the difference between the crystallinity of boron nitride fabricated by the gas phase reaction and that of the one prepared by the solid state reaction.

The methods of preparation of boron nitride used were as follows; (1) gas phase reaction of boron trichloride with ammonia on a SiC resistor heated at 900 or 1050°C[2], (2) decomposition at 800 or 1000°C of the complex formed by the reaction of boron trichloride with ammonia in gas phase at room temperature[3], (3) solid-gas reaction of boron oxide coated on tri-calcium phosphate with ammonia at 800 or 1000°C for four hours[4], (4) solid-gas reaction of sodium tetraborate with ammonia at 800 or 1000°C for two hours, and (5) solid-solid reaction of boron oxide with sodium amide (mixing ratio by mole, 1:3) at 800°C in nitrogen[5,6].

Interlayer spacings of (002), and La- and Lc-dimensions of crystallite of boron nitride fabricated by the methods mentioned above were measured using an automatic recording X-ray spectrometer. As the observed diffraction maximum is not corrected for polarization and absorption, the true value may slightly become less than the measured one. La-dimension, the width of the graphite-like layer, was obtained from (10) band or (100) line, and Lc-dimension, the thickness of the parallel packet of layers, was obtained from (002) line.

TABLE I. BORON NITRIDE FABRICATED IN A VARIETY OF WAYS

| Starting material | Reaction temp. °C | $d_{002}$ Å | La Å | Lc Å |
|---|---|---|---|---|
| 1) $BCl_3+NH_3$ | 900 | 3.619 | 45 | 12 |
| | 1050 | 3.591 | 49 | 13 |
| 2) Decomposition of the complex ($BCl_3\cdot 4NH_3$) | 800 | 3.624 | 56 | 14 |
| | 1000 | 3.594 | 68 | 14 |
| 3) $B_2O_3+NH_3$ | 800 | 3.389 | 71 | 45 |
| | 1000 | 3.339 | 290 | 66 |
| 4) $Na_2B_4O_7+NH_3$ | 800 | 3.349 | 265 | 88 |
| | 1000 | 3.339 | 1160 | 282 |
| 5) $B_2O_3+NaNH_2$ | 800 | 3.389 | 243 | 115 |

The result of X-ray measurement is summarized in Table I. The crystallinity of boron nitride fabricated at 1000°C is more developed than that at 800°C. Interlayer spacing of the nitride fabricated in gas phase is larger than that of the nitride prepared in solid-gas and solid-solid reaction, while La- and Lc-dimensions of the former being smaller than those of the latter. Boron nitrides fabricated at 800°C in the reaction of boron trichloride with ammonia and in the reaction of boron oxide on tri-calcium phosphate with ammonia were heated at 1400, 1600, 1800 and 2000°C in nitrogen atmosphere of 200 mmHg. The relation between La- and Lc-dimensions of these nitride is shown with the values of starting materials in Fig. 1.

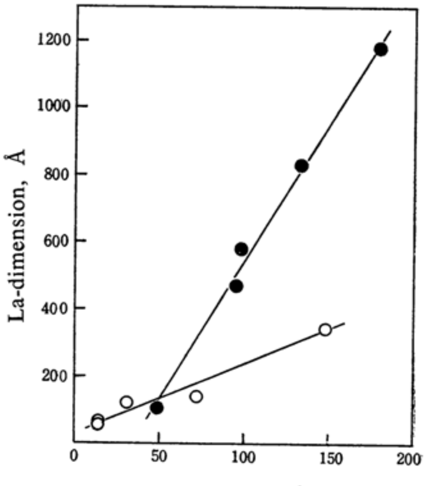

Fig. 1. Crystallite growth of boron nitride by heat treatment.

○ Boron nitride fabricated by the reaction of $BCl_3$ with $NH_3$

● Boron nitride fabricated by the reaction of $B_2O_3$ with $NH_3$

It is shown from Fig. 1 that crystallization of boron nitride formed in solid phase is preferable to that of the nitride in gas phase. It seems that boron nitride formed by gas phase

---

1) R. S. Pease, *Acta Cryst.*, 5, 356 (1952).

2) Th. Renner, *Z. anorg. u. allgem. Chem.*, **298**, 22 (1959).

3) F. Meyer and R. Zappner, *Ber.*, **54B**, 560 (1921).

4) K. M. Tayler, U. S. Navy, Bureau of Ordnance Research Contract NOrd 10982 (1949).

5) J. Kamlet, U. S. Pat. 2865715 (1958).

6) H. Tagawa and O. Itouji, This Bulletine, in press (1962).

reaction and that prepared by solid phase one correspond to non-graphitizing and graphitizing carbons respectively.

*Research Laboratory*
*Nippon Carbide Industries Co., Inc.*
*Uozu, Toyama*