CHEMISTRY LETTERS, pp. 691-692, 1985.

THE SYNTHESIS OF BORON NITRIDE AND BORON CARBIDE BY PYROLYSIS OF BORIC ACID/1,2,3-PROPANETRIOL CONDENSATION PRODUCT

Hiroaki WADA, Shuichi ITO, Kazuyuki KURODA, and Chuzo KATO*
Department of Applied Chemistry, Waseda University, Ohkubo, Shinjuku-ku, Tokyo 160

Both boron nitride and boron carbide were synthesized by the pyrolysis of the boric acid/1,2,3-propanetriol condensation product above 1300 °C in N_2, whereas the thermal treatment in an Ar flow yielded boron carbide.

Polymer pyrolysis is now considered as one of the important methods of preparing various ceramics such as SiC, Si_3N_4, and SiC-B_4C.[1] Boron nitride (BN) was also prepared by using pyrolytic process of a B-N containing polymer.[2] During the study of the thermal stability of borate esters of polyhydroxy alcohols, we found that the borate ester of 1,2,3-propanetriol could be used as a precursor of BN ceramics. Though the preparation and properties of the borate ester of 1,2,3-propanetriol have been reported,[3] its thermal treatment has not yet been investigated. Therefore, we here report the synthesis of BN and B_4C by the thermal treatment of boric acid/1,2,3-propanetriol ester.

The condensation product was prepared by heating an equimolar mixture of H_3BO_3 and 1,2,3-propanetriol at 150 °C in an evaporator. A glassy colorless transparent product was obtained. It showed spinnability on heating. Chemical analysis of the product showed that 1:1 (H_3BO_3:1,2,3-propanetriol) ester was formed (Found: B, 10.48; C,35.73; H,5.01%; Calcd for $(C_3H_5O_3B)n$: B,10.82; C,36.08; H,5.06%). The IR spectrum of the condensation product dissolved in $CHCl_3$ indicated that the dehydration was complete and that both the bonded B-O and C-O absorptions were observed. The product (ca. 1.5 g) was put into an alumina boat, which was then placed in a mullite tube and heated to various temperatures (900-1400 °C) in a N_2 or Ar flow at a rate of 500 cm^3 min^{-1}. The heating rate was 7 °C min^{-1} up to 600 °C, and 5 °C min^{-1} above 600 °C.

When the condensation product was heated under 1200 °C, only B_2O_3 was detected regardless of the gas used and the heating time. The color of the heat-treated samples was black, suggesting that the decomposition of the product produced amorphous carbon and B_2O_3.

When the product was heated above 1300 °C in a N_2 flow for 2 and 4 h, BN and B_4C were formed as shown in Figs. 1a-c. The crystallinity increased with the increases of heating temperature and heating time. However, BN formed in this process was not well crystallized even at 1300 °C. The d_{002} peak at $2\theta=26.6$ ° was very broad. Moreover, the d_{102} peak which was characteristic of the three-dimensional order of BN was absent. This indicated the low crystallinity of the formed BN. The XRD patterns also revealed that small amount of B_4C was formed in this process.

The color of the heat-treated samples was black when heated at 1300 °C, whereas it became gray at 1400 °C. This indicated that the peak at 26.6 ° was mainly ascribed to BN rather than graphite. This was in consistent with the IR spectra. The intensity of the absorption bands around 1400 and 800 cm^{-1} due to BN[4] increased with the increase of heating temperature compared to the peak at about 1080 cm^{-1} assigned to B_4C.[4]

When the borate ester was heated in an Ar flow at 1400 °C for 2 h, boron carbide was detected by XRD (Fig. 1d) and IR. The additional and distinct peak at 2θ=26.6 ° was ascribable to graphite since there was no possibility of forming BN in an Ar flow.

In the XRD patterns, additional peaks except B_4C, BN, and graphite were observed. These peaks were ascribed to $Al_4B_2O_9$ ($2Al_2O_3 \cdot B_2O_3$)[5] or $Al_{18}B_4O_{33}$ ($9Al_2O_3 \cdot 2B_2O_3$)[6] formed by the solid reaction between the ester and the alumina boat. The formation of the oxide was also confirmed by X-ray fluorescence analysis. This result was in agreement with the phase diagram of B_2O_3 and Al_2O_3.[7]

The results indicated that organoborate esters could be used as a precursor for the preparation of boron-containing ceramics.

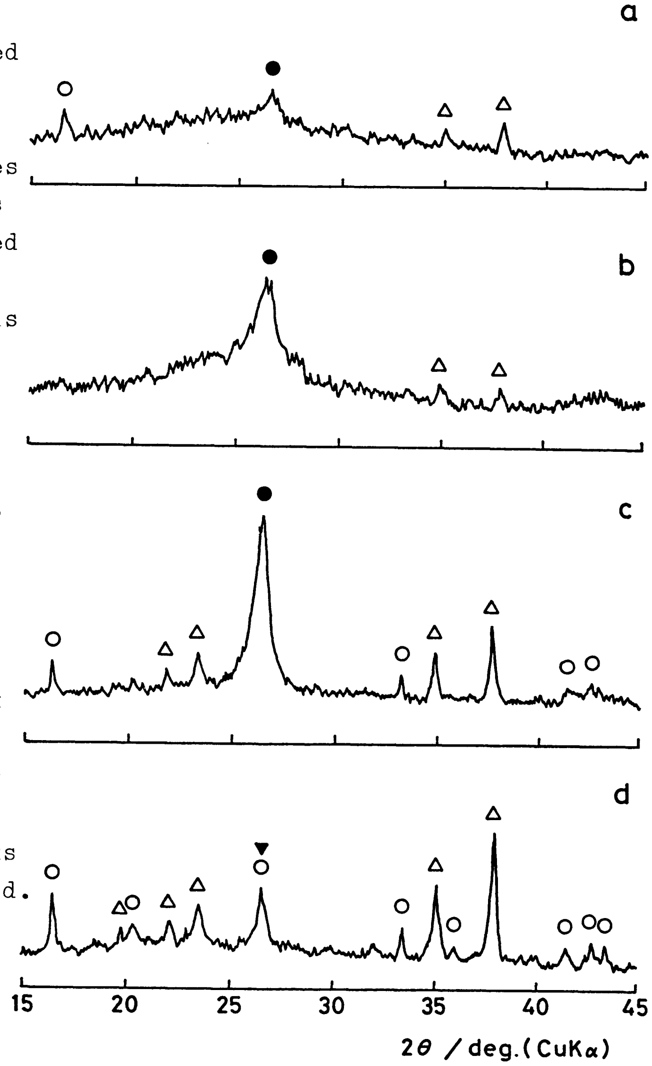

Fig. 1. XRD patterns of heat-treated samples of H_3BO_3/1,2,3-propanetriol condensation product pyrolyzed at (a) 1300 °C,2 h in N_2, (b) 1300 °C, 4 h in N_2, (c) 1400 °C, 4 h in N_2, and (d) 1400 °C, 2 h in Ar.

● BN △ B_4C ▼ graphite
○ $Al_4B_2O_9$ and/or $Al_{18}B_4O_{33}$

This work was supported by the Kawakami Memorial Foundation.

References

1) R. W. Rice, Am. Ceram. Soc. Bull., 62, 889 (1983).
2) I. Taniguchi, K. Harada, and T. Maeda, Japan Kokai, 51-53000 (1976).
3) H. Steinberg, "Organoboron Chemistry, Vol.1 Boron-oxygen and Boron-sulfur Compounds," Interscience, New York (1964), Chap. 5.
4) E. G. Brame, Jr., J. L. Margrave, and V. W. Meloche, J. Inorg. Nucl. Chem., 5, 48 (1957).
5) JCPDS cards, 29-10.
6) JCPDS cards, 32-3.
7) P. J. M. Gielisse and W. R. Foster, Nature, 195, 69 (1962).

(Received January 31, 1985)