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

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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 $2\theta=26.6$ ° 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.

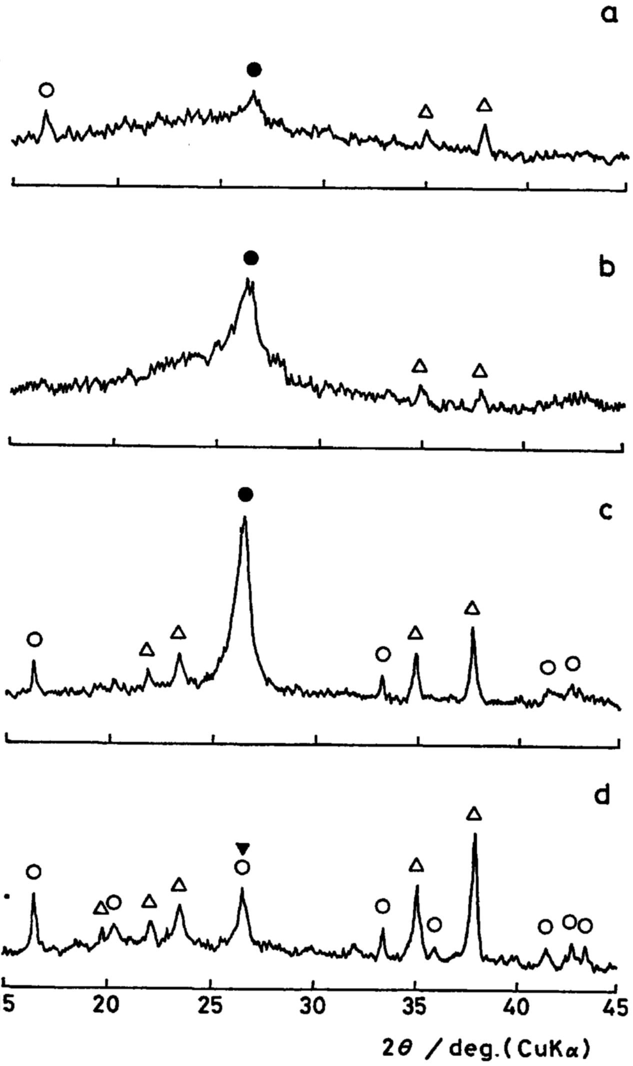

Fig. 1. XRD patterns of heat-treated samples of H_3BO_3/1,2,3-propanetriol condensation product pyrolyzed at (a) 1300 °C, 2 h in N_2, (b) 1300 °C, 4 h in N_2, (c) 1400 °C, 4 h in N_2, and (d) 1400 °C, 2 h in Ar.

● BN △ B_4C ▼ graphite

○ $Al_4B_2O_9$ and/or $Al_{18}B_4O_{33}$

This work was supported by the Kawakami Memorial Foundation.

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(Received January 31, 1985)