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論 文

Synthesis of boron carbide microcrystals from saccharides and boric acid

Akihiro Sudoh, Hidetaka Konno❖, Hiroki Habazaki and Hajime Kiyono

With the precursors prepared from saccharides, such as glucose and cellulose, and boric acid, microcrystals of boron carbides were synthesized at relatively low temperatures of 1500-1600°C by 1 h treatment in an argon atmosphere. Hydrothermal treatment at the stage of precursor preparation was found to be effective to form the precursors which readily decompose to boron carbides in the shape of micrometer-sized crystals. Although a small amount of free carbon is contained in the products and substituted-type boron carbides may be included, this process is interesting: precursor preparation is very simple and the raw materials are inexpensive, above all the process is not hazardous.

KEYWORDS : Boron carbide crystal, Saccharide borate ester, Glucose, Cellulose, Hydrothermal treatment

1. Introduction

Boron carbide is one of the hardest materials and industrially useful. Commercial processes for the production of boron carbide powder are based on the reaction between B_2O_3 and carbon[1]. When carbon is used both as a reducing agent and a reactant, the process requires heat treatment at around 1700°C or higher. The process using magnesium metal as a reducing agent of B_2O_3 in the presence of carbon produces boron carbide at lower temperature, 1000-1200°C, but formed MgO and impurities must be removed by costly post-treatment. Recently, a low temperature process in an autoclave has been reported but raw materials are toxic[2], so that it is unlikely that the process is developed on a commercial scale. We have reported that boron carbide/carbon composites are synthesized from esters of monosaccharides, such as glucose and mannose, and phenylboronic acid[3] or boric acid[4] under relatively mild conditions, *e. g.* 1 h treatment at 1400°C under flowing argon. In these previous works, mole fractions of boron in the stock solutions were not sufficiently large; the maximum mole ratio was B:monosaccharide = 2:1[3),4)]. Accordingly, the formed boron carbide was crystalline particles of sub-micrometers to several micrometers mixed in irregular-shaped carbon matrices. So far the reason why the microcrystals are formed from these esters is not explained, but the method can be developed to a process to synthesize boron carbide micro-crystals less contaminated with carbon by increasing mixing ratio of borate. Thus, this paper is aimed to propose a simple and relatively low cost process to produce boron carbide micro-crystals, and not to investigate detailed synthesis mechanism.

In the present work, precursors were formed with cellulose, a type of polysaccharide, as well as glucose aiming at making good use of abandoned biomass. In addition, hydrothermal treatment was applied to form precursors, expecting the promotion of ester formation which may be favorable for the conversion of precursor to boron carbides[3),4)].

2. Experimental

2.1 Precursor preparation

Commercially available GR grade glucose (GL, $C_6H_{12}O_6$), cellulose (CL, $(C_6H_{10}O_5)_n$) and boric acid (BA, H_3BO_3) were used as raw materials. The cellulose was microcrystalline powder for thin-layer chromatography, and the composition was C: 42.5, H: 6.3, O: 51.2 mass % or C: 27.1, H: 48.3, O: 24.6 mol % by elemental analysis. Boric acid and glucose were dissolved into distilled water at a mole ratio, BA/GL, of 4/1 or 5/1, in which the total borate concentration was about 1.6 mol dm^{-3}. The cellulose was suspended in about 1.6 mol dm^{-3} boric acid solution to be a ratio of four borate molecules per one unit of C_6. Details of the preparation of precursors are summarized in **Table 1** with precursor codes. One GL molecule or one unit of C_6 in CL can form an ester with maximum two borate ions[3]. Therefore, GB(2) of BA/GL = 2/1 was prepared by the same method with GB(4) as a reference material. For GB(2) characteristic bands of borate in FT-IR spectra markedly reduced, supporting the formation of ester.

2.2 Characterization

The precursors were put into a graphite boat and heated to 1000-

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Table 1 Conditions of precursor preparation and the boron content of precursor.

Precursor code	GB(4)	GB(4)Ht	GB(5)Ht	GB(4)Mix	CB(4)Ht	CB(4)Mix
Glucose(GL)/g*1	7.28	7.28	5.23	7.28		
Cellulose(CL)/g*1					6.85	6.85
Boric Acid(BA)/g*1	10.00	10.00	10.00	10.00	10.00	10.00
Mole ratio						
BA/GL or CL*2	4/1	4/1	5/1	4/1	4/1	4/1
Mixed state	Solution	Solution	Solution	Powder	Suspension	Powder
Pretreatment	None	Hydrothermal*3	Hydrothermal*3	None	Hydrothermal*3	None
Final treatment	Drying at 180°C	Drying at 180°C	Dryng at 180°C	Mixing*4	Drying at 180°C	Mixing*4
Boron content/mass%						
Analyzed	12.8	11.8	14.3	12.2	10.3	13.9
Calculated*5	12.2-12.8	12.2-12.8	13.5-14.5	12.2-12.8	12.8-13.5	12.8-13.5

*1 In 100 cm^3 of distilled water except for the powder mixtures.
*2 Per one C_6 unit.
*3 Hydrothermal: Solution or suspension was heat treated at 120°C for 2 h in an autoclave.
*4 Mixing: Powder mixture was heated at 180°C for 1 h in an oven with mixing every 5 min by a spatula.
*5 Lower value is assuming the dehydration of the excess H_3BO_3 to 100% of HBO_2 and higher value to B_2O_3 (*cf.* text *3.1.*).

1600°C at 300 K h^{-1} and kept for 1-10 h at each temperature in a flow of argon. Hereafter, the products are referred to as GB(4)Ht-1500 and so on, where the first symbol is the precursor code in **Table 1**, and the second term heat treatment temperature (HTT) in Celsius. Unless otherwise described treatment time is one hour.

The precursors and products were melted with K_2CO_3 and Na_2CO_3 at 800°C in a Pt crucible, cooled to ambient temperature, and dissolved in concentrated HCl. The HCl solution obtained was diluted and analyzed for boron by inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICPS-IV). The precursors and products were characterized by transmission Fourier transform infrared spectroscopy (FT-IR, JASCO FT-IR-350), X ray diffraction (XRD, Rigaku RAD-X RINT2000, Cu Kα, $\lambda = 0.15418$ nm, $2\theta = 10\text{-}90°$ at 2 deg min^{-1} or 0.02 deg step scan), ^{11}B magic angle spinning nuclear magnetic resonance (MAS-NMR, Bruker MSL-300, 4 T, pulse 4 μs, repetition time 4 s, MAS 14 kHz), thermogravimetry (TG, SII TG/DTA32, 10 K min^{-1} in pure argon), scanning electron microscopy (SEM, JEOL JSM-6300F, 2 kV), and transmission electron microscopy (TEM, JEOL JEM2000ES, 200 kV).

3. Results and discussion

3.1 Characterization of precursors

The aqueous solutions containing GL and BA became viscous by heating above 100°C and slurry started to precipitate with time mainly due to esterification and melting of glucose; finally light brown glass-like materials were obtained. These can be used as precursors but are not convenient to handle. Therefore, drying at 180°C was adopted as the final treatment to obtain powder precursors, as described in **Table 1**, and it was also applied to the preparation of CB(4)Ht.

Glucose melts at around 150°C but does not decompose below 200°C as curve (a) in **Fig.1**, and dehydration of boric acid starts from around 100°C as curve (b). Simply mixed powder of BA/GL = 2/1 decomposes as curve (c), showing the superposed behavior of (a) and (b), which indicates that glucose and boric acid decompose independently. In contrast, GB(2) starts to decompose from around 100°C but the mass loss is much smaller than that of mixed powder as curve (d), showing the effect of ester formation. When esterification is completed, GB(2) is theoretically expressed as $H_2[(C_6H_8O_{10})\{B(OH)_2\}_2]$, though it is uncertain that this form of compound is actually formed by the procedure in **Table 1**. Supposing that two H_2O molecules are removed from this form by dehydration, it results in the loss of 13.5 mass %. This value is attainted at around 275°C of the curve (d) in **Fig.1**, and a large mass loss emerges above 300°C. Accordingly, the initial part of curve (d) suggests that the structure of GB(2) is similar to that described above and condensation polymerization takes place up to about 300°C. This explains slow thermal decomposition of GB(2) and small mass loss at elevated temperatures. In the case of cellulose, the situation will be more complicated and cross-linking of esters may also occur by dehydration.

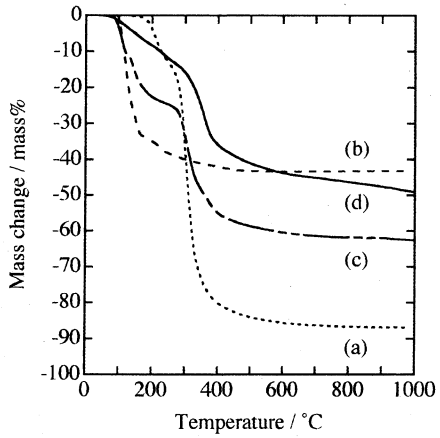

Fig.1 Thermogravimetric curves at 10 K min^{-1} in pure argon: (a) glucose, (b) boric acid, (c) mixed powder of BA/GL = 2/1, (d) GB(2) (*cf.* text *2.1.*)

When there is no interaction between the esters and the excess

amounts of boric acid added, borate may be present as metaboric acid, HBO_2, and boron oxide, B_2O_3, in the precursors, since the mass loss of boric acid at 180°C (curve (b) in **Fig.1**) is 34 mass % and larger than the loss by dehydration from H_3BO_3 to HBO_2. The analyzed boron content of the precursors is shown in **Table 1**, where the calculated values are also shown based on the compositions of $C_6H_{14}O_{10}B_2$ for glucose ester, $C_6H_{12}O_9B_2$ for cellulose ester, and HBO_2 or B_2O_3 for the excess borate. The analyzed values are the averages of a few data and most of them are close to the calculated values, though some values are slightly deviated from the calculated. If the excess borate reacted with the esters by dehydration, boron content is nearly the same with the calculated values in **Table 1**.

3.2 Formation and characterization of boron carbides from glucose-based precursors

Yield by 1 h heat treatment and boron content of the products from glucose-based precursors are shown in **Fig.2**. With all precursors, the yield steeply decreases in a HTT range between 1200 and 1400°C and reaches to a steady value of around 10 mass %. In response to this, the boron content increases markedly. These drastic changes are owing to the formation of boron carbides by pyrolysis, which is confirmed by XRD as shown in **Fig.3** for GB(4)Ht, for example. Diffraction peaks which resemble B_4C (JCPDS 35-798) are distinguishable for GB(4)Ht-1300. In the diffraction pattern for GB(4)Ht-1400 these peaks and a small carbon 002 peak are observed but no other peaks. Above this HTT, carbon peak is not distinguishable. The results by ^{11}B MAS-NMR were parallel to those by XRD as shown in **Fig.4**, in which standard spectra for reagent B_4C (99 %, Kishida Reagent Chemicals, Japan) and B_2O_3 (99.9 %, Soekawa Chemical, Japan) are also shown. For the products below 1300°C sharp peaks due to B_2O_3 around 0 ppm are observed but there are no side bands which are characteristic of boron carbides. In the spectrum for GB(4)Ht-1300 sharp peaks of B_2O_3 remain but the side bands are also distinguished, indicating the formation of boron carbides. The spectrum for the products above 1300°C coincides with that of reagent B_4C, showing that the boron species other than boron carbide are not predominant in these.

The results from the precursors GB(4) and GB(4)Mix compared unfavorably with those from GB(4)Ht, especially the results from GB(4)Mix was poor. Diffraction peaks of B_2O_3 are clearly observed for GB(4)-1400 and GB(4)Mix-1400 as shown in **Fig.5**, while no such peaks are observable for GB(4)Ht-1400 (**Fig.3**). Boron content is much lower than corresponding products from GB(4)Ht (**Fig.2**). Boron content of these products increased by prolonged heat treatment but diffraction peaks of B_2O_3 remained even after 10 h treatment. In addition, carbon 002 peak remained by 1 h treatment at 1500°C. Consequently, single phase of B_4C (by XRD) was formed from GB(4) by 1 h treatment at 1600°C but not from GB(4)Mix. Thus, GB(4) and GB(4)Mix are less reactive than GB(4)Ht. In point of homogeneity, GB(4) and GB(4)Ht are comparable because both prepared from solution and the final treatment condition was the same (**Table 1**). These results demonstrate

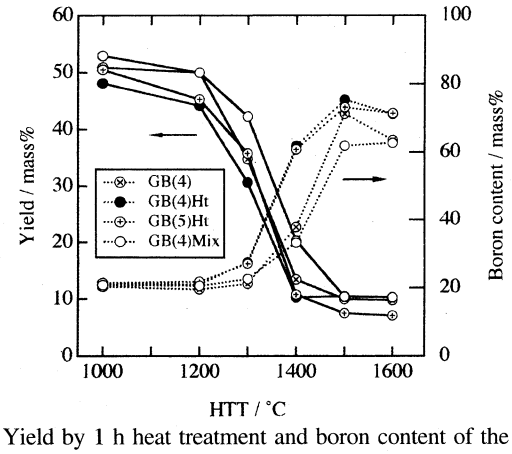

Fig.2 Yield by 1 h heat treatment and boron content of the products from glucose-based precursors.

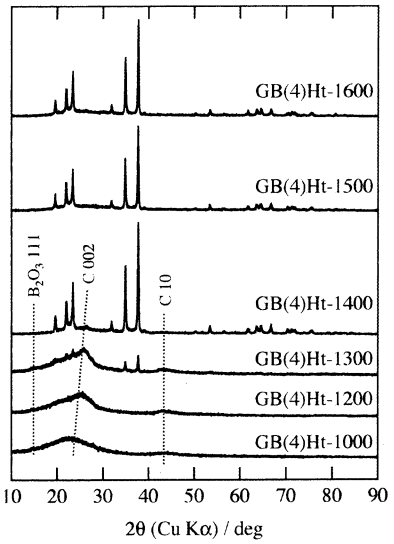

Fig.3 XRD pattern of the products from GB(4)Ht. Diffraction peaks without index are all assigned to B_4C (JCPD 35-798).

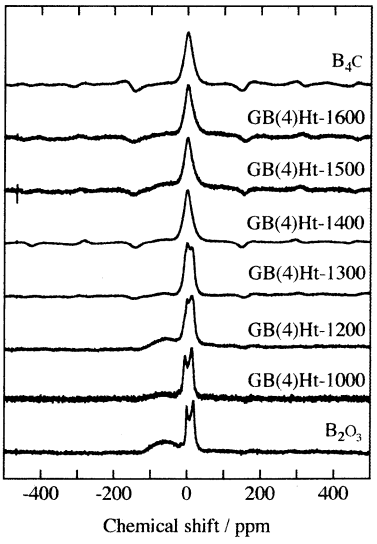

Fig.4 MAS-NMR spectra of the products from GB(4)Ht.

effectiveness of the hydrothermal treatment for precursor preparation, suggesting that the hydrothermal treatment enhances ester formation.

As shown in **Fig.2**, boron content of the products at HTT = 1500-1600°C (single phase by XRD and MAS-NMR) was lower than 78.3 mass % of B_4C. With the intention of increasing boron content of the products, GB(5)Ht was prepared and heat treated. Naturally, boron content in this precursor was highest (**Table 1**) but the content in the products was nearly the same with that from GB(4)Ht (**Fig.2**). Further, the yield above 1400°C was lowest of all (**Fig.2**), suggesting that evaporation of borate was prominent in this precursor. As described above, one glucose molecule can form an ester with two borate ions, so that in case of GB(5)Ht the third excess borate may be free.

3.3 Formation and characterization of boron carbides from cellulose-based precursors

Fig.6 shows yield after 1 h heat treatment and boron content of the products from CB(4)Ht and CB(4)Mix. There is no distinctive difference in the decomposition behavior of these two precursors, and the results are generally the same with that of glucose-based ones. The XRD patterns for the products, however, were clearly different as shown in **Fig.7**. Strong diffraction peaks of B_2O_3 are present in the pattern for CB(4)Mix-1400 and they were clearly distinguished after 10 h treatment, whereas they are very weak for CB(4)Ht-1400. Carbon 002 peak is broad for CB(4)Mix-1400 and sharp for GB(4)Ht-1400. These characteristic differences depending on the precursors prepared by hydrothermal method and mixing method (**Table 1**) are similar to the results for glucose-based precursor (**Figs.3** and **5**), but they are more intense for the cellulose-based precursors. This indicates that in case of CB(4)Mix, cellulose and borate independently decompose to carbonaceous materials and B_2O_3, and then react at higher HTT, while the formation of boron carbides from CB(4)Ht proceeds mainly through direct pyrolysis of the integrated materials. Diffraction peaks of B_2O_3 and carbon are observed in CB(4)Mix-1500 but no such impurity peaks in the pattern of CB(4)Ht-1500. Accordingly, it is reasonably concluded that the hydrothermal treatment is effective also in the formation of cellulose-based precursor.

3.4 Morphology and structure of boron carbide crystals

SEM images of single phase boron carbide (by XRD) from glucose-based and cellulose-based precursors are shown in **Figs.8** and **9**, respectively. It is obvious that the present process produces microcrystalline boron carbide, and depending on the precursor the following features are observed:

(a) Size of crystals from GB(4)Ht and GB(5)Ht is about a few to 10 μm, and large plate-like crystals are also formed.

(b) GB(4)gives similar type crystals to those from GB(4)Ht and GB(5)Ht, but also forms agglomerated sub-micrometer

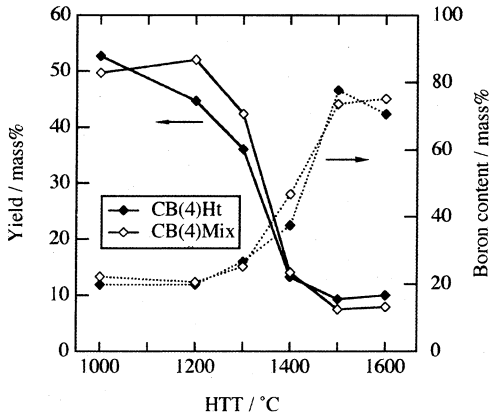

Fig.6 Yield by 1 h heat treatment and boron content of the products from cellulose-based precursors.

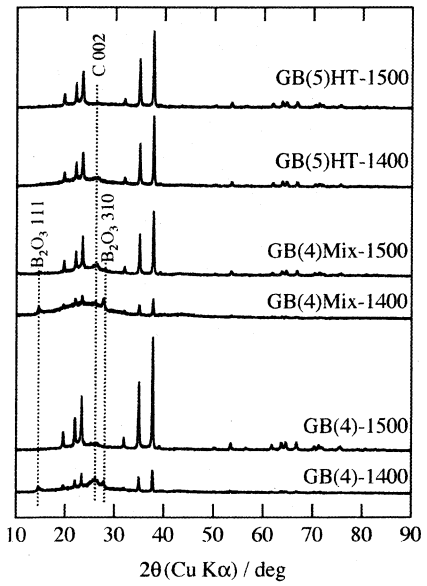

Fig.5 XRD patterns of the products from different precursors. Diffraction peaks without index are all assigned to B_4C (JCPDS 35-798).

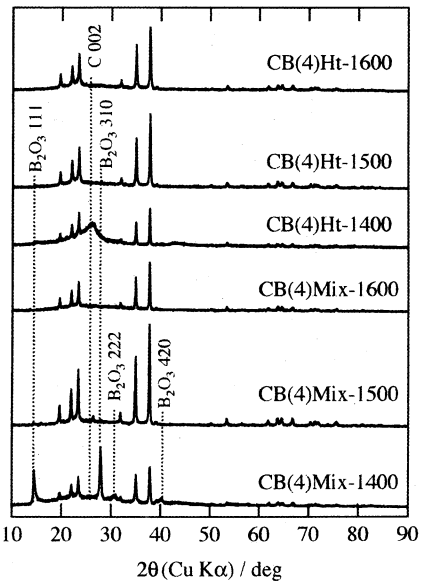

Fig.7 XRD patterns of the products from cellulose-based precursors. Diffraction peaks without index are all assigned to B_4C (JCPDS 35-798).

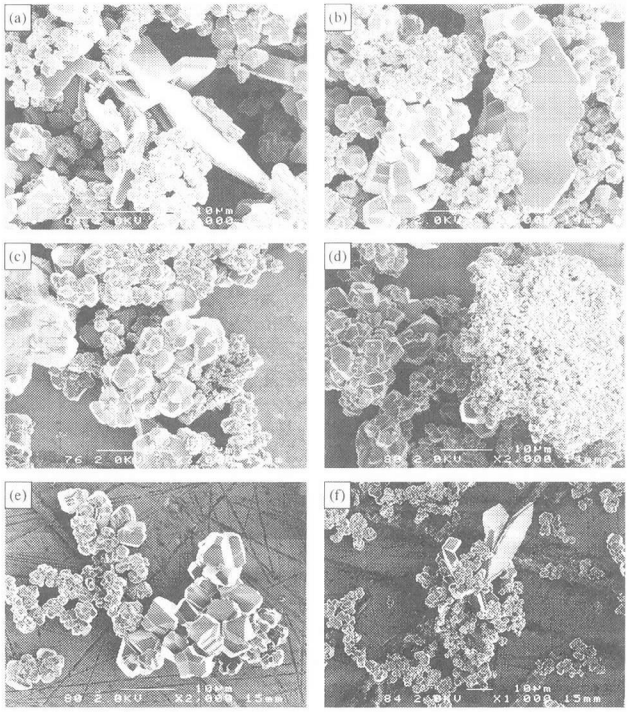

Fig.8 SEM images of the products from glucose-based precursors which were single phase by XRD: (a) GB(4)Ht-1500, (b) GB(4)Ht-1600, (c) GB(4)-1500, (d) GB(4)-1600, (e) GB(5)Ht-1500, and (f) GB(5)Ht-1600. Bars are 10 μm.

crystals. Plate-like crystals are not observed.

(c) Crystals from CB(4)Ht are generally much smaller than those from the glucose-based precursors and sub-micrometer-sized particles are predominant.

By selected area electron diffraction using TEM these crystals were found to be polycrystalline, though nearly idiomorphic types were also observed by SEM. There is a tendency for larger crystals to grow from the precursors prepared from solution and by hydrothermal treatment, but detailed mechanism why such crystals are formed is not explained at present. It is only presumed that the precursors GB(4)Ht and GB(5)Ht melt to form a matrix having uniform composition during the heating process and crystalline particles are deposited from it during heating at constant temperature and on cooling.

The boron content of the products in **Figs.8** and **9** was lower than the stoichiometric one (**Figs.2** and **6**), but hexagonal lattice constants were $a = 0.5602$ nm and $c = 1.2083$ nm for GB(4)Ht-1500, and $a = 0.5599$ nm and $c = 1.2070$ nm for GB(4)Ht-1600, which are close to 0.56003 nm and 1.2086 nm of B_4C (JCPDS 35-798). This indicates that actually boron carbide crystal is formed, though amorphous free carbon is contained. There is a wide diversity of detailed crystalline structure for boron carbide solid solution[1]. The rhombohedral crystalline structure of boron carbide is commonly drawn by icosahedral B_{12} linked by direct covalent bonds and inter-icosahedral chains of C_3. It is reported, however, that the central position in the C-C-C chain is partially substituted by boron atom[5)-9)].

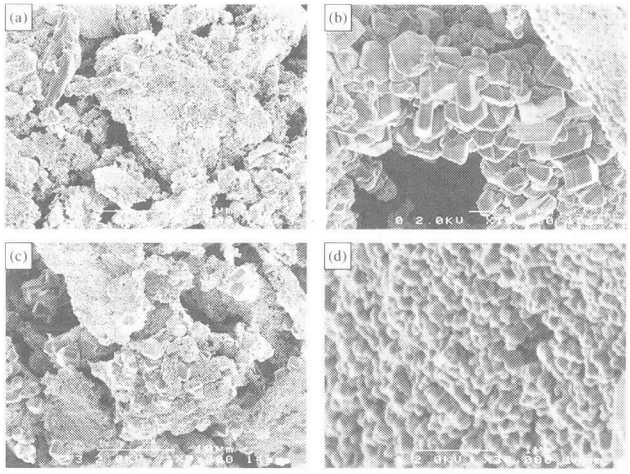

Fig.9 SEM images of the products from CB(4)Ht which were single phase by XRD: (a) (b) CB(4)Ht-1500, and (c) (d) CB(4)Ht-1600. Bars are 10 μm for (a) and (c), and 1 μm for (b) and (d).

Conclusive evidence on the detailed crystalline structure was not obtained from additional measurements by FT-IR and Raman spectroscopy. Therefore, substituted-type boron carbides may be included.

4. Summary

Boron carbide microcrystals were synthesized from the precursors composed of glucose or cellulose and boric acid under relatively mild conditions of 1 h treatment at 1500-1600°C in an argon atmosphere. The thermal decomposition behavior of precursor, and the structure and morphology of products strongly suggest that hydrothermal treatment at the stage of precursor preparation enhances ester formation between saccharides and borate, leading to the precursors which readily decompose to boron carbides in the shape of micrometer-sized crystals. Although a small amount of free carbon is contained in the products and substituted-type boron carbides may be included, this process is interesting: precursor preparation is very simple and the raw materials are inexpensive, above all the process is not hazardous.

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