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SYNTHESIS OF C/B₄C COMPOSITES FROM SUGAR-BORIC ACID MIXED SOLUTIONS

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B/C composites containing crystalline B₄C particles were synthesized at 1400°C from the precursor composed of sugar-borate complexes. The precursors prepared from aqueous solutions of glucose and boric acid were found to be advantageous to the formation of B₄C at low temperatures.

Keywords: boron carbide; B/C composites; glucose; boric acid

INTRODUCTION

B/C-composite materials are potentially useful as oxidation-resistant carbon materials, neutron absorbers, host materials for lithium intercalation, semiconductors, and so on. Previously we have reported a process to form B/C composites containing B₄C from sugar-organoborane complexes which were synthesized in organic solvents [1]. It was found that B₄C started to form at around 1300°C from these precursors, showing that B₄C can be synthesized with much lower energy. The process is promising, but the use of organic solvents, which are volatile and/or not decomposed easily in the environment, should be avoided with the aim of developing a harmless, low cost process. In the present work, we report the results using aqueous solutions of glucose and boric acid.

EXPERIMENTAL

Commercially available GR grade glucose (GL, C₆H₁₂O₆) and boric acid (BA, H₃BO₃) were used as raw materials. GL and BA were dissolved into distilled water in a mole ratio of 2:1 to 1:2, and the mixed solutions were

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heated at 200°C in air for 2.5 h. By this procedure, caramel-like precursors (GL-BA), which were easily crushed to pieces, were obtained. These precursors were put into a graphite boat and heated to 1200–1400°C at 300 K h⁻¹ and kept for 1 h at each temperature in a flow of Ar. Hereafter, GL-BA with the mole ratio of 2:1 treated at 1200°C is referred to as GL-BA(2:1)1200, and so on.

The precursors and products were melted with K₂CO₃ and Na₂CO₃ in a Pt crucible, cooled to ambient temperature, and dissolved in conc. HCl. The HCl solution obtained was diluted and analyzed for boron by inductively coupled plasma atomic emission spectrometry (ICP-AES). The precursors and products were characterized by X ray diffraction (XRD), magic angle spinning nuclear magnetic resonance (MAS-NMR), Raman spectroscopy, thermo-gravimetry (TG), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

One GL molecule can form a complex (or ester) with maximum two borate ions. The aqueous solutions containing GL and BA became viscous by heating above 100°C and slurry started to precipitate with time due to esterification; finally light brown glass-like materials were obtained. These can be used as precursors but are not convenient to handle. Therefore, the solutions were heated at 200°C for 2.5 h to obtain powder precursors, as mentioned above. The analytical boron content of GL-BA(1:1) was

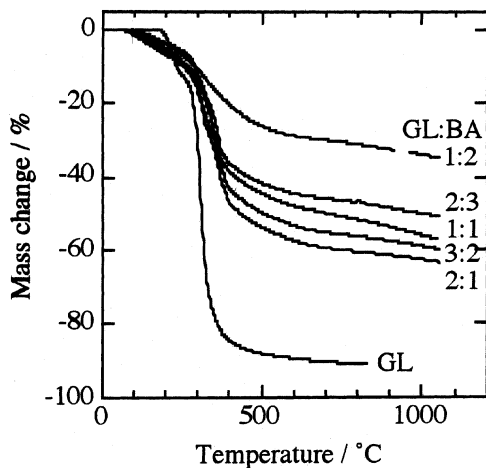


FIGURE 1 Carbonization curves.

5.0 mass%, and that of GL-BA(1:2) 9.4 mass%, on average. These values are slightly larger than the calculated boron content of each complex, 4.8 and 8.1 mass%, so that the precursors were slightly decomposed, probably by dehydration, during the preparation.

Decomposition curves of GL-BA and GL at 10 K min⁻¹ in a flow of Ar are shown in Figure 1. Major mass loss of GL-BA occurred between 300 and 400°C similar to GL. The yield at 1000°C became smaller with increasing GL:BA mole ratio but was still larger than that of sugar-organoborane complexes (ca. 35 mass% [1]).

XRD patterns of the products formed from different GL-BA at 1200°C are shown in Figure 2. Peaks of B₄C (JCPDS 35-798) are distinguishable for GL/BA ≤ 1 even at this temperature, though B₂O₃ is a major boron species. The results clearly show that higher boron content is favorable to the formation of B₄C. For GL-BA(2:1)1400, however, weak peaks of B₄C were observed and no B₂O₃ peaks appeared.

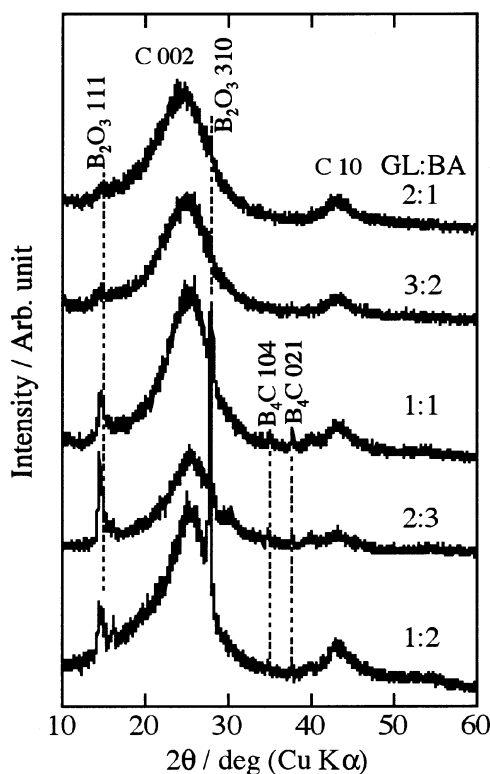


FIGURE 2 XRD patterns of the products from different GL-BA at 1200°C.

XRD patterns of GL-BA(1:2)1300 – GL-BA(1:2)1400 are shown in Figure 3. Crystalline B_2O_3 decreased markedly above 1300°C and no B_2O_3 peaks were observed for GL-BA(1:2)1400. XRD pattern of the product at 1400°C from a powder mixture of GL:BA = 1:2 is also shown in Figure 3. Large B_2O_3 peaks are observed in this sample, which indicates that the complex formation is a very effective and necessary process to form B_4C at low temperatures. Raman spectra of B_4C for GL-BA(1:2)1350 and GL-BA(1:2)1400 were much more intense than those for the products from sugar-organoborane complexes [1]. MAS-NMR spectrum of GL-BA(1:2)-1400 is shown in Figure 4. The spectrum agrees well with that of commercially available B_4C including the side band structure, showing that the boron species other than B_4C were trace amounts in GL-BA(1:2)1400. In contrast to this, in the spectrum of the product at 1400°C from the sugar-organoborane complex, broad shoulder peak was observed at the right hand side of the B_4C peak. This was considered to be due to the presence

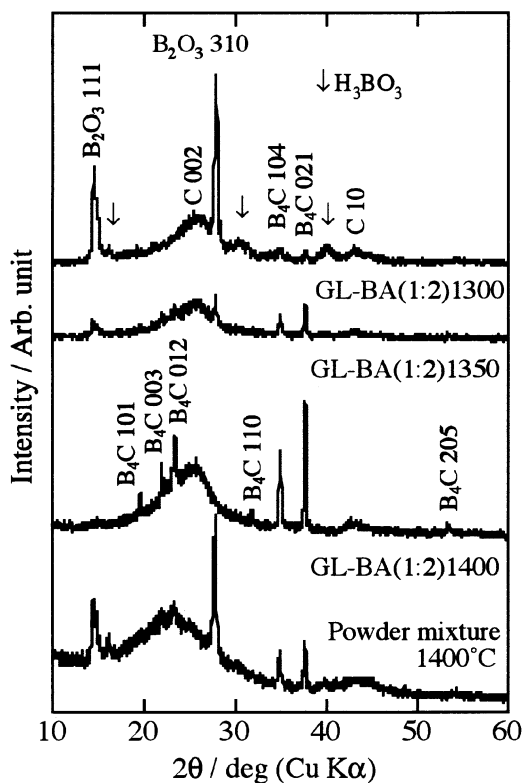


FIGURE 3 XRD patterns of GL-BA(1:2) treated at different temperatures.

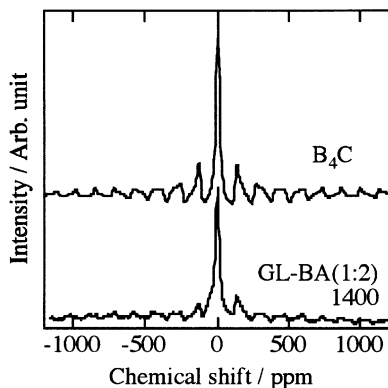


FIGURE 4 MAS-NMR spectra.

of dissolved boron species in a carbon matrix [1,2]. Differences between the present precursors and the sugar-organoborane complexes can be attributed to the different borate compounds used, that is, boric acid and phenylboronic acid. The mechanism that dissolved boron species are formed with the latter, however, is not clear at present.

The average boron content of GL-BA(1:2)1400 was about 26 mass%, but the analytical values varied widely: the scattering was very different from the results for precursors and the products at 1350°C and lower. This is probably due to sampling, since B₄C crystals were formed and dispersed in the products randomly. SEM photographs of GL-BA(1:2)1400 are shown in Figure 5. There were many crystals of a few micrometers in size in various parts of the carbon matrix. They were identified to be single crystals of B₄C by TEM and selected area electron diffraction, although the stoichiometry

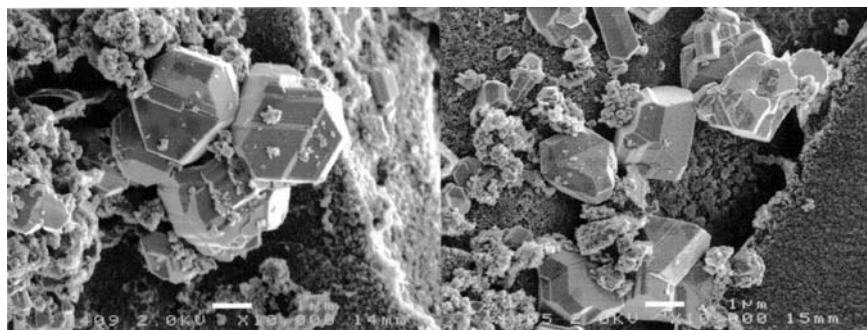


FIGURE 5 SEM photographs of GL-BA(1:2)1400. Bars are 1 μm.

of B_4C must be examined more precisely. The crystalline particles in micrometer size were not observed in the products from the sugar-organoborane complexes under the same heat treatment condition. Thus, the present method produces a mixture of pure B_4C crystals and carbon. When the present process is considered to an industrial process of B_4C production, separation of B_4C crystals from matrix carbon is a problem to be solved.

In sum, with the precursors prepared from aqueous solutions of glucose and boric acid, single crystals of B_4C were formed at as low temperature as $1400^\circ C$; the temperature is about 1400 K lower than the process used for industrial production. Most of the methods to produce B_4C are reported to require $1700^\circ C$ and higher [3–5]. Preparation of the precursor from aqueous solution is very simple and the raw materials are inexpensive. Above all the process is not hazardous.

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