Journal of Metals, Materials and Minerals, Vol. 29, No. 3, pp. 48-53, 2019

Phase formation of boron carbide powder synthesized from glutinous rice flour

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Received date:
29 September 2018
Revised date:
15 February 2019
Accepted date:
23 March 2019

Keywords:
Boric acid
Glutinous rice flour
Phase formation
Boron carbide

Abstract

Boron carbide is an attractive material because of its very high hardness and low density. A number of synthesis processes to produce various forms of boron carbide powders have been reported. In this study, the feasibility of boron carbide synthesis using an inexpensive carbon source, glutinous rice flour, was investigated. Boric acid and glutinous rice flour with the molar ratios, ranging from 2:1 to 4:1, were homogeneously mixed with deionized water at 80°C. The mixtures were dried and pyrolyzed at 700°C for 2 h in air. The phase present and the carbon: boron oxide molar ratio of the pyrolyzed precursor were determined in order to control boron and carbon contents for the synthesis process. The precursor was synthesized under an Ar flow in a tube furnace at 1350°C - 1450°C for 1, 3 and 5 h. Phase analysis, chemical bonding and morphology of the synthesized powder were identified by X-ray diffraction, Fourier-transform infrared spectroscopy and scanning electron microscopy, respectively. It was found that formation of B_4C as a major phase was observed at 1450°C, though unreacted B_2O_3 and carbon still persisted in the final product. In addition, the composition with large number of hydroxyl group showed the B_4C phase formation at lower temperature and shorter soaking time.

1. Introduction

Boron carbide (B_4C) is one of the hardest ceramic materials, next to diamond and cubic boron nitride. It is well known for its excellent properties such as low density, high hardness, high melting point, good wear resistance, elastic modulus, good chemical stability, and high neutron absorption cross section [1,2]. The combination of these properties makes B_4C an ideal material for numerous applications such as ceramic armor, abrasive powder, cutting tools, nuclear and aerospace applications [3].

B_4C powder can be synthesized by various methods [4] such as magnesiothermic reduction, synthesis from elements, vapor phase reactions, synthesis from polymer precursors, and carbothermic reduction. The most widely used method for synthesizing B_4C powder on an industrial scale is carbothermic reduction. This process is carried out in an electric arc furnace using boron oxide (B_2O_3) and carbon black as starting materials at a high temperature of approximately 2000°C. The overall reaction is illustrated in equation 1.

$$2B_2O_3\ (l,g) + 7C\ (s) \rightarrow B_4C\ (s) + 6CO\ (g) \qquad (1)$$

This process has several problems including carbon residue in the final product due to boron loss by volatilization and agglomeration of the synthesized powder caused by the high synthesis temperature. This agglomerated and extremely hard B_4C powder has to be ground to gain desirable particle size for the next step of fabrication process. Therefore, the development of low temperature synthetic route is required to achieve low cost manufacturing.

In recent years, low temperature synthesis of B_4C powder from boric acid and a variety of organic precursors such as citric acid [5], glycerin [6], polyvinyl alcohol [7], sucrose [8,9], cellulose [10,11], and starch [10] have been intensively studied. By these processes, B_4C powder can be synthesized at a much lower temperature than that of the traditional process. This may be caused by the formation of borate ester bonds during the condensation process which facilitates the reaction kinetics to form boron carbide at a lower temperature. Vijay et al. [9] successfully synthesized B_4C powder by the carbothermic reduction process using a mole ratio between boric acid and sucrose equal to 3.38. The formation of crystalline B_4C was observed at 1600°C for 10 min with a free carbon content of 2.5 wt%. Zahid et al [11] studied the effect of structural homogeneity of the precursor on low-temperature synthesis of B_4C using cellulose as a carbon source dissolved in ethylene glycol. The formation of crystalline boron carbide was observed at 1200°C. However, utilization of glutinous rice flour, which is an inexpensive and environment-friendly carbon source for B_4C powder synthesis, has not been reported. As an organic starch with –OH functional groups in its structure, glutinous rice flour can react with boric acid to form B-O-C esterification bonding,

DOI: 10.14456/jmmm.2019.33

enhancing the low temperature synthesis of B_4C. In this study, the feasibility of boron carbide synthesis using an inexpensive carbon source from Thai glutinous rice flour was investigated. The effects of starting composition and synthesis temperature on the phase formation of the synthesized boron carbide powder are discussed.

2. Experimental

2.1 Material preparation

Boric acid (99.5%, Fisher Chemical) and glutinous rice flour (d_{50}~13 micron, commercial grade, Thailand) were used as boron and carbon sources, respectively. Particle morphologies of the starting materials are shown in Figure 1. Boric acid consisted of > 200 μm clusters whereas agglomerates of 3-7 μm particles were observed in the glutinous rice flour. In this study, 7 starting precursor compositions were prepared by adjusting the molar ratios between boric acid and glutinous rice flour = 2:1, 2.5:1, 2.75:1, 3:1, 3.5:1, 3.75:1, and 4:1. These precursor compositions were named P2-P4, according to the molar ratio of boric acid in the compositions. Boric acid and glutinous rice flour were separately dissolved in distilled water by continuously stirring at 80°C. The solutions were homogeneously mixed together and further stirred at 80°C for 2 h. The precursors were dried in an oven at 100°C for 24 h followed by heat treatment at 700°C for 2 h in air. The pyrolyzed precursors were placed in graphite crucibles and synthesized at 1350-1450°C for 1-5 h in a tube furnace with an Ar flow rate of 3 ml/min.

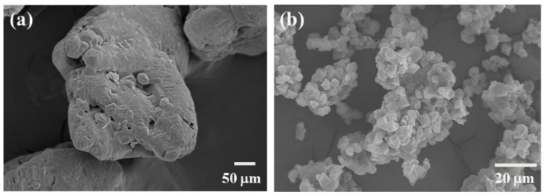

Figure 1. SEM images of starting materials (a) boric acid (b) glutinous rice flour.

2.2 Characterizations

Chemical functions in the starting materials, precursors and pyrolyzed precursors were analyzed by Fourier transform infrared spectroscopy (FTIR: Nicolet, model Impact 400, USA) using KBr tablets at a spectra range of 400-4000 cm^{-1}. The C/B_2O_3 mole ratio (ψ) of the pyrolyzed precursors was calculated according to equation 2

$$\psi = (5.8 \times m_2)/(m_1 - m_2) \qquad (2)$$

where m_1 is the total weight of the pyrolyzed precursor and m_2 is the weight of carbon in the pyrolyzed precursor. B_2O_3 was removed by treating the pyrolyzed precursor in 80°C hot distilled water so that carbon weight (m_2) could be measured [10-12]. The B_4C peak intensity ratio of each component (I_{B4C}, I_C and I_{B2O3}) in the XRD pattern was estimated from equation 3;

$$B_4C \text{ peak intensity ratio} = (I_{B4C}/I_{B4C}+I_C+I_{B2O3}) \qquad (3)$$

where I_{B4C}, I_C and I_{B2O3} denote the main peak intensities in an XRD pattern of B_4C ((021) reflection at 2θ ~ 37.8°), carbon (amorphous halo at 2θ ~ 26°) and B_2O_3 ((310) reflection at 2θ ~27.8°), respectively. Phase identification was carried out at room temperature using an X-ray diffractometer (XRD: Bruker, D8 Advance, Germany) operated at 40 kV and 40 mA with monochromatized Cu-K_α (λ = 1.5418 Å) radiation at a scanning rate of 1°/min. The morphology of the synthesized powder was observed using a scanning electron microscope (SEM: JOEL, JSM-6480LV, Japan) operated at 20.0 kV.

3. Results and discussion

3.1 FTIR spectra of precursors

The FTIR spectra of the starting materials were analyzed and compared with those of the precursors, as shown in Figure 2. For the boric acid spectrum, the broad bands at 3000-3500 and 1300-1600 cm^{-1} corresponded to the O-H and B-O stretching vibration, respectively, whereas the strong band at 1198 cm^{-1} was assigned to the bending vibration of B-OH [13-15]. The glutinous rice flour spectrum revealed the appearance of bands at 3000-3600 cm^{-1}, 2800-3000 cm^{-1}, 1650 cm^{-1} and 1000-1200 cm^{-1} which were attributed to the O-H, C-H, C=O and C-O-C stretching vibrations, respectively [16-17]. The presence of –OH and –CO functional groups in the glutinous rice flour accommodated the homogenous condensation reaction with boric acid to produce an appropriate precursor for B_4C synthesis. FTIR spectra of the 7 precursor compositions were similar to each other, but different from the starting materials. Compared to the starting materials, the FTIR spectra of all precursors revealed the additional stretching vibration bands of the B-O-C bond at 1022, 1080, 1105 and 1158 cm^{-1}, indicating the formation of cross-linkages between polymeric chains in the glutinous rice flour and the boric acid after mixing with boric acid [5,6]. FTIR spectra of the pyrolyzed precursors are shown in Figure 3. The appearance of B-C bonding in the pyrolyzed precursors is in good agreement with the previous studies [18-19].

The C/B_2O_3 molar ratios of precursors pyrolyzed at 700°C for 2 h in air are shown in Figure 4. It was found that the molar ratio of carbon to boron oxide increased with the increasing proportion of glutinous rice flour in the starting composition. According to the stoichiometric carbothermic reaction (1) between boron oxide and carbon to form boron carbide, the C/B_2O_3 molar ratio of the pyrolyzed precursor should be close to 3.5 so that, P2.5, P2.75 and P3 were selected for the further study.

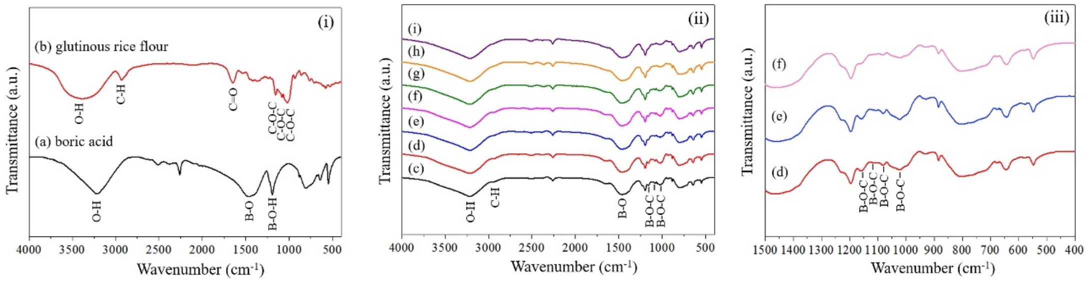

Figure 2. FTIR spectra of (i) (a) boric acid and (b) glutinous rice flour, (ii) (c) P2, (d) P2.5, (e) P 2.75, (f) P3, (g) P3.5, (h) P3.75 and (i) P4 and (iii) magnified image of (ii).

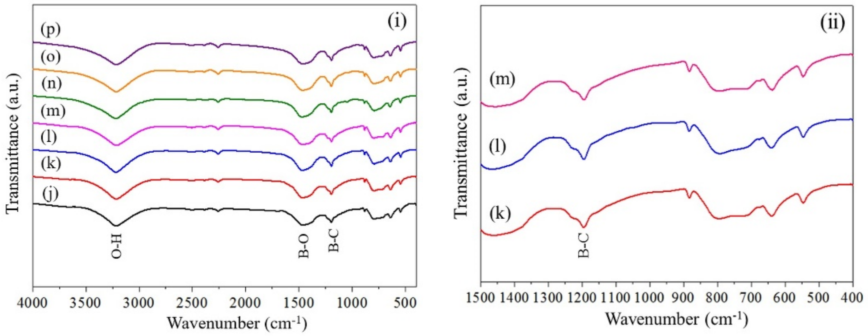

Figure 3. FTIR spectra of pyrolyzed precursors at 700°C of (i) (j) P2, (k) P2.5, (l) P 2.75, (m) P3, (n) P3.5, (o) P3.75 and (p) P4 and (ii) magnified image of (i).

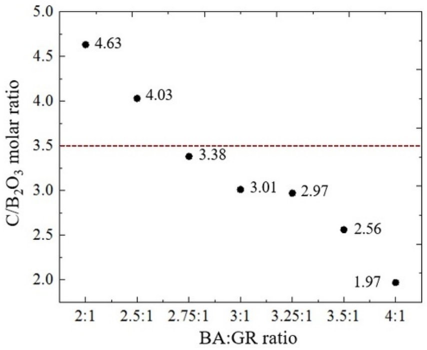

Figure 4. C/B_2O_3 molar ratios of the precursors pyrolyzed at 700°C for 2 h.

The morphology of the precursors; P2.5, P2.75 and P3 shown in Figure 5(a-c) indicated a variety of particle and/or agglomerate sizes of boric acid dispersed in a carbon matrix after the condensation process. During pyrolysis, the boric acid decomposed to B_2O_3 which could be removed by washing in hot deionized water, thus leaving the carbon component in the pyrolyzed precursors. Figure 5(d-f) shows SEM images revealing the porous carbon structure in the pyrolyzed precursors. The significant distinction in pore structure between the three compositions was not detected but compared to the previous study [20] which showed more uniformed pore distribution, the precursor preparation process in the present study might need to be adjusted.

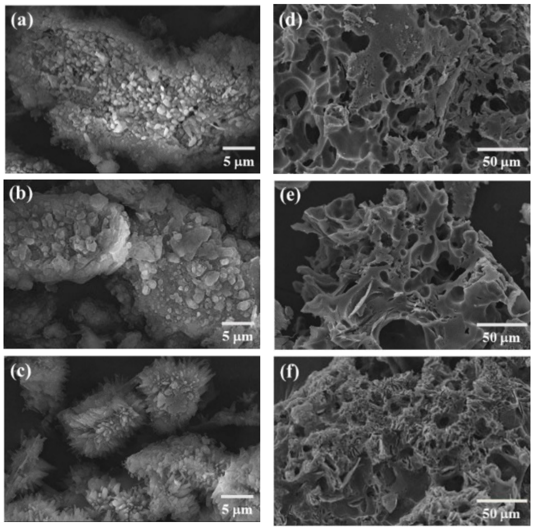

Figure 5. SEM images of (a-c) precursors and (d-f) pyrolyzed precursors after washing with hot deionized water: (a-d) P2.5, (b-e) P2.75 and (c-f) P3.

3.2 Phase analysis of the synthesized powder

The evolution of B_4C peak intensity ratios of P2.5, P2.75, and P3 at 1350, 1400°C and 1450°C for 1, 3 and 5 h are summarized in Figure 6. All three compositions showed similar results where B_4C peak intensity ratios increased with the increasing synthesis temperatures and soaking times. This was probably attributed to an increase in reactivity of the reaction (1) at higher temperature. At 1350°C B_4C peak intensity ratios of the three synthesized powders were not significantly different. At a higher temperature with longer soaking time, the B_4C peak intensity ratios obtained from P2.5 were higher than those from P2.75 and P3. P2.5 as the starting composition with a large number of hydroxyl groups possibly reacted with nearby boric acid to form a high amount of B-O-C condense product and this enhanced the kinetics of the B_4C reaction.

Figure 7 shows the XRD patterns of P2.5, P2.75 and P3 synthesized at 1350, 1400 and 1450°C for 5 h. The B_4C phase formation of all three samples increased with the increasing synthesis temperature. At 1450°C, rhombohedral B_4C (JCPDS #00-035-0798) was detected as a major phase in P2.5 and P2.75, while unreacted carbon (JCPDS #00-026-1076) and B_2O_3 (JCPDS #00-013-0570) also remained in the powder. Similar results have been reported by Kakiage *et al.* [20] who synthesized B_4C powder from H_3BO_3-poly (vinyl alcohol). It was explained that the higher number of hydroxyl groups in the high PVA precursor improved the degree of dispersion of H_3BO_3 in the PVA network chains. With this assumption, higher number of contacts between B and C was expected in the carbon-rich pyrolyzed composition of P2.5 which enhancing the conversion rate to form B_4C.

3.3 Morphology of the synthesized powder

Particle morphology of P2.5 synthesized at 1450°C for 5 h is displayed in Figure 8. The synthesized powder was agglomerated and consisted of ~10-25 μm equiaxed crystals. B_4C particles with a rhombohedal shape and size of ~20 μm were also observed. In addition, the residual unreacted B_2O_3 and C were detected by EDS analysis. More uniformity of B and C species dispersed in the precursor are required to improve the conversion rate of the final product.

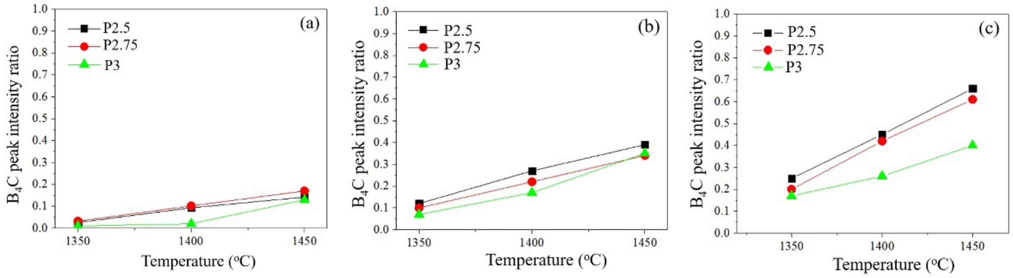

Figure 6. B_4C peak intensity ratios of P2.5, P2.75 and P3 synthesized at 1350, 1400 and 1450°C for (a) 1 h, (b) 3 h and (c) 5 h under Ar flow.

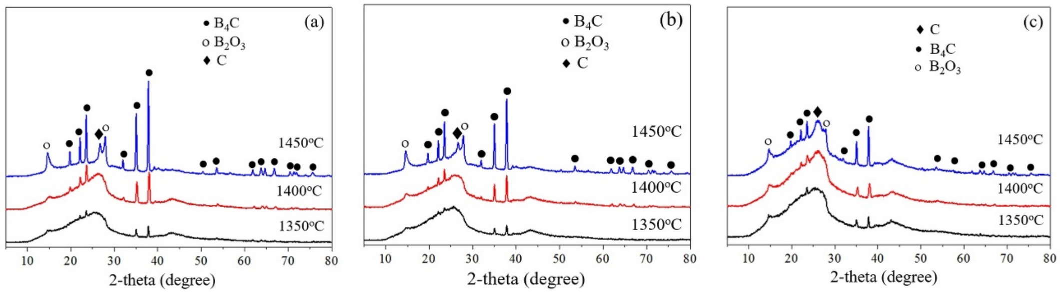

Figure 7. XRD patterns of powders synthesized at 1350°C, 1400°C and 1450°C for 5 h: (a) P2.5, (b) P2.75 and (c) P3.

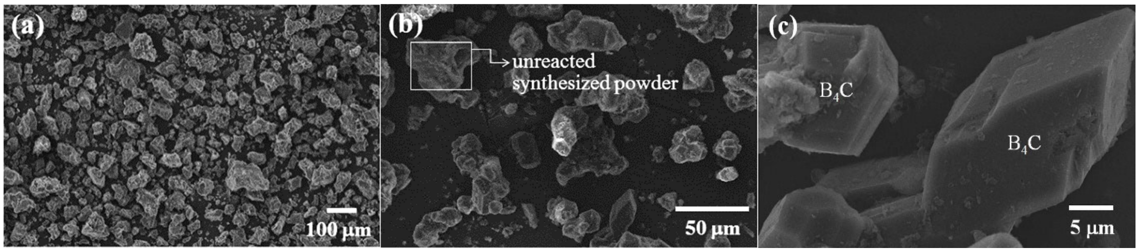

Figure 8. SEM images of P2.5 synthesized at 1450°C with soaking time 5 h (a) magnification 100X (b) magnification 500 X and (c) magnification 3000 X.

4. Conclusions

B_4C powder was synthesized using boric acid and glutinous rice flour as boron and carbon sources (molar ratios of acid: flour = 2:1 to 4:1) at 1350-1450°C for 1-5 h under an argon flow. In this study, at the synthesis temperature of 1350°C for 1 h, rhombohedral B_4C appeared as a minor phase. The XRD peak intensity of B_4C increased with the increasing synthesis temperature and soaking time. B_4C was the major phase observed at 1450°C, though unreacted B_2O_3 and carbon still persisted in the final product. Compared to P2.75 and P3, phase formation of crystalline B_4C in P2.5, which consisted of a large number of hydroxyl group, was observed at lower temperature and shorter soaking time.

5. Acknowledgements

The authors would like to acknowledge financial support from The 100th Anniversary Chulalongkorn University Fund for Doctoral Scholarship. Highly thankful to Department of Materials Science, Faculty of Science, Chulalongkorn University and National Metals and Materials Technology Center for the characterization equipment.

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