

Synthesis of High Purity Micron Size Boron Carbide Powder from B₂O₃/C Precursor

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Abstract— Among the refractory carbides, next to carbides of tungsten, titanium and silicon carbide, boron carbide (B₄C) has of late assumed great significance as a strategic material because of its high hardness, low density, and high cross section for neutron absorption, chemical inertness, and etc. The main applications of this material include military industries, nuclear industries, solid fuels for rockets, coating resistant component, and etc. In this research, boron carbide has been produced by sol-gel method from inexpensive raw materials such as boric acid and citric acid in micron particle size. Aqueous solution of boric acid in presence of citric acid forms a stable gel under controlled pH condition (pH=2-3). The gel pyrolyzed at 600, 650, 700 and 750 °C temperatures under vacuum. From XRD patterns it was found that the ratio of B₂O₃ to C in the precursor powder pyrolysed at 650 °C was better compare to the other temperatures for production of composite precursor with carbon matrix and boron oxide as reinforcement. Those composite precursors heated under vacuum at 5 °C /min up to 1350, 1450 and 1500 °C and kept 2.5 hrs. Final product has been characterized by X-ray diffraction (XRD), particle size analysis (PSA), scanning electron microscopy (SEM) and chemical analyses. The purity of product for 1.6 and 1.9 ratios of raw materials is 86.14% and 91.26% (weight percent), respectively. By using this method boron carbide powder with D90 equal to 3.43 micron can be produced.

Index Terms— boron carbide, boric acid, citric acid, powder synthesis, sol_gel

I. INTRODUCTION

Boron carbide (B₄C) is a highly refractory and hard material that is of great interest for both its structural and electronic properties. The boron carbide structure is composed of icosahedra units that are linked by both direct covalent bonds and by three-atom chains. The most widely accepted structural model for B₄C (B₁₂C₃) has B₁₁C icosahedra with C-B-C intericosahedral chains. However, single phase boron carbides are also known with carbon concentrations ranging from 8.8 to 20 atom%, and localized phases of varying composition may exist in a single material. This range of concentrations is made possible by the substitution of boron and carbon atoms for one another within both the icosahedra and the three-atom chains[1-4].

Boron carbide is an important non-metallic material with useful physical and chemical properties. The most important properties of boron carbide include its high-temperature stability, high hardness, high cross-section for neutron capture, high modulus of elasticity, low density, chemical inertness, and excellent high-temperature thermoelectric properties. This combination of properties make boron carbide a strong candidate for numerous high technology applications including uses as an abrasive powder for polishing and lapping, wear resistant parts, ceramic armors, and as reinforcement in metal matrix composites used in sporting equipments. It is also used as a neutron moderator in nuclear reactors because of high reactivity with neutron and high neutron absorption cross section of the ¹⁰B, boron carbide is currently used as a neutron absorber material (control rods) in the majority of nuclear plant such as pressurized water reactor (PWR) and liquid metal fast breeder reactor (LMFBR), and potentially, for power generation in deep space flight applications [5-9].

For these reasons, extensive amount of researches have been conducted over the past decade to produce boron carbide powders. Various synthetic processes to produce variety forms of boron carbide are known. Boron carbide can be synthesized from elemental boron and carbon directly. The high cost of these elements makes this method economically unattractive. Other synthesis routes include metallotermic and carbothermic processes such as carbon-thermal reduction of boron oxide (B₂O₃) over 1000 °C, reduction of BCl₃ by CH₄ at a temperature of 1500 °C with laser, thermal decomposition of a mixture of pure carbon and boron trichloride in an atmosphere of hydrogen, and gaseous reaction between BCl₃ and a methane- hydrogen mixture in r. f. argon plasma [10-13].

Recently, boron carbide has been synthesized by co-reduction route using BBr₃ and CCl₄ as the source materials at a low temperature of 480 °C and new selective synthesis routes to boron carbide and boron nitride based on the use of new polymer systems, poly[2-(vinyl) pentaborane] and poly [B-vinylborazine], as precursors. Mira belli et al., reported that 2(H₂C=CH)B₅H₈ will undergo thermal polymerization to vinlypentaborane oligomers and that these species can be converted to pure boron carbide with high ceramic yields under mild conditions. Isao et al., reported that boric acid and 2-hydroxy benzyl alcohol (HBA) were used as the B and C sources of B₄C. H₃BO₃ and HBA in DMF solution gave a phenolic resin-B₂O₃ hybrid. The hybrids swelled

upon heating, and the swelled hybrids could be easily ground into fine powders. Heat treatment of the powdered hybrids at 1500°C in Ar atmosphere for 4 hrs led to the formation of B_4C powders. Among the methods, carbothermal reaction and magnesiothermal reaction are widely used as main techniques for the production of B_4C powders [14-17]. Magnesiothermic reduction of B_2O_3 in the presence of carbon is one of the industrial processes used for preparing boron carbide. Although fine powders can be obtained, this process is unsatisfactory for the production of high purity powders because powders are easily contaminated by magnesium compounds. Furthermore, even the repeated digestions with hot acids can not purify powders completely because the removals of magnesium compounds are extremely difficult. The most commercially and industrially viable method is reduction of boric acid with carbon black at a temperature over 1750°C in electric arc furnaces. The product thus obtained is hard and consists of excess unreacted carbon. The hard mass is crushed and pulverized to the requisite mesh size and purified by chemical and thermal oxidation method because of their contamination from grinding media [18, 19].

For production of boron carbide matrix composites a boron carbide powder composed of normal particle size distribution with low impurity is needed. There is therefore a need for developing a technique to produce rapidly and inexpensively B_4C powders. The present research addresses this need.

II. EXPERIMENTAL PROCEDURE

The materials used were boric acid (H_3BO_3 , E. Merck, D-64271 Darmstadt) and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Merck KGaA, 64271 Darmstadt, Germany). In the first step, aqueous solution of boric acid (2.5 M) was prepared by dissolving boric acid in distilled water at 90°C . Citric acid was added to the boric acid solution and the solution was heated up to 120°C to remove excess water and conversion to a gel. The pH was kept in 2-3 range by adding ammonia solution (25%). Under this condition, a "golden yellow colored" gel was obtained and then dried in an oven. The molar ratio of boric acid to citric acid with respect to overall reduction of boron oxide by carbon ($2\text{B}_2\text{O}_3 + 7\text{C} = \text{B}_4\text{C} + 6\text{CO}$) was kept at 1.6. In the second, the derived gel from 1.6 ratios of raw materials was heated under vacuum at 600, 650, 700, 750°C , and held for 2 hrs at each temperature to obtain spongy black precursors. The precursors easily crushed to powder form. They were then formed to specimens with 12mm diameter and 5 mm thickness by cold pressing under a pressure of 20 MPa. The specimens were put in a graphite dies with exit gas ability. The specimen then heated up to 1350, 1450 and 1500°C with heating rate of $5^{\circ}\text{C}/\text{min}$ and held for 2.5 h. The 1.9 ratio of raw materials was also selected to investigate the effect of composition.

The powder products were characterized by x-ray diffractometry (XRD) and particle size analyzer methods. They were also analyzed to determine free carbon contents. The quantity of free carbon in boron carbide is

difficult to determine because of the low atomic number of carbon which renders electron microprobe analysis imprecise, and because of the similarity between chemical proportions of carbon for graphite and boron carbide which makes chemical analysis unreliable. The progressing of the overall reduction reaction in the specimens was determined by comparing the $I_{\text{B}_4\text{C}}/I_{\text{C}}$ (I is intensity of peak).

Recently, a new commercial method for determination of free carbon has been reported. In this method an amount of boron carbide powder containing some free carbon was weighed and taken as W_1 . It was then heated to 700°C for 30 min in air. It was assumed that all free carbon and a part of boron carbide powder are oxidized during this heat treatment. So, the remaining powder, W_2 , was washed with hot water to remove the oxidized part of boron carbide, namely B_2O_3 . The resulting powder was then dried and weighed as W_3 . The difference $W_2 - W_3 = W_4$ yields the amount of B_2O_3 and therefore the oxidized boron carbide (W_5). The sum of $W_3 + W_5 = W_6$ gives total boron carbide and therefore the difference $W_1 - W_6 = W_7$ yields the amount of residual free carbon [18].

II. RESULTS AND DISCUSSION

By mixing boric acid and citric acid with pH controlling in the range of 2-3 using heating and vaporization of excess water, different gels was formed. The gels was dried in oven and pyrolyzed in vacuum for 2h under temperatures of 600, 650, 700 and 750°C . XRD patterns, Fig.1, show that all peaks are correspond to cubic B_2O_3 . Also the XRD patterns, Fig.2, at 1250 and 1350°C , shows carbon peaks which indicate that carbon exist in amorphous form in the precursor.

The XRD patterns show that intensity of B_2O_3 peak is higher at 650°C compare to the same peak at other temperatures. Based on literature, under vacuum or inert atmosphere the boron carbide formation reaction temperature is around 1130°C . but in this reaction the diffusion of reacting species is likely to become sluggish thus calling for higher temperature for reaction to proceed at a reasonable rate. As mentioned in experimental section, the samples were heated up to 1250, 1350, 1450 and 1500°C with a heating rate of $5^{\circ}\text{C}/\text{min}$ under vacuum and held for 2.5 hrs. The XRD patterns of product at 1350°C present that B_2O_3 and C remain unreacted also the rate of boron carbide formation is low in 1350°C and below temperatures (Fig.2). Whereas, at 1450 and 1500°C the unreacted B_2O_3 is not seen in the product, (Fig.2). From the XRD patterns given in Fig.2, it is evident that the ratio of $I_{\text{B}_4\text{C}}/I_{\text{C}}$ is higher at 1500°C compare to other temperatures.

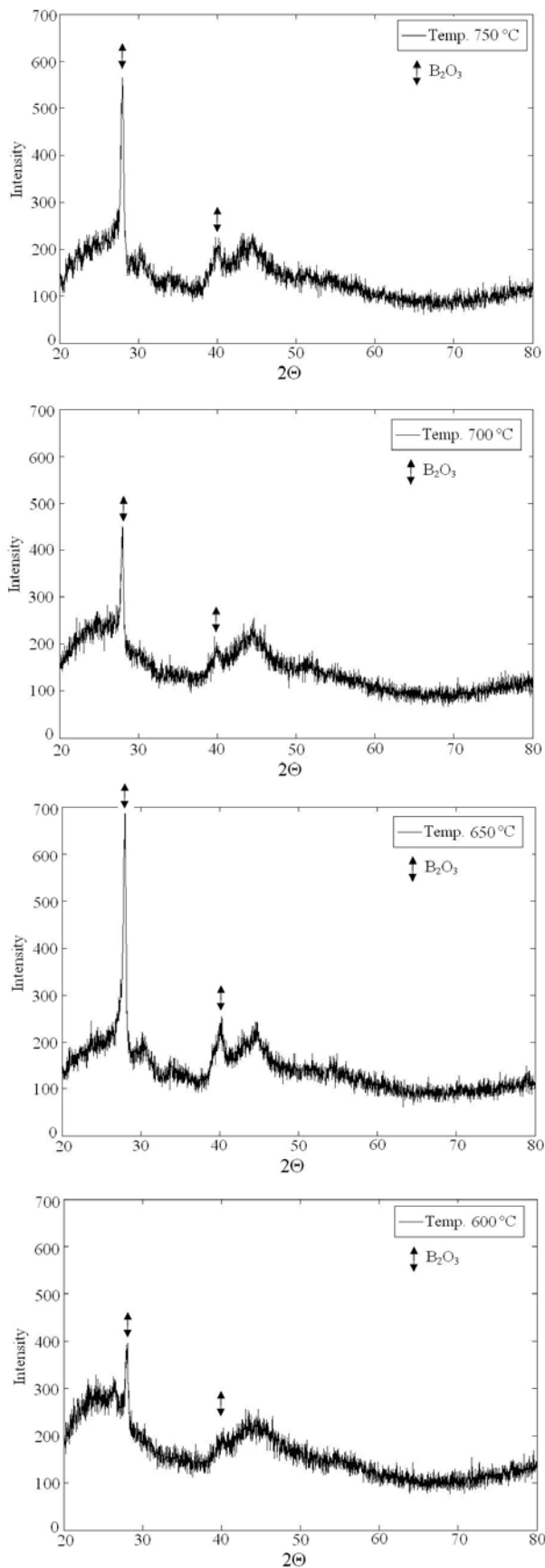


Fig. 1. XRD patterns of the precursors produced from 1.6 ratio of boric acid/citric acid at temperatures of 600, 650, 700, and 750 ° C.

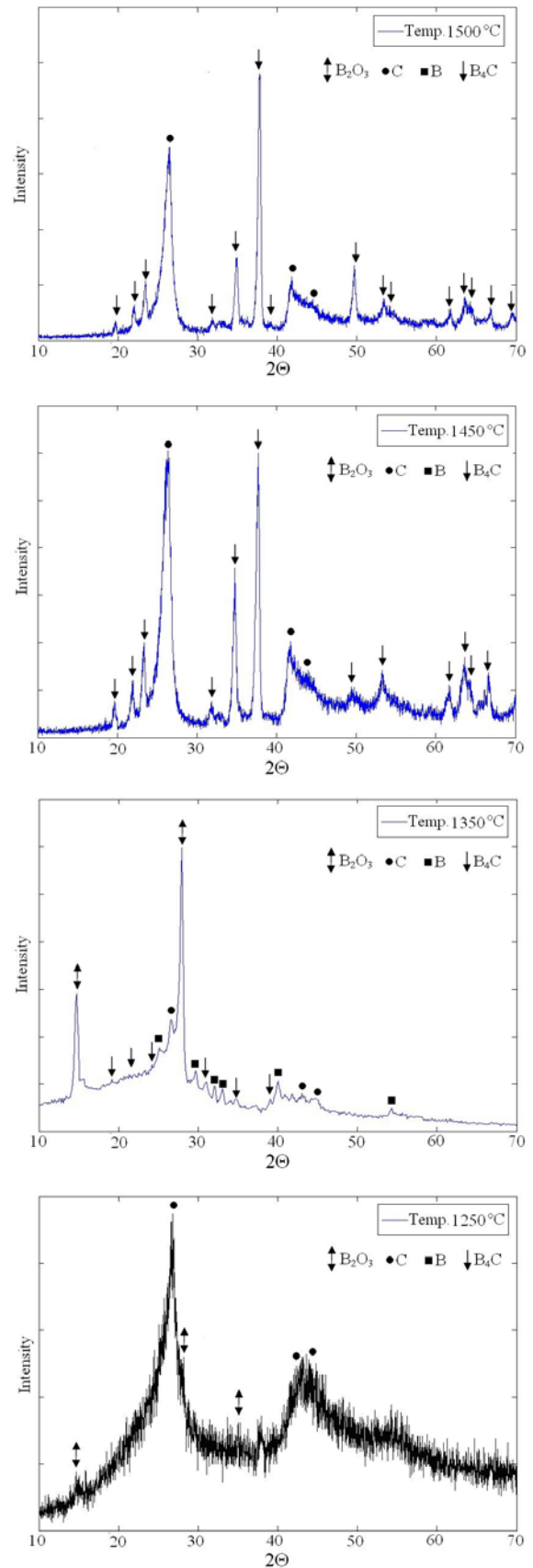


Fig. 2. XRD patterns product obtained by heating the pyrolyzed gel precursor powder and boric acid/citric acid=1.6 up to 1250, 1350, 1450, and 1500 ° C.

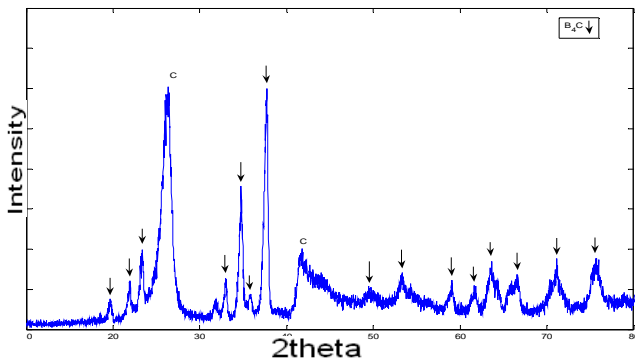


Fig. 3. XRD pattern of the boron carbide powder produced by heating of the pyrolyzed gel precursor powder boric acid/citric acid=1.6 up to 1450 ° C for 1.5 h.

This indicates that at this temperature more reaction has taken place. This is due to the fact that formation of B_4C is very sensitive to temperature. At lower temperatures B_4C may hardly form which lets boron to exit from the system. The effect of time on B_4C formation reaction at 1450 °C was investigated. According to XRD patterns Fig.2 and Fig.3, the ratio of I_{B_4C}/I_C has been increased with time. Therefore, more amount of B_4C has been formed. Comparison of XRD patterns at 1450 and 1500 ° C, Fig.2, show that the value of I_{B_4C}/I_C has been increased with temperature. Thus, the effect of temperature in B_4C formation is more than time effect.

Quantity of free carbon in production at 1500 ° C (2.5h) is about 13.86%.

The presence of free carbon in the product suggests that some boron has been lost during reaction. For compensation of boron loss, a composition with excess boric acid (1.9) was used. In this case the amount of free carbon was measured to be about 8.74%.

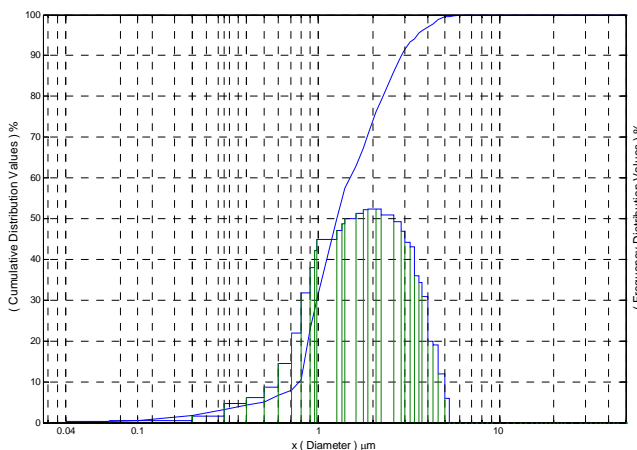
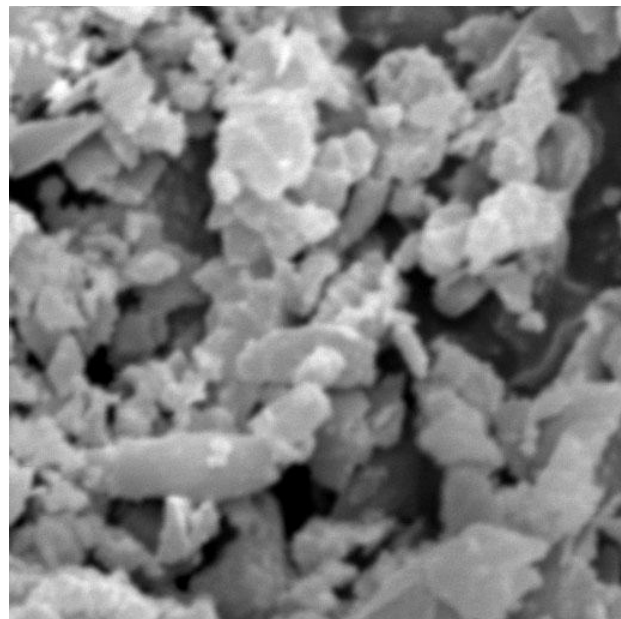
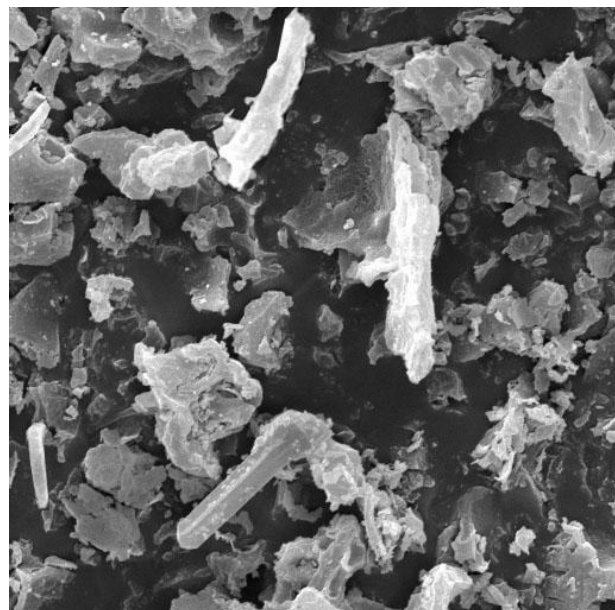


Fig.4. Particle size distribution of the product obtained after heating the pyrolyzed gel precursor up to 1450 ° C, holding 2.5 h and 1.6 ratios.



SEM MAG: 2.00 kx DET: SE Detector HV: 25.0 kV VAC: HiVac DATE: 06/21/05 Device: MV2300 Vega ©Tescan Obducat CamScan

Fig. 5. SEM photomicrograph of boron carbide powder produced at 1500 ° C for 2.5 hrs and ratio of 1.6.



SEM MAG: 2.00 kx DET: SE Detector HV: 25.0 kV VAC: HiVac DATE: 06/21/05 Device: MV2300 Vega ©Tescan Obducat CamScan

Fig. 6. SEM micrograph of the final product with boric acid/citric acid of 1.9 heated at 1500 ° C for 2.5 hrs.

The particle size of the product obtained after heating the precursor powder up to 1450 ° C, holding for 2.5 h and 1.6 ratio of raw materials were analyzed. The results showed that particles are consisted of $D_{10}=0.59$, $D_{50}=1.56$ and $D_{90}= 3.43$ micron (Fig.4). The results of the present investigation show that, for minimizing the free in the product excess boric acid must be used. Because the final product is in powder form it doesn't need further milling process. Also leaching and purification processes, as used

in conventional production methods of boron carbide are not necessary in this method.

Figure 5 illustrates a SEM image from the powder produced at 1500 °C for 2.5 hrs and ratio of 1.6. From the figure, it can be seen that the particles have distorted elliptical, plate like, and polyhedral shapes. However, some particles with sharp edges can also be seen in the image. However, by increasing the boric acid/citric acid ratio and same heating time at temperatures of 1500 °C, the resultant powders had irregular shapes (Fig. 5 and 6). As can be seen from the Fig.6, by increasing the boric acid/citric acid ratio and heating time some needle – shape B₄C particles have formed. This type of particles form as a result of solid-gas interfacial reactions.

CONCLUSION

Almost uniform and high purity micron size boron carbide powder can be produced by using boric acid to citric acid ratio of 1.6 of raw materials without any need to milling and leaching processes in compare to conventional method. Compare to the reaction time and temperature of other methods and also the composition of final product, it can be stated that mixing of B₂O₃ and carbon is more homogenous in this method. Therefore, the kinetics of process has been improved. The effect of temperature on B₄C formation is more effective than time. The B₄C powder produced by this process is composed of particles with different shapes and with a narrow size distribution. By increasing the boric acid/citric acid ratio some needle–shape B₄C particles have formed.

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