JMEPEG (2008) 17:44–49
DOI: 10.1007/s11665-007-9125-0

©ASM International
1059-9495/$19.00

The Effect of Time, Temperature and Composition on Boron Carbide Synthesis by Sol-gel Method

A.M. Hadian and J.A. Bigdeloo

(Submitted July 26, 2005; in revised form April 29, 2006)

To minimize free carbon residue in the boron carbide (B_4C) powder, a modified sol-gel process is performed where the starting materials as boric acid and citric acid compositions are adjusted. Because of boron loss in the form of $B_2O_{2(g)}$ during the reduction reaction of the stoichiometric starting composition, the final B_4C powders contain carbon residues. Thus, an excess H_3BO_3 is used in the reaction to compensate the loss and to obtain stoichiometric powders. Parameters of production have been determined using x-ray diffraction analysis and particle size analyses. The synthesized B_4C powder using an excess boric acid composition shows no trace of carbon.

Keywords boric acid, boron carbide, citric acid, sol-gel

1. Introduction

Covalently bonded solids based on boron, carbon, or nitrogen comprise the hardest materials presently known. Among this, B_4C comes third after diamond and cubic BN, with the advantages of being easily synthesized and being stable up to very high temperatures (Ref 1, 2). Boron carbide has a complex structure based on B_{12} icosahedra and three atom linear chain building blocks (Ref 3). Boron carbide is an important nonmetallic material with useful physical and chemical properties. Its high melting point, high-modulus, large-neutron capture section, low density, chemical inertness, outstanding thermal, and electrical properties make boron carbide a strong candidate for high-technology applications such as nuclear, Space, microelectronics, military, and medical industries (Ref 4). Boron carbide can be synthesized by a variety of high temperature methods. It can be synthesized from elemental boron and carbon directly. The high cost of these elements has made this method economically unattractive (Ref 5). Other synthesis route are metallotermic and carbothermic processes; carbon-thermal reduction of boron oxide (B_2O_3) over 1000 °C (Ref 6); reduction of BCl_3 by CH_4 at a temperature of 1500 °C with laser; thermal decomposition of a mixture of pure carbon and boron tricloride in an atmosphere of hydrogen; gaseous reaction between BCl_3 and a methane-hydrogen mixture in r.f.argon plasma (Ref 7-9).

Recently, boron carbide has been synthesized by co-reduction route by using BBr_3 and CCl_4 as the source materials at low temperature of 480 °C (Ref 6) and new selective synthesis routes to boron carbide and boron nitride based on the use of the new polymer systems, Poly [2-(vinyl) pentaborane] and poly [B-vinylborozine], as precursors. Mira belli et al., reported that $2(H_2C{=}CH)\ B_5H_8$ will undergo thermal polymerization to vinylpentaborane oligomers and that these species can be converted to pure boron carbide (B_4C) 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 B_4C. H_3BO_3 and HBA in DMF solution gave a phenolic resin-B_2O_3 hybrid. The hybrids swelled on heating, and the swelled hybrids could be easily ground into fine powders. Heat treatment of the powdered hybrids at 1500 °C in Ar for 4 h led to the formation of B_4C powders (Ref 8). Magnesiothermic reduction of B_2O_3 in the presence of carbon is one of the industrial processes which is used for preparing boron carbide (Ref 10, 11). 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 cannot purify powders completely because the removal of magnesium compounds is extremely difficult (Ref 12). The most commercially viable and industrial method is from 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 of 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 (Ref 13, 14). Due to crucial role of free carbon residue in B_4C powder characteristics, in the present report, we focused on the minimization of the free carbon residue in the final B_4C products using a H_3Bo_3 excess (carbon deficient) composition. Some parameters in the carbothermal reduction process of H_3BO_3 for the production of the carbon-free B_4C powders have been determined experimentally using x-ray diffraction (XRD), particle size analyzer (PSA), and determination of free carbon suggesting an optimum starting composition.

2. Experimental procedure

The materials used were boric acid (H_3BO_3, E. Merck, D-64271 Darmstadt) and citric acid (C6H8O7.H2O, Merck

---

A.M. Hadian and **J.A. Bigdeloo,** Department of Metallurgy & Material, Faculty of Engineering, University of Tehran, Tehran, Iran. Contact e-mail: hadian_a@yahoo.com.

KGaA, 64271 Darmstadt, Garmany). 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 ($2B_2O_3 + 7C = B_4C + 6CO$) was kept at 1.6. In second step, the derived gel from 1.6 ratios of raw materials was heated under vacuum at 600, 650, 700, 750 °C, and held for 2 h at the temperature. The spongy black precursor was obtained. The spongy black precursors easily crushed to powder form. They were then formed to specimens with 12 mm 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 1250, 1350, 1450, and 1500 °C

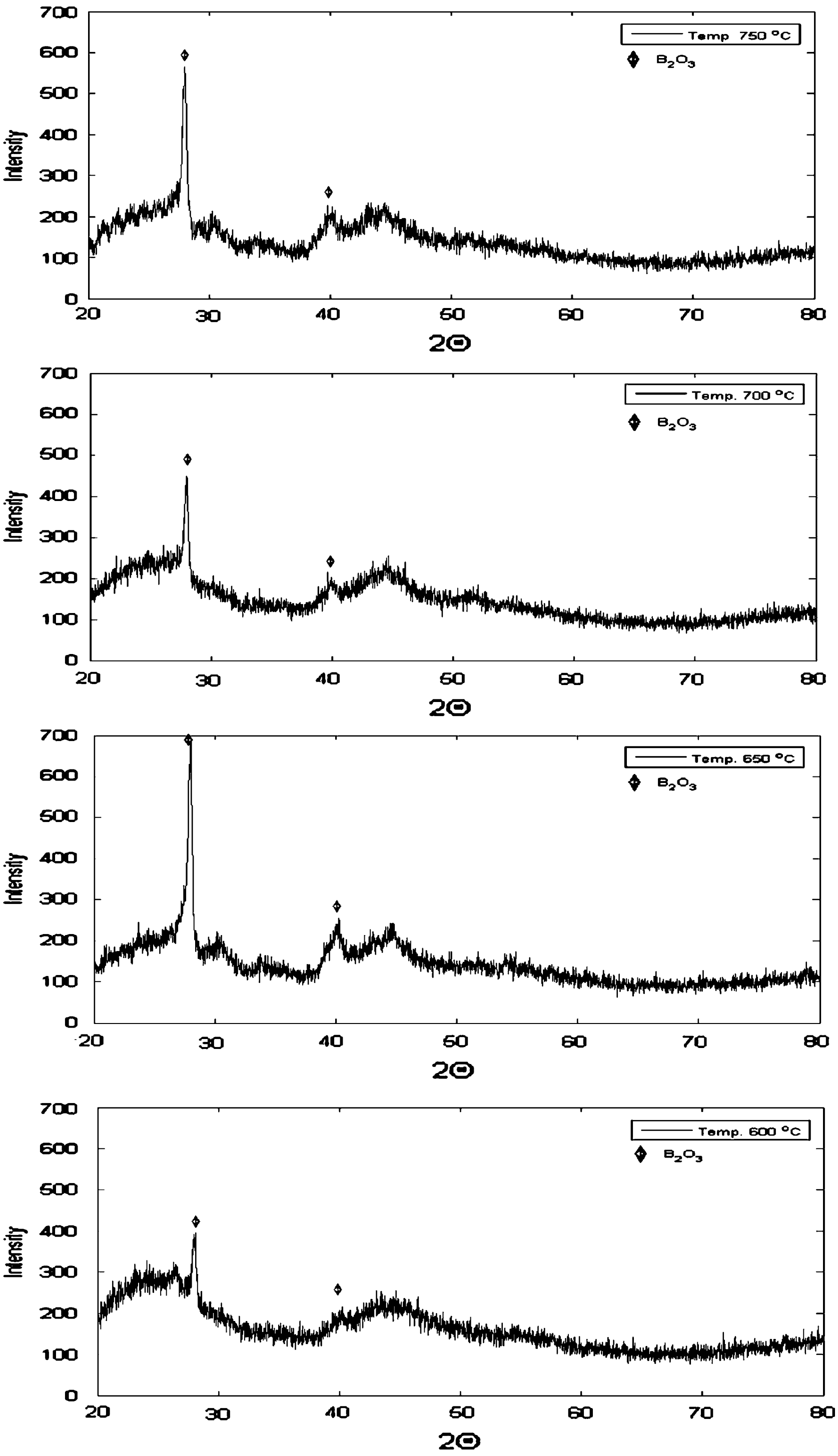

Fig. 1 XRD patterns of the precursors produced from the 1.6 ratio of boric acid/citric acid at temperatures of 600, 650, 700, and 750 °C

with 5 °C/min and held for 2.5 h. The 1.9 and 2.2 ratio of raw materials for investigation of composition effect also performed for 2.5 and 3.5 h. The powder products were characterized by XRD and particle size analyze by Particle Size Analyzer (CILAS 1064). 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 (Ref 10). The progressing of the overall reduction reaction in the specimens was determined by comparing the I_{B_4C}/I_C.

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, viz 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 (Ref 4).

3. Results and discussion

The XRD patterns of the dried gels obtained from reaction of boric acid with citric acid with ratio 1.6 and pyrolized at 600, 650, 700, and 750 °C for 2 h are shown in Fig. 1. The figure shows that the XRD patterns are similar to the pattern of cubic

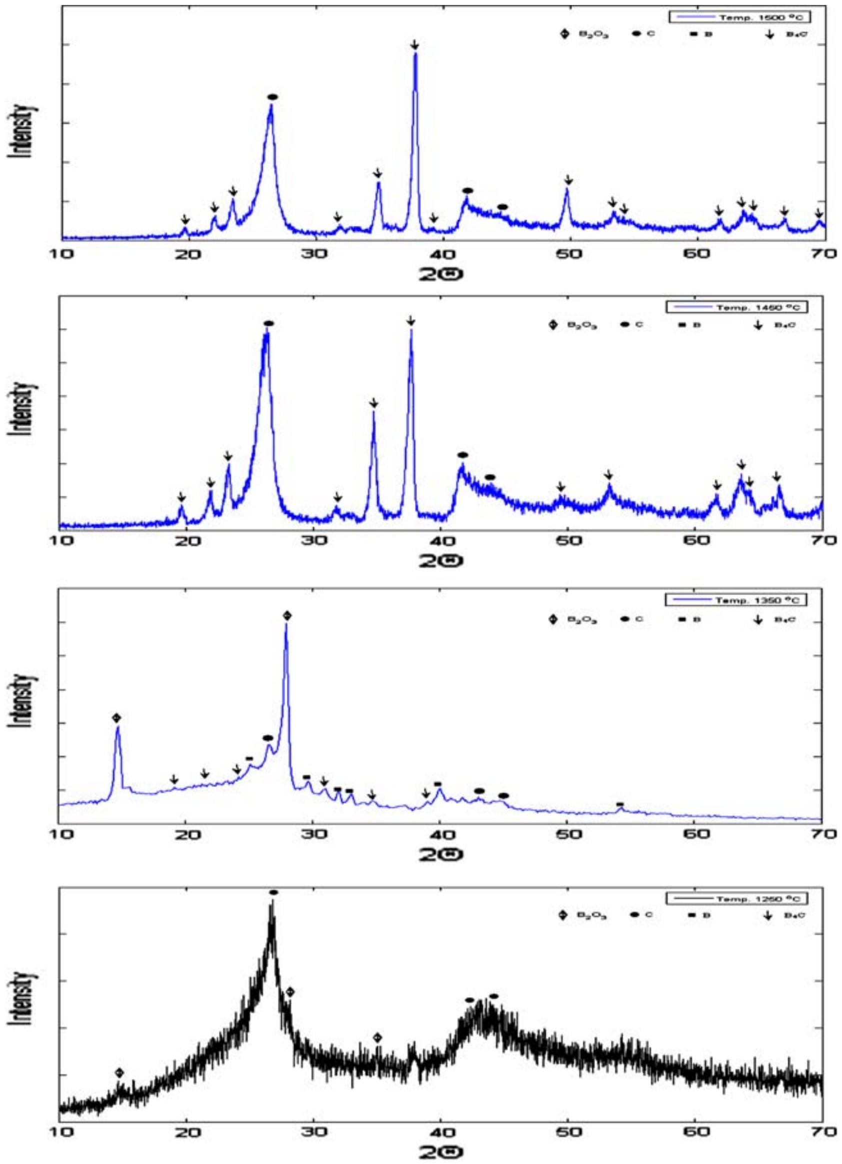

Fig. 2 XRD pattern of the product obtained by heating the pyrolyzed gel precursor powder and boric acid/citric acid = 1.6 up to 1250, 1350, 1450, and 1500 °C for 2.5 h

boron oxide. On the other hand, since the precursor produces carbon containing phase such as B_4C and free carbon at elevated temperatures (Fig. 2). It can be concluded that this precursor contains carbon which is in amorphous shape in addition to B_2O_3. Since the primary mixing is in solution form, it is expected that the mixture is more homogenous while compared to conventional mixing methods. Therefore the reactant surfaces increases resulting in increased kinetic of the reactions. From Fig. 1, it can be seen that the intensity of B_2O_3 peaks obtained at 650 °C is higher while compared to other temperatures. Therefore, this temperature (650 °C) was selected as optimum temperature for primary pyrolis process for all the gels with different raw materials ratio.

The precursor from primary pyrolis with stoichiometric composition was heated in a tube furnace under vacuum for 1250, 1350, 1450, and 1500 °C with a heating rate of 5 °C/min and held for 2.5 h. at temperature.

Figure 2 shows the XRD patterns taken from samples prepared at different temperatures. From the figure, it is evident that no reactions have occurred.

At 1250 °C the product contains B_2O_3 and C. By increasing the temperature to 1350 °C it looks that some reactions have taken place, but untreated B_2O_3 and C are seen yet. Whereas, at 1450 and 1500 °C no B_2O_3 is observed and the only impurity seen is C. This indicates that at 1450 °C and higher temperatures the reaction is completed and in accordance with other reports, the basic impurity is unreacted carbon (Ref 3-6). The presence of free carbon indicates some boron loss. This is due to removing of boron by such reaction products as carbon monoxide resulting in changes in stoichiometric condition of the reaction (Ref 9). Therefore, the end product will contain considerable amount of free carbon which alters its properties. In this research work, the amount of free carbon has been minimized by using excess of boric acid in the starting materials.

For this purpose, the boric acid to citric acid ratios of 1.9 and 2.2 was investigated. With respect to the XRD patterns shown in Fig. 3 and 4, it can be found that by increasing the above-mentioned ratio, even at lower temperatures such as 1350 °C, the reacted peaks of B_4C is more clear with higher intensity.

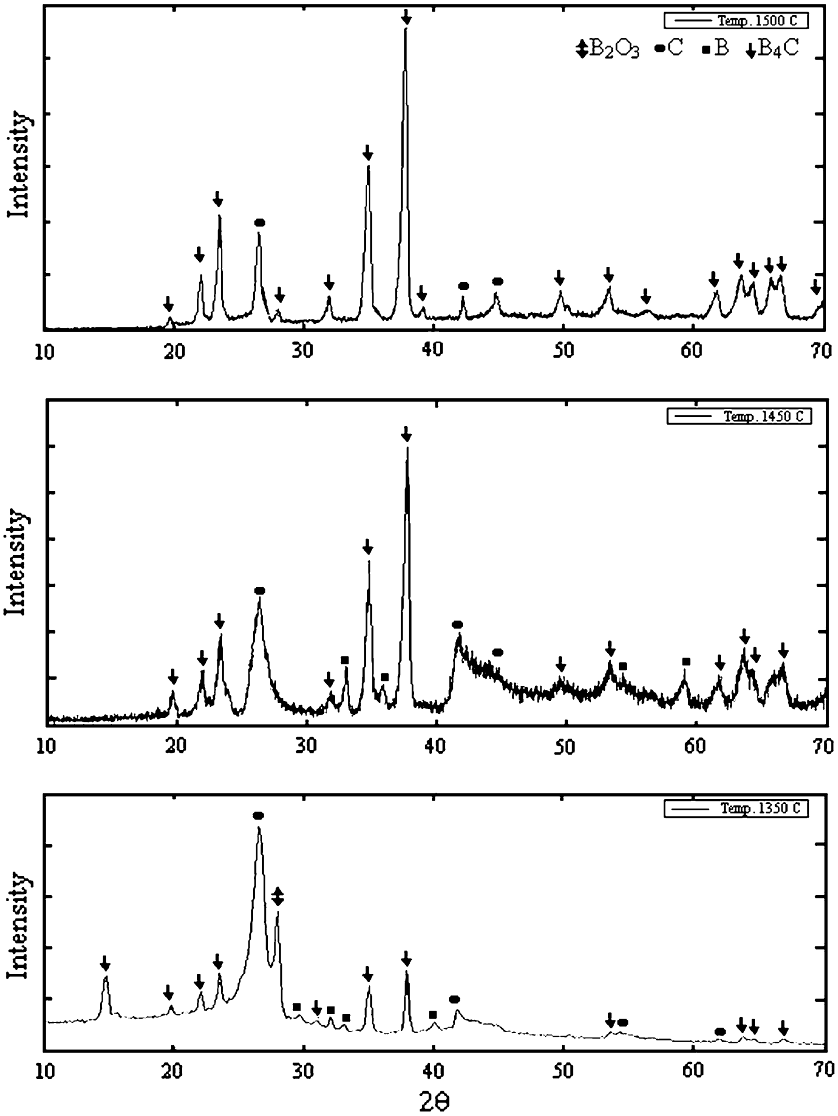

Fig. 3 XRD pattern of the product obtained by heating the pyrolyzed gel precursor powder and boric acid/citric acid = 1.9 up to 1350, 1450, and 1500 °C for 2.5 h

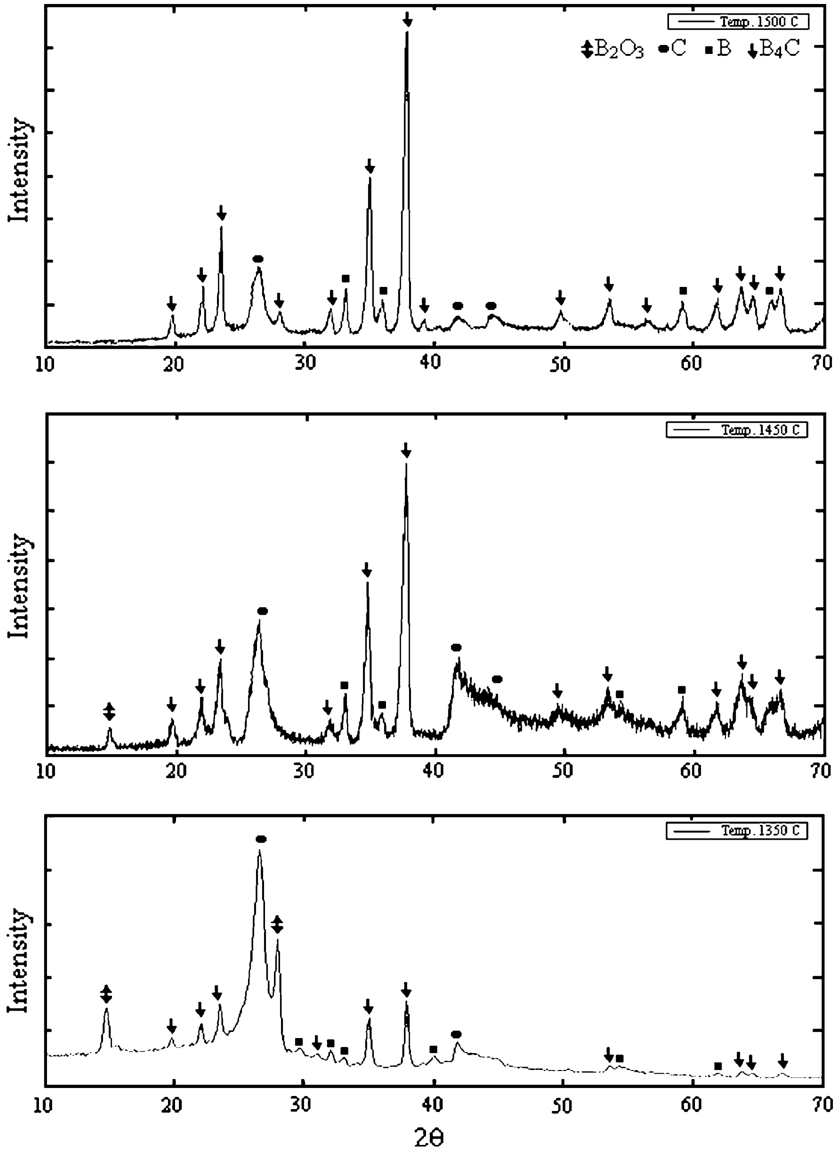

Fig. 4 XRD pattern of the product obtained by heating the pyrolyzed gel precursor powder and boric acid/citric acid = 2.2 up to 1350, 1450, 1500 °C for 2.5 h

While, at 1450 °C and with ratio of 1.9, free boron can even be seen.

For 1.9 ratio at 1500 °C the end products include B_4C and free carbon, meaning that under this condition the reaction is completed. Whereas, for 2.2 ratio, even at 1500 °C that reaction of B_2O_3 and boron is not completed and these materials can be seen in the XRD pattern.

In order the reaction to be completed, the reaction time was increased up to 3.5 h. According to Fig. 5, presence of free carbon was observed weakly. With respect to these results, it can be concluded that by increasing the ratio of the raw materials the necessary time to be completed increases at a certain temperature. The reason for the needed longer time is that at temperatures higher than 1350 °C, B_2O_3 may form a glassy shell which prevents the exit of $CO_{(g)}$ resulting the rate of the reaction to be reduced. Hence, for ratio of 1.9 and 2.5 h, the temperature has to be increased to 1500 °C and higher, but for ratio of 2.2, in addition of increasing temperature to 1500 °C, the reaction time has to be increased to 3.5 h too.

With respect to the XRD patterns given in Fig. 3, 4, and 5, it can be seen that by increasing the raw material ratio in the primary composition the carbon peak starts to weakening in a manner that at 2.2 ratio no carbon peak is observed. By analyzing free carbon and comparing with previous works (Table 1) it can be concluded that this technique allows for higher purity at lower ratio (2.2) while compared to carbothermal method in which the raw material ratio is 3.5 (for boric acid to carbon) and 2.9 (for B_2O_3 to carbon). Moreover, this method requires shorter reaction time. As mentioned previously, this is mainly due to effectiveness of primary mixing in increasing contact surfaces resulting in higher reaction kinetics. According to Table 1, by increasing composition at constant temperature, the particle size increases at D_{90} (diameter at 90%) and D_{50}, but decreases at D_{10}.

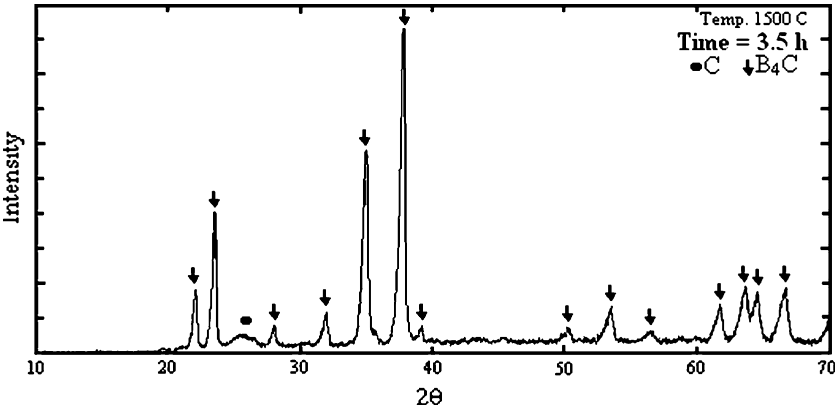

Fig. 5 XRD pattern of the product obtained by heating the pyrolyzed gel precursor powder and boric acid/citric acid = 2.2 up to 1500 °C for 3.5 h

Table 1 Free carbon and particle size analysis of selected samples

				Composition of particle size distribution (μm)		
Ratio	**Time (h)**	**Temperature (°C)**	**C_{free}%**	**D_{10}**	**D_{50}**	**D_{90}**
1.6	2.5	1500	21.64	0.69	1.19	3.17
1.9	2.5	1500	8.74	0.58	1.71	3.40
2.2	3.5	1500	2.38	0.38	2.38	4.43

4. Summary

It was found that 650 °C is the optimum temperature for obtaining a homogeneous mixture of B_2O_3 and C with highest B_2O_3 to C ratio. By optimizing the composition of starting material, reaction temperature and heat-treatment process, micron size boron carbide powder was produced.

References

1. D. Simeone, C. Mallet, P. Dubuisson, G. BaldiNozzi, and C.Gervais, Study of Boron Carbide Evolution Under Neutron Irradiation by Raman spectroscopy, *J. Nuclear Mater.*, 2000, No. 277, p 1–10
2. G. de With, High Temperature Fracture of Boron Carbide: Experiments and Simple Theoretical Models, *J. Mater. Sci.*, 1984, **19**, p 457–466
3. Z.L. Arbary and C.D. Reynolds, U.S. patent, No. 4,215,088, "Method for Fabricating Boron Carbide Articles", July. 29, 1980
4. C.H. Jung, M.J. Lee, and C.J. Kim, Preparation of Carbon Free B_4C Powder from B_2O_3 Oxide by Carbothermal Reduction Process, *Mater. Lett.*, 2003, **58**(5), p 609–614
5. E.G. Gray, Patent Specification, No. 687946, "A process for the Production of Boron Carbide", Feb. 22, 1950
6. B.V.S. Subba Rao, A.D. Manohar, R.M. Rao, K. Somaraju, and R.K. Basu, *Ceramic powder for high-tech-applications*, Sangam Books, 1998, p 83–88
7. A. Sinha, T. Mahata, and B.P. Sharma, Carbothermal Route for Preparation of Boron Carbide Powder from Boric Acid-Citric Acid Gel Precursor, *J. Nuclear Mater.*, 2002, **301**, p 165–164
8. M. Carlsson, F.J. Garcia-Garcia, and M. Johnsson, Synthesis and Characterization of Boron Carbide Whiskers and Elongated Platelets, *J. Crystal Growth*, 2002, **236**(3&4), p 466–476
9. F. Thevenot, Boron Carbide-A Comprehensive Review, *J. Euro. Ceram. Soc.*, 1990, **74**(6), p 205–225
10. A. Alizadeh, E. Taheri-Nassaj, and N. Ehsani, Synthesis of Boron Carbide Powder by a Carbothermic Reduction Method, *J. Euro. Ceram. Soc.*, 2004, **24**(10-11), p 3227–3234
11. B.V.S. Subba Rao, A.D. Manohar, R.M. Rao, K. Somaraju, and R.K. Basu, *Ceramic powder for high-tech-applications*, Sangam Books, 1998, p 82–83
12. D.K. Bose, K.U. Nair, and C.K. Gupta, Production of High Purity Boron Carbide, *High Temp. Mat. Proc.*, 1986, **7**(2&3), p 133–140
13. L. Shi, Y. Gu, L. Chen, and Y. Qian, A Low Temperature Synthesis of Crystalline B_4C Ultrafine Powders, *Solid State Commun.*, 2003, **128**(1), p 5–7
14. S. Mondal and A.K. Banthia, Low-Temperature Synthesis Route for Boron Carbide, *J. Euro. Ceram. Soc.*, 2005, **25**(2–3), p 287–291