

Production of Boron Carbide by Carbothermal Reduction of Boron Oxide and Petroleum Coke

H. Amini^{a*}, M. A. Azarfar^b, A. H Dehcordi^c and A. Malekpour^d

*Author for correspondence

Tehran-Nuclear Science and Technology Research Institute science^{a,c} & Research branch Islamic Azad University,
Nuclear Engineering^{a,b}, Isfahan university^d,
Islamic Republic of Iran,
E-mail: hbamini@aeoi.org.ir

ABSTRACT

Boron carbide, B₄C, is the third hardest known material next to diamond and boron nitride. Reasonable cost of production, low density, and high chemical inertness makes boron carbide an attractive material for micro-electronic, military, space and medical applications. Boron has a high neutron absorption cross section and hence any compound containing boron, especially if it has a good mechanical strength, is of great interest in nuclear industry. Other properties of B₄C make this compound to be highly used in nuclear reactor.

Using reduction reaction of boron oxide by carbothermal process, B₄C, free of impurities, was produced. Boron loss during the process, in the form of B₂O₂ gas; a common problem in B₄C production, was minimized by adjusting the stoichiometry of feeding materials. Likewise, carbon residue was eliminated by taking appropriate composition at the starting point. The result of number of experiments showed that production of boron carbide is highly dependent on the phase change of reactant boron oxide from solid to liquid and from liquid to gaseous boron hypo-oxides and then the interaction with carbon and carbon monoxide.

Keywords: Boron carbide, carbothermal process, reaction

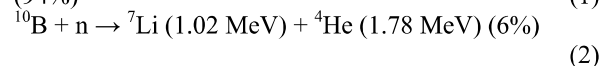
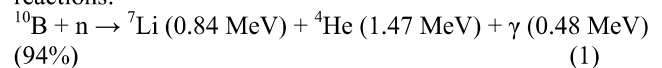
1. INTRODUCTION

Boron carbide with covalent bonded solids based on boron and carbon has ability to accommodate a large variation in carbon composition without undergoing a basic structural change [1, 2]. The boron carbide structure is composed of icosahedra units by three-atom chains. The structure (B₁₂C₃) is the ideal archetype, but boron carbide actually exists over a widely varying compositional range B_{12+x}C_{3-x} (0.06 < x < 1.7) [3].

B₄C comes third after diamond and cubic BN, with the advantages of being easily synthesized and stable up to very high temperatures [4, 5]. Boron carbide is an important ceramic material with useful physical, chemical, nuclear 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;

Favourable chemical properties include a high resistance to chemical attack, such as dilute and concentrated acids and alkali, and to the water. This combination of properties make boron carbide a strong candidate for various fields include grinding, lapping, polishing and producing other boron containing materials such as titanium boride, and excellent high temperature thermoelectric, wear resistant parts, ceramic armors, and as reinforcement in metal matrix composites used in sporting equipments [6,7,8].

The neutron absorption property of B₄C is due to the presence of the ¹⁰B isotope which takes in the following nuclear reactions:



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) [9, 10].

Boron carbide can be synthesized by metallothermic or carbothermic processes. The metallothermic process is a method that uses directly synthesized essential elements boron and carbon. The high cost of elemental boron makes this route economically unattractive. The second process, carbothermic method, involves inexpensive starting materials, such as boric acid (H₃BO₃) or boron anhydride (B₂O₃), borax (Na₂B₄O₇), which can be reduced by using carbon to produce boron carbide the powder prepared by this method has morphology and surface characteristics suitable for obtaining dense ceramic bodies [8,11].

Here, the reaction of commercial B₄C powders is expressed as follows [12];



$\Delta H^\circ = 1812 \text{ kJ/mol}$, at 2200 _ 2500 °C.

This reaction, however, requires an extended period of time because the rate of heat conduction is quite slow and the process is highly endothermic.

2 Topics

The carbothermic reduction can be carried out in an electric arc furnace or a resistance furnace.

Although, the production rate of electric arc furnace is much greater than that of resistance furnaces. But, this process production has excessive amount of free carbon because the control of temperature above 2300 K is not possible. This leads to vaporization of boron source, in form B_2O_3 and B_2O_2 , from the system affecting the B/C ratio. Therefore, high amount of free carbon (10 to 12%) is created in the final product of B_4C . During the reaction the temperature attained in resistance furnace is considerably lower than that of electric furnace, resulting in much less boron source loss. Thus, the free carbon content is easily controlled in resistance furnace [8, 13].

The objective of this work is to obtain select the production method that the minimization of the free carbon residue in the final B_4C products and using a B_2O_3 excess (carbon deficient) composition. Some parameters in the carbothermal reduction process of B_2O_3 for the production of the carbon-free B_4C powders have been determined experimentally using X-ray diffraction (XRD).

2. Experimental procedure

The materials used were boron trioxide (B_2O_3) obtained boric acid (H_3BO_3 , E. Merck, D-64271 Darmstadt) and powdered petroleum coke (98.5% C, 0.5% S, 0.02% N). The first powder was used as a source of boron and the last powder was used as reducing agent. In the first step, boric oxide has also been produced such as by the slow dehydration of boric acid in an oven at 225°-250° C for two hour then crushed to powder form. As per molar quantities Powder mixtures, boron oxide and petroleum coke, with add 20% excess boron oxide, as initial materials should be mixed in a laboratory ball mill for 1 h. They were then formed to specimens with 12 mm diameter and 5 mm thickness by cold pressing under a pressure of 1000 kPa. Some specimens were put in a graphite dies with exit gas ability (resistance furnace) then heated up to 1650 and 2250 °C for 1 hour. In Arc furnace some specimens were placed in a graphite crucible kept in steel reactor. The steel reactor consisted of a tight flange at the top with provisions for the inlet/outlet of argon gas. Two graphite electrode above crucible product arc and rapidly the temperature received above 2300K.

After completion of the reaction, the end product was removed from the graphite crucible and treated with hot water and dilute HCl to remove unreacted boron trioxide, and oxides. Again the final product was thoroughly washed with triple distilled water and treated with ethanol to remove moisture. Then the powder was dried at 150°C for 1 h (in an oven).

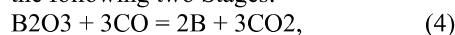
The synthesized powders were characterized by XRD (STOE STADI MP). The carbon, hydrogen, and sulphur contents of the product were determined by chemical analysis (CHNS Analyzer VARIO EL, Germany).

The progressing of the overall reduction reaction in the specimens was determined by comparing the I_{B_4C}/I_C ratio in all the specimens, where I_{B_4C} and I_C denote the intensity of peak 100 of B_4C ($2\theta=37.8$) and the intensity of peak 100 of graphite ($2\theta=26.5$) respectively. It is obvious that the higher the I_{B_4C}/I_C ratio, the higher the volume fraction of formed boron carbide and the lower the free carbon.

3. Results and discussion

Figs. 1 and 2 show boron carbide is produced in arc furnace at temperature above 2200°C in 2 minutes. In order to increasing the temperature in Arc furnace at condition of constant voltage, the amperage should be increased. Increasing the temperature causes that the rate of boron production in equation (4) increases. Whereas, the utilization rate of boron in equation (5) stay unchanged, as shown in Fig. 2 by boron picks.

The conversion of boron anhydride to boron carbide occurs in the following two Stages:



The first stage reduction becomes thermodynamically feasible above 1400°C, therefore with increasing the temperature boron production is increased, but second stage requires time for diffusion elements and produced boron carbide. Although Temperature beyond 2000°C has been recommended for an enhanced rate of reduction Accompanied by the formation of boron carbide,

Figs. 3 and 4 show production of boron carbide in resistance furnace at temperatures 1650°C and 2000°C respectively in 1 hours and 10 minutes. I_{B_4C}/I_C ratio in Fig. 4 more than that of Fig. 3. As a result, the utilization of B_2O_3 increases with increasing temperature and the amount of its utilization depends on temperature and experiments show that B_2O_3 is completely utilized.

Process of boron carbide production depends on both time and temperature. Also the reactant molar in feed, B/C ratio, is crucial to the manufacturing of stoichiometric boron carbide. Heat transfer and heating rate and mass transfer have a substantial influence on the mechanism of overall reaction boron carbide production. It is also observed that, the carbon conversion increase with increasing the temperature and in excess of boron oxide. For slow heating rates, reactants react via classical nucleation, growth mechanism due to the reaction proceeding through a liquid boron path [14]. For higher temperature range the reaction proceed via gaseous route. There is a change in mechanism at about 1700°C, which is believed to be the result of competition between B_2O_3 (l) and B_2O_2 (g) reacting with carbon. The liquid phase reaction dominates at lower temperature while the gas phase reaction dominates at higher temperature [15].

Fig (5), fig (6) show XRD chemical purified boron carbide and modified method for production of boron carbide.

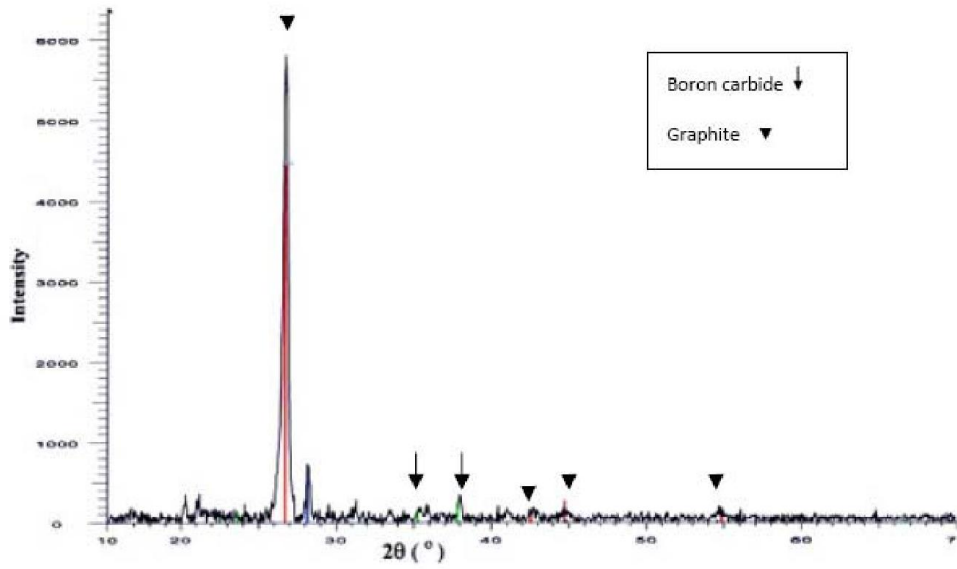


FIG1. Production boron carbide tin arc furnace 100A, constant voltage

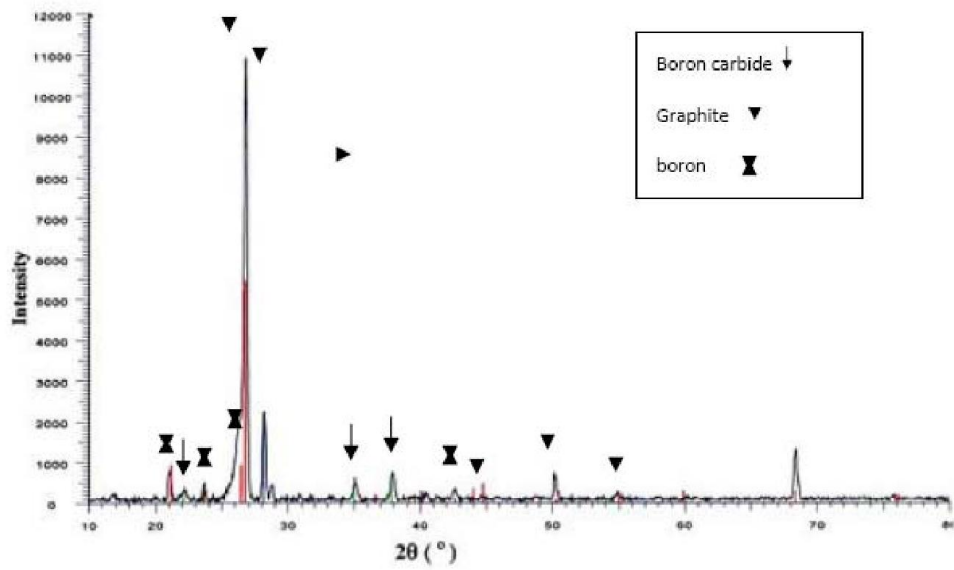


FIG2. Production boron carbide tin arc furnace 150 A, constant voltage

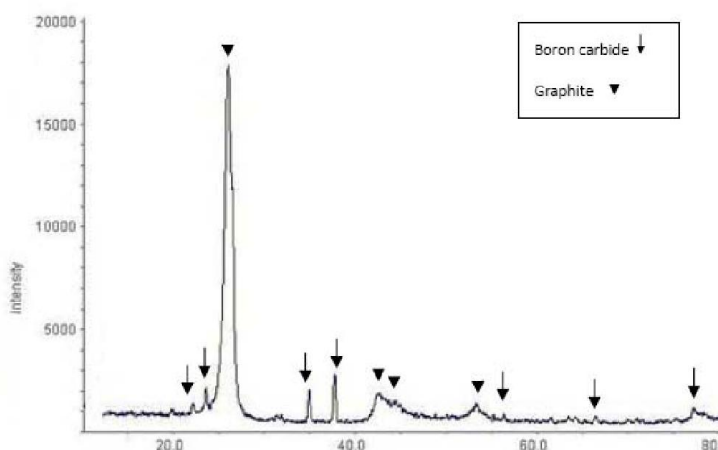


Fig3. Production of boron carbide in resistance furnace at temperatures 2000°C, 10 min

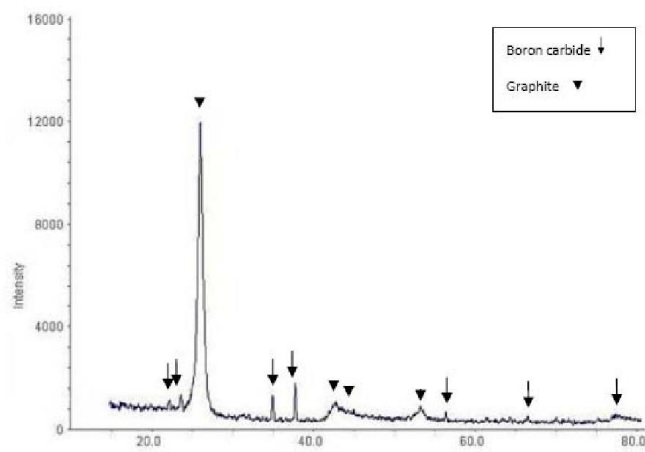


Fig4 . Production of boron carbide in resistance furnace at temperatures 1650°C, 1 hour

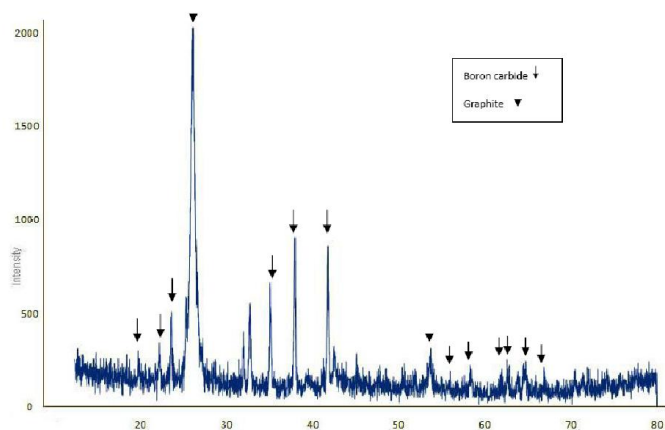


Fig5 .purified boron carbide is produced in Arc furnace temperature above 2200°C, 10 min, B/C=4

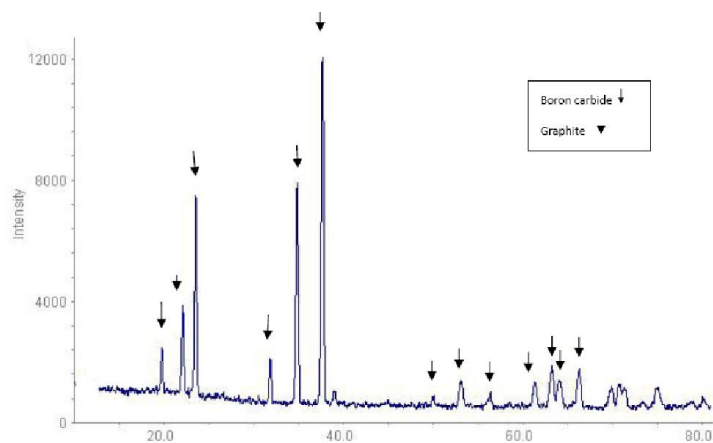


Fig6 .purified boron carbide is produced in resistance furnace temperature 2000, 1hour, B/C=3

4. CONCLUSION

Process of boron carbide production depends on both time and temperature. Although the effect of temperature on rate of formation B_4C is more effective than time but the time and suitable reactant molar in feed, B/C ratio, needed for complication reaction and to minimize free carbon residue.

For production pure boron carbide resistance furnace is suitable because the temperature in resistance furnace during the reaction is considerably lower than that of arc furnace, resulting is much less boron loss. Thus, the reduction reaction is easily controlled.

REFERENCES

- 1- Musiri M. Balakrishnarajan, Pattath D. Pancharatna and Roald Hoffmann, Structure and bonding in boron carbide: The invincibility of imperfections, *New J. Chem.*, 2007, 31, 473–485
- 2- A.M. Hadian and J.A. Bigdeloo, The Effect of Time, Temperature and Composition on Boron Carbide Synthesis by Sol-gel Method, *Journal of Materials Engineering and Performance*, 2008, 17, 44–49
- 3- D. Gosset and M. Colin, *J. Nucl. Mater.*, 1991, 183, 161.
- 4- 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
- 5- G. de With, High Temperature Fracture of Boron Carbide: Experiments and Simple Theoretical Models, *J. Mater. Sci.*, 1984, 19, p 457–466

- 6- D. Segal, Chemical preparation of powders, *Material Science Technology*, 1991, vol. 4, pp. 205-211,.
- 7- D. Gosset and B. Provot, Boron carbide as a potential inert matrix; an evaluation, *Progress in Nuclear Energy*, vol.38, 2001, pp. 263-266,.
- 8- G. Goller, C. Toy, A. Tekin and C.K. Gupta, The Production of Boron Carbide by Carbothermic Reduction, *High Temperature Materials & Processes*, 1996, pp. 117-122.
- 9-A.N. Caruso, P.A. Dowben, S. Balkir, Nathan Schemmb, Kevin Osberg, R.W. Fairchild, Oscar Barrios Floresb, Snjezana Balaz, A.D. Harken, B.W. Robertson and J.I. Brand, The all boron carbide diode neutron detector: Comparison with theory, *Materials Science and Engineering*, B 135:2 , pp. 129, 2006
- 10- Mahagin, D.E., and Dahl, R.E., Nuclear Applications of Boron and Borides, in *Boron and Refractory Borides*, Matkovich, V.I., Ed., Berlin-Heidelberg: Springer, 1977, pp. 613–632
- 11- Gray, E. G., Process for the production of boron carbide. U.S.Patent 2,834,651, 13 May 1958.
- 12- K.A. Schwetz, A. Lipp, in: *Ullmann's Encyclopedia of Industrial Chemistry*, vol. A4, Wiley, 1985, p. 295.
- 13- Scott, J., "Arc Furnace Process for the production of boron carbide ,," U.S. Patent No. 3,161,471, 1964
- 14- Weimer, A. W., Moore, W. G., Roach, R. P., Hitt, J. E., and Dixit, R. S., "Kinetics of Carbothermal Reduction Synthesis of Boron Carbide," *Journal of the American Ceramic Society*, Vol. 75, 1992.
- 15- Weimer, A. W., *Thermochemistry and Kinetics*, Chapman and Hall, London, 1997.