ISSN 1061-3862, International Journal of Self-Propagating High-Temperature Synthesis, 2009, Vol. 18, No. 1, pp. 60–63. © Allerton Press, Inc., 2009.

Synthesis of Boron Carbide by Calciothermic Reduction Process*

L. J. Berchmans[a], V. Mani[b], and K. Amalajyothi[c]

[a] *Electropyrometallurgy Division, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, 630006 India*

[b] *Department of Chemistry, St. Joseph's College, Tiruchirappalli, Tamil Nadu, 620002 India*

[c] *Department of Electrochemical Engineering, Center for Education, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, 630006 India*

e-mail: ljberchmans@yahoo.com

Received September 24, 2008

Abstract—Boron carbide (B_4C) powders were synthesized by calciothermic reduction process from the mixtures of borax (or boron trioxide), petroleum coke, and calcium. The synthesized materials were characterized by XRD, SEM, and chemical analysis.

Keywords: metallothermic reduction, XRD, SEM, chemical analysis.

PACS: 81.05.Mh, 81.16.Be, 81.20.Ka

DOI: 10.3103/S1061386209010129

1. INTRODUCTION

Boron carbide (B_4C) is a boron-containing compound [1] with a high melting point (2450°C), outstanding electroconductivity (9.2 mho), low specific gravity (2.52 g cm^{-3}) [2], large neutron capturing cross section (3850 barn), chemical inertness, and unique thermal properties. It was found to be one of important candidate materials for high tech applications [3]. The B_4C crystal has a rhombohedral lattice (*hR* 15, s.g. *R*3*m*) consisting of the 12-atomic icosahedral units located at the corners of a rhombohedral unit cell connected by the C–B–B or C–B–C chains along the cell diagonal [4]. In the B–C system, B_4C is known as an equilibrium compound [5]. Due to low carbon content, B_4C can be expected to decrease the number of carbon species formed during oxidation. The properties of B_4C as a function of carbon content have been discussed in [6–9]. The neutron absorption property of B_4C is due to the presence of the ^{10}B isotope which takes part in the following nuclear reaction:

$$^{5}_{10}\mathrm{B} + {}^{1}_{0}n \longrightarrow {}^{2}_{4}\mathrm{He} + {}^{3}_{7}\mathrm{Li} + 2.4\mathrm{Mev}.$$

For thermal neutrons, the absorption cross section is 3850 barn, which makes the material an excellent candidate for use in thermonuclear reactors. At higher energies, the cross section of the most of other elements becomes very low, whereas that of ^{10}B is known to monotonically decrease with increasing energy [10, 11].

For production of B_4C, many processes have been attempted and these have led to formation of $B_{12}C_3$ composites [12–14]. Such materials can be synthesized using a chemical vapor deposition process [15, 16] or carbothermic reduction process [17, 18]. Different carbon sources—such as dextrose, sucrose, starch, glycerol, polyvinyl alcohol, etc.—have been employed for preparation of B_4C powders. Magnesiothermic reduction [19, 20], laser-induced reduction, metallothermic micropyretic process [21], soft chemical methods [22–26], plasma-enhanced chemical vapor deposition [27], dc magnetron sputtering, and thermal evaporation technique [28] have also been tried. But in all cases, the synthesis was accompanied by a marked loss of boron.

In this work, we made an attempt to synthesize boron carbide powders from inexpensive and readily accessible raw materials.

2. EXPERIMENTAL

Boron carbide has been synthesized by the reaction between boron-containing compounds—borax $Na_2B_4O_7$ and boron trioxide B_2O_3—and a carbon releasing agent, powdered petroleum coke (petcoke). As per molar quantities, the reactants were mixed and finely ground to obtain a uniform powdered mass. Then it was placed in a graphite crucible kept in an inconel reactor. The inconel reactor consisted of a tight flange at the top with provisions for the inlet/outlet of argon gas. The whole assembly was then heated in an electric furnace. The reaction vessel was connected to the argon gas line and the reduction was carried out in controlled conditions, for a predetermined period of 5 h at 1000°C. After completion of the reaction, the end product was removed from the graphite crucible and treated with hot water

* The article is published in the original.

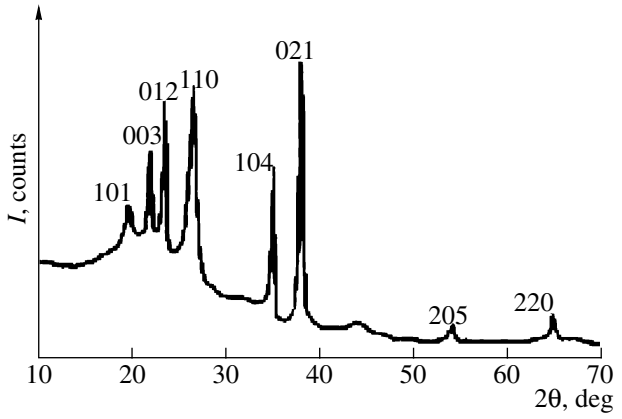

Fig. 1. Diffraction pattern of the product formed in the borax + petcoke + Ca mixture.

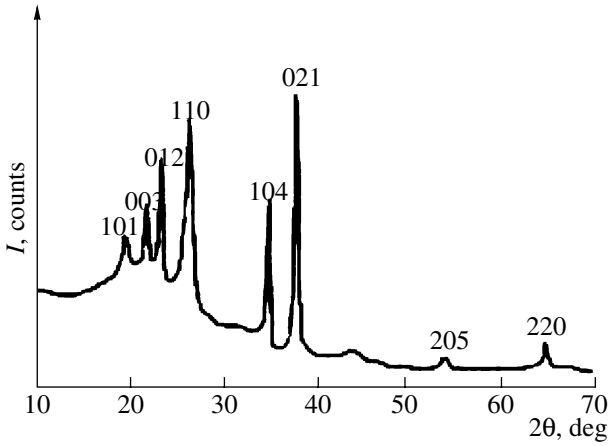

Fig. 2. Diffraction pattern of the product formed in the B_2O_3 + petcoke + Ca mixture.

and dilute HC1 to remove unreacted boron trioxide, borax, 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).

For the determination of residual free carbon content a chemical treatment was done with sulfochromic acid. In this technique, free carbon was estimated by taking 1 g of B_4C powder which was leached with 100 ml of a solution of sulfochromic acid. The latter was prepared by dissolution of $K_2Cr_2O_7$ in conc. H_2SO_4. During this treatment, free carbon was oxidized and removed from the solution, so that the remaining precipitate gave B_4C. The final product was black in color. The synthesized powders were characterized by XRD (Philips 8030 X-ray diffractometer). The carbon, hydrogen, and sulfur contents of the product were determined by chemical analysis (CHNS Analyzer EL 111, Germany). The morphology of synthesized crystals was examined by SEM (JEOL-JSM-3.5 CF, Japan).

3. RESULTS AND DISCUSSION

Calcium as an excellent reducing agent is being widely used in many metallurgical operations. Calcium is used as a reducing agent in the extraction of other metals like uranium [29, 30], zirconium [31], and thorium. It is also used in the preparation of TiC [32] and niobium powders [33]. Petroleum coke is used because it is low in ash, sulfur, and volatile compounds [34]. It is reported that the use of petcock as a reducing agent may result in fuel savings of 66% and a CO_2 emission avoidance of 15% [35].

3.1. XRD Analysis

The diffraction patterns of the products formed in the borax-containing (Fig. 1) and B_2O_3-containing (Fig. 2) mixtures provide useful information about the product and accompanying impurities.

The lattice parameters of product were determined using the following expression:

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{1}{c^2},$$

where d is the density, a and c are lattice parameters, and h, k, l the Miller indices.

The size L of product crystallites was determined using the Debye-Scherrer formula as given below:

$$L = \frac{0.9\lambda}{\beta\cos\Theta},$$

where $\beta = \Delta/2$ (Δ is the full width at half maximum for a given diffraction peak) and $\theta = 1/2\ 2\theta$.

The X-ray density d of B_4C was determined using the well-known formula:

$$d = mZ/Va^3.$$

The XRD data for B_4C obtained in two different routes are presented in Table 1. Our lattice parameters well agree with the reported values: a = 5.65 Å and c = 12.16 Å [36–39]. The mean crystallite size L was found to vary within the range 21–23 nm, depending on the type of starting mixture. The nanosize of B_4C powders is an important property for their use as a neutron capture material in the nuclear industry.

3.2. Chemical Analysis

The data of chemical analysis (Table 2) show that the product obtained from the borax + petcoke + Ca mixture contains a higher amount of nitrogen, sulfur, hydrogen, and carbon as impurities. The product formed in the B_2O_3 + petcoke + Ca mixture is seen to contain a considerable amount of carbon as an impurity,

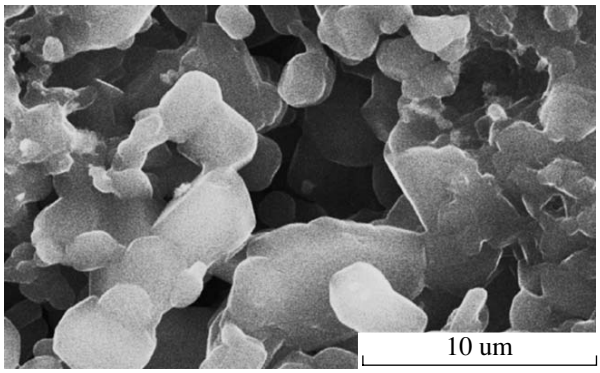

Fig. 3. SEM image of the product formed in the borax + petcoke + Ca mixture.

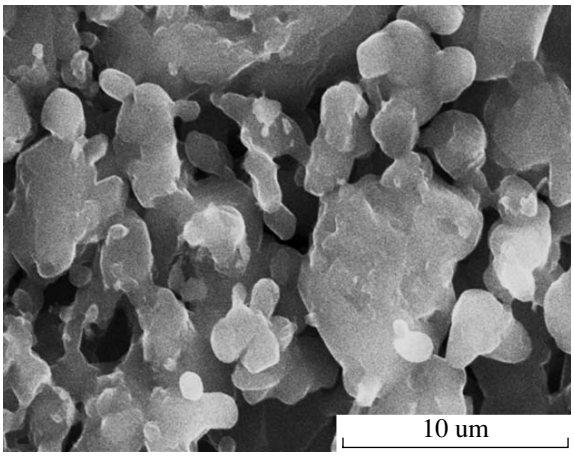

Fig. 4. SEM image of the product formed in the B_2O_3 + petcoke + Ca mixture.

while the nitrogen, sulfur, and hydrogen contents are negligibly small.

3.3. SEM Data

The SEM images of the synthesized products (Figs. 3, 4) show an uneven distribution of B_4C particles comprising of large faceted aggregates with some small incrustations on their surface. The large faceted aggregates are formed due to moisture absorption by the samples and also due to the presence of impurities as detected by XRD and chemical analysis.

4. CONCLUSIONS

Fine B_4C powders have been successfully synthesized in a low-temperature process from readily accessible raw materials.

REFERENCES

1. Lee, K.W. and Harris, S.J., *Diamond Relat. Mater.*, 1998, vol. 7, p. 1539.
2. Subramanian, C, Roy, T.K., Murthy, T.S.R.Ch., Sengupta, P., Kale, G.B., Krishnainah, M.V., and Suri, A.K., *Ceram. Int.*, in press.
3. Amberger, E., Stumpf, W., and Buschbeck, K.-C, Boron, in *Gmelin Handbook of Inorganic Chemistry,* Berlin: Springer, 1981.
4. Chauet, O., Forro, D.E.L., Aselage, T.L., and Zuppiroli, L., *Phys. Rev. B*, 1996, vol. 53, p. 14450.
5. *ASM Hand Book Vol. 3: Alloy Phase Diagrams*, Baker, H., Ed., Metals Park, OH: ASM International, 1992.
6. Werheit, H., *Mater. Sci. Eng. B*, 1995, vol. 29, nos. 1–3, pp. 228–232.
7. Nihara, K., Nakahira, A., and Hirai, H., *J. Am. Ceram. Soc.*, 1984, vol. 67, pp. C13–C14.
8. Lezhava, D., Darsavelidze, G., Gabunia, D.O., *et al.*, *J. Solid State Chem.*, 2006, vol. 179, pp. 2934–2938.
9. Merzhanov, A.G., *Russ. Chem. Bull.*, 1997, vol. 46, no. 1, pp. 1–27.
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. Roy, T.K., Subramanian, C, and Suri, A.K., *Ceram. Int.*, 2006, vol. 32, pp. 227–233.
12. Bougoin, M., Thevenot, F., Dubois, J., and Fantozzi, G., *J. Less-Common Met.*, 1985, vol. 111, pp. 257–271.
13. Thevenot, F, *J. Eur. Ceram. Soc.*, 1990, vol. 6, pp. 203–225.
14. Oliveira, J.C. and Conde, O., *Thin Solid Films*, 1997, vol. 307, pp. 29–37.
15. Sezer, A.O. and Brand, J.I., *Mater. Sci. Eng. B*, 2001, vol. 79, pp. 191–202.
16. Spohn, M.T., *Am. Ceram. Soc. Bull.*, 1993, vol. 72, no. 6, p. 88.
17. Scott, J.J., US Patent 3 161 471, 1964.
18. Spohn, M.T., *Am. Ceram. Soc. Bull.*, 1993, vol. 72, no. 6, p. 88.
19. Thevenot, F., in *Advanced Ceramics*, Ganguly, C, Roy, S.K., and Roy, P.R., Eds., vols. 56–57, 1991, p. 59.
20. Mohanty, R.M., Balasubramanian, K., and Seshadri, S.K., *J. Alloys Comp.*, 2007, vol. 441, pp. 85–93.
21. Mondal, S., andBanthia, A.K., *J. Eur. Ceram. Soc*, 2005, vol. 25, pp. 287–291.
22. Shi, L., Gua, Y., Chen, L., Qiana, Y., Yanga, Z., Ma, J., *Solid State Commun.*, 2003, vol. 128, pp. 5–7.
23. Sinha, A., Mahata, T., and Sharma, B.P., *J. Nucl. Mater.*, 2002, vol. 301, pp. 165–169.
24. Sudoh, A., Konno, H., Habazaki, H., and Kiyono, H., *Carbon*, 2007, vol. 45, pp. 1373–1375.
25. Han, W., Bando, Y., Kurashima, K., and Sato, T., *Chem. Phys. Lett.*, 1999, vol. 299, pp. 368–372.
26. Pender, M.J. and Sneddon, L.G., *Chem. Mater.*, 2000, vol. 12, pp. 280–283.

27. Ma, R. and Bando, Y., *Chem. Phys. Lett*, 2002, vol. 364, pp. 314–317.
28. Method for Converting Uranium Oxides to Uranium Metal, US Patent 4717420, 1988.
29. Vol'skii, A.N., Sterlin, Ya.M., Sokolov, V.S., Gulyaeva, V.N., and Savenkova, A.G., *journal*, 2002, vol. 93, pp. 563–568.
30. Abdelkader, A.M., and El-Kashif, E., *ISIJ Int.*, 2007, vol. 47, no. 1, pp. 25–31.
31. Barbandel, D.V., Mishra, R., and Junej, J.M., *J. Therm. Anal. Calorim.*, 2004, vol. 78, pp. 775–780.
32. Toru H. Okabe, T., Park, I., Jacob, K.T., and Waseda, Y, *J. Alloys Comp.,* 1999, vol. 288, pp. 200–210.
33. Hackett, G.A., Zondlo, J.W., and Svensson, R., *J. Power Sources*, 2007, vol. 168, pp. 111–118.
34. Halmann, M., Frei, A., and Steinfeld, A., *Energy*, 2007, vol. 32, pp. 2420–2427.
35. Lye, R.G., Hollox, G.E., and Venables, J.D., in *Anisotropy in Single Crystal Refractory Compounds*, New York: Plenum Press, 1968.
36. Hollox, G.E., *Mater. Sci. Eng.*, 1968–1969, vol. 3, p. 121.
37. McKenna, P.M., *Met. Program.*, 1939, vol. 36, p. 152.
38. Pfau, H., and Rix, W., *Z. Metallkd.*, 1954, vol. 45, p. 116.
39. Leion, H., Mattisson, T., and Lyngfelt, A., *Fuel*, 2007, vol. 86, pp. 1947–1958.