AIChE

Production of B_4C Coatings by CVD Method in a Dual Impinging-Jet Reactor: Chemical Yield, Morphology, and Hardness Analysis

Mustafa Karaman, N. Aslı Sezgi, and H. Önder Özbelge
Dept. of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

DOI 10.1002/aic.11900

β-rhombohedral boron carbide (B_4C) was deposited on a tungsten substrate from a BCl_3—H_2—CH_4 gas mixture in a dual impinging-jet chemical vapor deposition reactor. On-line FTIR analysis of the product stream proved the formation of $BHCl_2$ and HCl as by products, in a competing parallel reaction. A maximum of 13% chemical yield of boron carbide was observed, and the yield was found to have increasing trend with an increase in temperature. XRD analysis proved the existence of rhombohedral B_4C phase at 1300°C without any other B_4C phases or impurities. At this temperature, the formation of 5-fold icosahedral boron carbide crystals up to 30 micron sizes was observed. Such highly symmetric crystalline regions were observed to have a very high hardness value of 4750 kg/mm^2 as revealed from the microhardness analysis. The change in product morphology at low substrate temperatures resulted in a decrease in the hardness values. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2914–2919, 2009

Keywords: chemical vapor deposition, ceramics, boron carbide, refractory carbides

Introduction

Among the refractory carbides family, boron carbide occupies a special place due to its excellent mechanical, physical, and chemical properties. It exhibits high hardness, high modulus, high wear resistance, and low density, together with high chemical and thermal stabilities. There is an increasing interest for boron carbide for high technology applications especially in military, nuclear, medical, and space industries. It is a potential p-type semiconductor material in the microelectronics industry.[1] All such high technology applications require high quality and well defined boron carbide, which usually necessitates a vapor deposition technology. Boron carbide exhibits different crystalline structures and the most stable phase of boron carbide is the rhombohedral phase with a stoichiometry of $B_{13}C_2$ and $B_{12}C_3$ (or B_4C). This phase exhibits a wide homogeneity range from 8 to 20 atomic % carbon concentrations, and the material properties are highly dependent on the chemical composition of the products. So that, for any high technology applications, it is crucial to keep the phase homogeneity within the required limits to produce well defined products with desired properties. Chemical vapor deposition offers the advantage of a well controlled deposition of high purity and single phase boron carbides.[2] It is possible to deposit films of uniform thickness and low porosity even on substrates of complicated shape in this process.[3] In the CVD process, various reactant gas mixtures containing boron, hydrogen, carbon, and halogen are used to deposit boron carbide on various substrates. Several reaction gas mixtures are BI_3—CH_4, BCl_3—CH_4—H_2, BBr_3—CH_4—H_2, and BCl_3—CCl_4—H_2.[4]

The extensive research on CVD of boron carbide usually focused on product morphology, microstructure, and chemical composition investigations with respect to various deposition conditions.[5–11] There are a limited number of studies on the kinetic analyses and they are usually based on thermodynamic considerations or experimental rate studies based on the deposition thicknesses per unit time.[12–14] The detailed

---

Correspondence concerning this article should be addressed to N. A. Sezgi at sezgi@metu.edu.tr

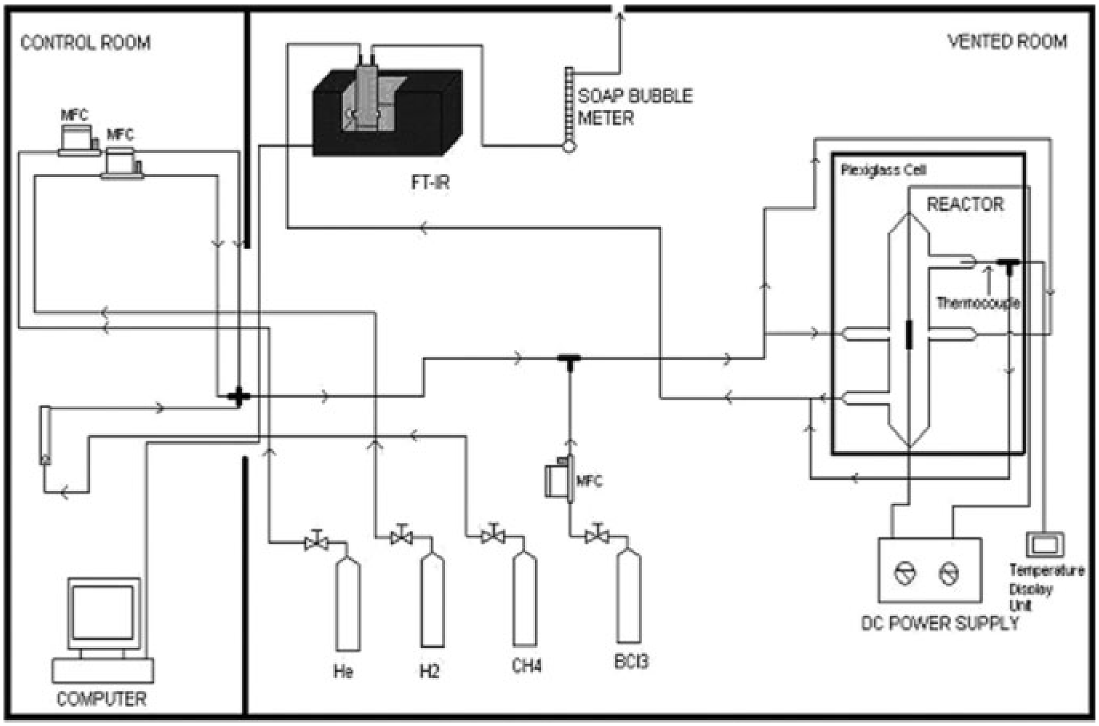

Figure 1. Schematic drawing of the experimental apparatus.

kinetic investigation requires combinatorial analysis of the product composition together with the chemical analysis of the reactor effluent gases, which was carried out previously by our research group using a dual impinging-jet reactor.[15,16] In other words, our research group has studied the chemical kinetics of B_4C deposition on a tungsten substrate in a dual impinging jet reactor in which diffusion limitations are minimized and has also obtained true experimental kinetic data.[16] Using the true kinetic data, reaction mechanism has been proposed and rate expressions have been obtained.[17] The impinging-jet reactor configuration is an ideal geometry especially in kinetic investigations because of the ability to minimize the mass transfer limitations on the reaction kinetics. Our earlier studies had also shown that the conversion values obtained in the impinging-jet reactor were at least five times higher than the conversion values obtained for the same reaction in a parallel flow CVD reactor.[18,19] Besides, the stagnation region produced as a result of jet impingement on the substrate surface leads to highly uniform and well mixed gas concentration distribution at the substrate leading well defined microstructures. The turbulent stagnation zone above the substrate surface may have great effect on the morphology of boron carbide deposited. The formation of by-product $BHCl_2$ was already proven by our group from the spectrophotometric analysis of the reactor effluent.[16] So, the estimation of the chemical yield of boron carbide becomes an important concern in terms of process economy and optimization, which is a missing analysis on the literature of the boron carbide CVD. The yield analysis of boron carbide deposition from the CVD and other techniques has not been available in the literature. In this study, it was aimed to investigate the effect of the deposition temperature and composition on chemical yield, together with the phase and morphology investigations of the boron carbide produced by the CVD method, using a previously optimized concentration of reactant gas mixture and to measure the hardness property of boron carbide synthesized at different temperatures.

Experimental

Boron carbide films were deposited on the tungsten substrate from a reactive gas mixture of BCl_3, CH_4, and H_2 in a dual impinging-jet reactor at different temperatures and initial compositions. The diagram of the experimental apparatus is given in Figure 1. Details of the reactor and the reactor system were published elsewhere.[16,17] Reactant gases, BCl_3, CH_4, and H_2 were fed to the reactor through the two orifices (0.5 mm diameter) in the middle of the reactor to provide well impingement on to the both sides of the tungsten substrate which hangs vertically between the two electrodes in the reactor. Flow rates of the reactant gases were controlled by mass flow controllers keeping the total volumetric flow rate at 200 sccm in all experiments. The tungsten substrate (3 cm length, 3 mm width) was heated to the desired reaction temperature resistively by applying DC power, and temperature measurements were carried out continuously at different locations over the substrate surface during the experiments by an optical pyrometer. The on-line chemical analysis of the reactor effluent was done by using a Perkin Elmer Spectrum One model Fourier Transform Infrared Spectrometer equipped with a Specac Sirocco Series heatable gas cell. The path length of the IR beam in the gas cell was variable which allowed the adjustment of best path length value for the specific experimental requirements. For the composition ranges utilized in this study, a path length value of 8 meters was adjusted. To obtain quantitative information on the compositions of the reactor inlet and outlet streams, the FTIR spectra of methane, boron trichloride, and hydrochloric acid were calibrated, before starting the actual experiments. The experiments were carried out with a methane mole fraction range of 0.018–0.042 and a boron trichloride mole fraction range of 0.023–0.0118, in excess hydrogen. The substrate temperature was changed between 1000 and 1400°C.

The product morphologies were characterized by XRD analysis (Philips PW 1840) and surface images of the films were obtained by SEM (JOEL JSM-6400). The microhardness measurements were carried out using a microhardness tester (Instron Tukon 2100B) having a diamond pyramid indenter. Before the hardness analysis, the samples were buried into bakalite molds and their top surfaces were polished with diamond paste having 3 μm particle sizes in a mechanical polisher (Metkon-Gripo).

Results and Discussion

The on-line FTIR analysis of the reactor effluent stream proved the formation of $BHCl_2$ and HCl as the only stable by-products. Together with the reactant gases BCl_3, CH_4, and H_2, and the solid product B_4C, there are altogether six chemical species involved in the reaction system. The following two overall independent reactions, boron carbide (1) and dichloroborane (2) formation reactions, are considered for the CVD of boron carbide;

$$BCl_3(g) + H_2(g) + 1/4CH_4(g) \Rightarrow 1/4B_4C(s) + 3\ HCl(g) \tag{1}$$

$$BCl_3(g) + H_2(g) \Rightarrow BHCl_2(g) + HCl(g) \tag{2}$$

In this study, the fractional yield was defined as the ratio of the actual amount of boron carbide deposited to the theoretical amount of boron carbide that would be produced for the complete conversion of the key component BCl_3 into B_4C.

$$\text{Percent yield } = \frac{R_{B_4C} \times MW_{B_4C} \times t}{1/4 \times F_o \times y_{BCl_3o} \times MW_{BCl_3}} \times 100$$

where R_{B_4C} is the formation rate of boron carbide and defined as,

$$R_{B_4C} = \frac{1}{4} F_o \frac{y_{CH_4o} - y_{CH_4}}{(\frac{3}{4} y_{CH_4} + \frac{1}{4}) y_{BCl_3o}}$$

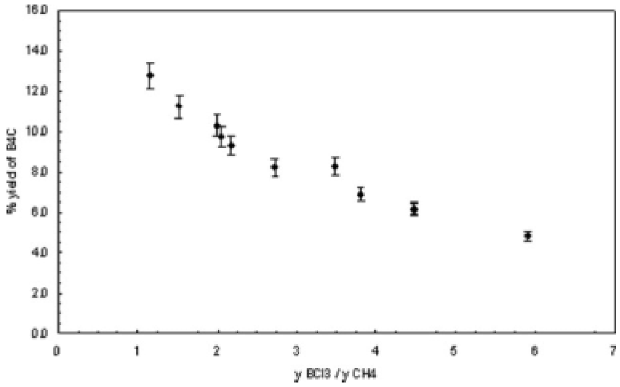

Figure 2. Effect of initial BCl_3/CH_4 mole ratio on B_4C yield (y_{BCl_3o} = 0.023–0.118, y_{CH_4o} = 0.018–0.042, in hydrogen, T = 1150°C).

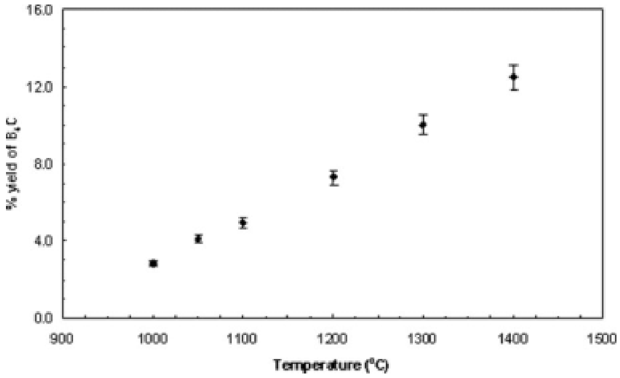

Figure 3. Effect of temperature on B_4C yield (y_{BCl_3o} = 0.081, y_{CH_4o} = 0.02, in hydrogen).

A more detailed analysis of reaction phenomena and stoichiometric calculations was presented in our previous publication.[16]

Effects of inlet molar ratio of BCl_3 to CH_4, and substrate temperature on boron carbide percentage yield are depicted in Figures 2 and 3, respectively. Boron carbide percentage yield decreases significantly with increasing BCl_3 to CH_4 inlet molar ratio. Our mechanism determination studies indicated that, among the many reaction mechanisms studied, the mechanism which involves the adsorption of BCl_3 on the substrate surface and the formation of dichloroborane in the gas phase gave the best agreement with the experimental data.[17] So that increasing inlet BCl_3 molar fraction does not cause significant increase in the formation rate of boron carbide. Low BCl_3 inlet molar fractions can be considered for high yields; however, great care should be taken into account to produce well defined boron carbide in the desirable homogeneity range. There is almost a linear increase in the boron carbide yield with increasing the substrate temperature. Boundary layer estimations, which are based on the empirical correlations presented by Martin[20] for the impinging-jet system used in this study revealed that the temperature changes from 1150°C to 300°C through a 0.38 mm distance from the substrate surface, so it is reasonable to assume a steep temperature gradient through the boundary layer in the gas next to the substrate surface. It may be expected that a change in surface temperature in this impinging-jet system may have smaller effect on the gas-phase kinetics and hence less impact on the reaction rates compared to the solid-phase kinetics in the formation of boron carbide. Therefore, the great increase of B_4C formation rate with temperature rise, when compared with the formation rate of $BHCl_2$, causes boron carbide yield to increase substantially.

The maximum boron carbide yield observed in the studied temperature and composition ranges in this study was 13%. Such poor yields are usually observed in CVD systems involving parallel side reactions. This low yield could be attributed to the high formation rate and selectivity of

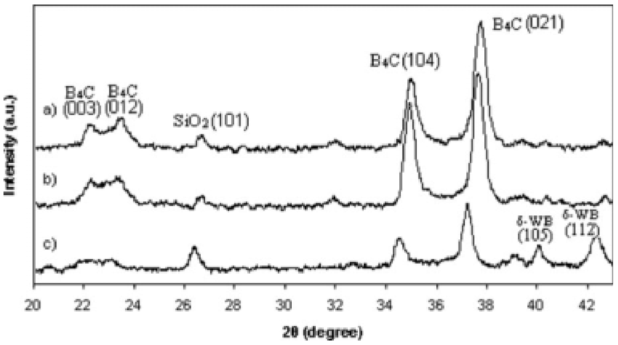

Figure 4. X-ray diffraction patterns of the samples produced at different substrate temperatures under atmospheric conditions with initial boron trichloride to methane molar ratio of 4.0 and with a temperature of: (a) 1300°C, (b) 1200°C, and (c) 1100°C.

competing dichloroborane formation reaction when compared with the boron carbide formation reaction. Also, boron carbide formation reaction may occur far from equilibrium within the studied temperature range, which may be another reason for observing poor yield.

Temperature had not only strong influence on the chemical yield of boron carbide but it also had great influence on the product composition and morphology. The change of the crystalline structure of the films with the substrate temperature was studied by powder XRD analysis and SEM. The X-ray diffractograms of the films produced at 1100, 1200, and 1300°C are shown in Figure 4. The most intense diffraction peaks were observed from the (021) and (104) reflections, which are both characteristics of rhombohedral boron carbide. However, there is a change in the 2θ angular position of both reflections with temperature variation. At 1300°C, (021) and (104) reflections are observed at 2θ angular positions of 37.8 and 34.95, respectively, which both correspond to technical grade rhombohedral $B_{12}C_3$ stoichiometry (JCPDS 35-798).[21] The diffraction peaks observed at 2θ angular positions of 22.3 and 23.5 belongs to the (003) and (012) reflections, respectively, which also corresponds to the rhombohedral boron carbide. With a decrease in temperature, the angular positions shift to lower 2θ angles at both reflections, implying a structure change. The reflections observed at 1200°C are more like the ones obtained at 1300°C, with an angular deviation of only 0.3° of 2θ. The shifts are especially significant at 1100°C, at which rhombohedral boron carbide reflections represent a $B_{13}C_2$ structure (JCPDS 33-225).[21] Therefore, it may be concluded that less carbon atom can be introduced into the B–C structure with a decrease in the substrate temperature. In the crystal structure of the rhombohedral boron carbide, 5-fold boron icosahedra are linked directly through covalent bonds and also by a chain of three atoms located on the principal body diagonal of the rhombohedron, as shown in Figure 5. 12-atom containing boron icosahedra together with the 3 atom diagonal chain builds up a 15-atom unit cell.[22] The change of the stoichiometry of our products with temperature change is possibly due to the replacement of one carbon atom with one boron atom in the C-B-C icosahedral chain, leading B-B-C structure, at lower temperatures.[23] The presence of δ-WB is observed only at 1100°C with the characteristic (105) and (112) reflections. At lower temperatures, boron contents of the films are higher and more boron atoms could have chance to diffuse through the substrate surface, forming tungsten boride phases at the interface. In addition to the δ-WB and r-B_4C peaks, the characteristic peak of SiO_2 at 2θ angular position of 26.5° was observed. The samples were made powder in a pestle made of quartz, which may possibly be scraped into the powder by harder boron carbide particles.

The change of surface morphology was also observed clearly after having SEM images of the samples produced at three different temperatures. With an increase in the substrate temperature, a great change in the microstructure was observed (Figure 6). At 1100°C, a few micron size pyramidal crystal facets are seen. At 1200°C, the grain size increases substantially up to around 5 μm. At this temperature, the surface of the pyramidal geometry is covered by tiny and uniform grains, which could be an indication of a second nucleation and growth mechanism. At 1300°C, at which the existence of only stoichiometric rhombohedral phase was proven by XRD analysis, the surface is covered by 10–40 micron size crystals having perfect 5-fold icosahedral symmetry (Figure 6c). This is a very striking observation because such large crystals having 5-fold symmetry are rare in nature and in the literature studies due to the lack of long-range translational symmetry for those crystals. It is known that, if the extremities of a single crystal are permitted to grow without any external constraint, the crystal assumes a regular geometric shape having flat faces, and its shape is indicative of the crystal system. The basic icosahedral units of rhombohedral B_4C structure might act as nuclei to build up large microscale icosahedral crystals with 5-fold symmetry.[24] Quite a number of massive 5-fold icosahedral crystals with a grain sizes larger than 30 micrometer can easily be seen in Figure 6c.

The mechanical properties of boron carbides consisting of such massive icosahedral crystals are believed to be improved further because of high degree of symmetry observed. Hardness is among the most important mechanical properties of boron carbide, together with high strength and low density. Hardness measurements were carried out for

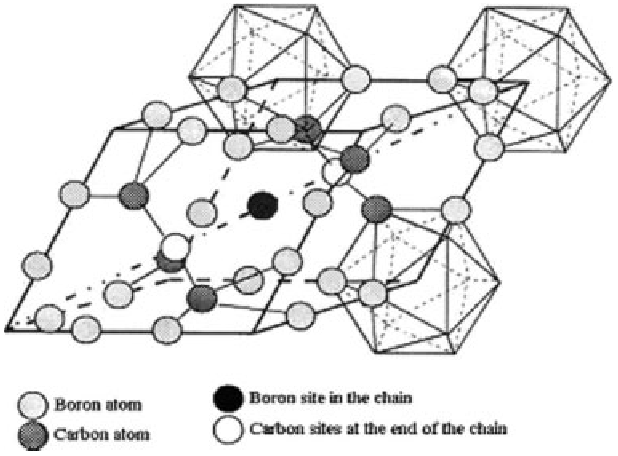

Figure 5. Rhombohedral structure of boron carbide.[20]

three different B_4C samples produced at 1100, 1200, and 1300°C, and the results are depicted in Table 1. There is an increasing trend in the hardness value with a temperature rise. This is a highly expected result considering above discussion, such that, temperature has strong influence on both chemical composition and microstructure. With temperature increase, B/C ratio of the boron carbide deposits decreases, due to the entrance of more carbon atom into the structure at higher temperatures, as revealed from the XRD analysis. In CVD synthesized boron carbide, hardness values increase with increasing carbon content within the phase homogeneity range.[4,25] It was concluded that the hardness increase with temperature is resulted from both, increase of bound-carbon content (not free graphite) and evolution in the microstructure of boron carbide with temperature. Especially, at 1300°C, the formation of large icosahedral B_4C crystals is believed to be one of the main reasons for the very high hardness value observed.

Table 1. Effect of Temperature on Vickers Hardness of Boron Carbide

Temperature (°C)	Vickers Hardness (kg/mm^2)
1100	3850
1200	4085
1300	4750

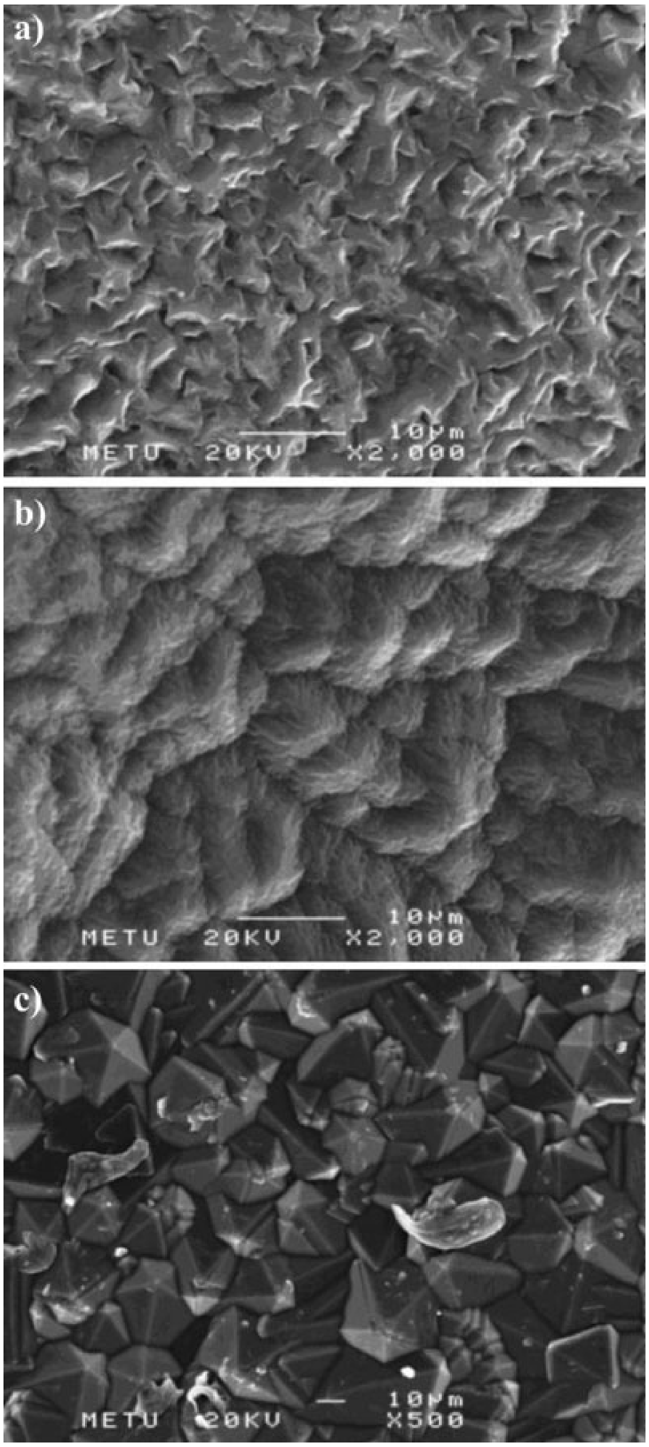

Figure 6. SEM images of the samples produced at different temperatures: (P = 1 atm., y_{CH_4}/y_{BCl_3} = 0.25, in hydrogen at reactor inlet) (a) 1100°C, (b) 1200°C, and (c) 1300°C.

Conclusions

The deposition of β-rhombohedral boron carbide on the tungsten substrate was achieved by a relatively simple process. Maximum boron carbide yield was observed at high substrate temperature and low inlet boron trichloride to methane molar ratio. The low yield values observed were attributed to the high formation rate and selectivity of competing dichloroborane formation reaction. The formation of massive 5-fold icosahedral boron carbide crystals up to 30 micron sizes was observed. Ultra high hardness value observed for these large crystals proved the improvement of mechanical properties due to the long range symmetry. Surface morphology and product composition changed with the change in deposition temperature. The change of the crystalline structure and the decrease in the carbon content of the deposits caused significant decrease in the measured hardness values.

Acknowledgements

The authors thank to The Scientific and Technological Research Council of Turkey (TUBITAK) (project no: Misag-217) and State Planning Organization of Turkey (project no: BAP-08-11-DPT2002K120510-IM-5) for their financial supports of this project.

Notation

R_{B_4C} = formation rate of boron carbide (gmol/min)
MW_i = molecular weight of component i (g/gmol)
t = deposition duration (sec)
F_o = total inlet molar flowrate (gmol/min)
x_i = conversion of BCl_3 to component i
y_{BCl_3o} = initial mole fraction of BCl_3

Literature Cited

1. Byun D, Spady BR, Ianno NJ, Dowben PA. Comparison of different chemical vapor deposition methodologies for the fabrication of heterojunction boron carbide diodes. *Nanostruct Mater*. 1995;5:465–471.
2. Sezer AO, Brand JI. Chemical vapor deposition of boron carbide. *Mater Sci Eng*. 2001;B79:191–202.

3. Bunshah RF. *Handbook of Hard Coatings*. Park Ridge, NJ: Noyes Publications, 2001.
4. Thevenot F. Boron carbide-A comprehensive review. *J Eur Ceram Soc*. 1990;6:205–225.
5. Cochran AA, Stephenson JB. Boron and boron carbide coatings by vapor deposition. *Metall Trans*. 1970;1:2875–2880.
6. Jansson U, Carlsson JO, Stridh B, Söderberg S, Olsson M. Chemical vapor deposition of boron carbides I: phase and chemical composition. *Thin Solid Films*. 1989;172:81–93.
7. Vandenbulcke LG. Theoretical and experimental studies on the chemical vapor deposition of boron carbide. *Ind Eng Chem Prod Res Dev*. 1985;24:568–575.
8. Vincent C, Vincent H, Mourichoux H, Bouix J. Characterization by XPS and SEM of reactive chemical vapor deposited boron carbide on carbon fibre. *J Mater Sci*. 1992;27:1892–1900.
9. Grigor'ev YM, Shugaev VA, Mukas'yan AS, Samoilenko NG, Shiryaev AA. The chemical vapor deposition of boron carbide from a BCl_3-C_7H_8-H_2 mixture on to heated support. *Russ J Inorg Chem*. 1991;36:1088–1091.
10. Oliveira JC, Oliveira MN, Conde O. Structural characterization of B_4C films deposited by laser-assisted CVD. *Surf Coat Technol*. 1996;80:100–104.
11. Vincent C, Vincent H, Scharff JP, Mourichoux H, Bouix J. Thermodynamic and experimental conditions for the fabrication of a boron carbide layer on high-modulus carbon fiber surfaces by RCVD. *Carbon* 1992;30:495–505.
12. Jansson U, Carlsson JO. Chemical vapor deposition of boron carbides in the temperature range 1300–1500 K at a reduced pressure. *Thin Solid Films*. 1985;124:101–107.
13. Ploog K. Composition and structure of boron carbides prepared by CVD. *J Crystal Growth*. 1974;24/25:197–204.
14. Grigor'ev YM, Zharkov AV, Mukas'yan AS, Shugaev VA. Macrokinetic relationships in forming boron carbide fibers by chemical vapor deposition. *Neorg Mater (translated)* 1992;29:344–348.
15. Dilek SN, Özbelge HÖ, Sezgi NA, Doğu T. Kinetic studies for boron carbide formation in a dual impinging jet reactor. *Ind Eng Chem Res*. 2001;40:751–755.
16. Karaman M, Sezgi NA, Doğu T, Özbelge HÖ. Kinetic investigation of chemical vapor deposition of B_4C on tungsten substrate. *AIChE J*. 2006;52:4161–4166.
17. Karaman M, Sezgi NA, Doğu T, Özbelge HÖ. Mechanism studies on CVD of boron carbide from BCl_3, CH_4 and H_2 gas mixture in a dual impinging jet reactor. *AIChE J*. 2009;55:701–709.
18. Sezgi NA, Ersoy A, Doğu T, Özbelge HÖ. CVD of boron and dichloroborane formation in a hot-wire fiber growth reactor. *Chem Eng Process*. 2001;40:525–530.
19. Sezgi NA, Doğu T, Özbelge HÖ. Mechanism of CVD of boron by hydrogen reduction of BCl_3 in a dual impinging-jet reactor. *Chem Eng Sci*. 1999;54:3297–3304.
20. Martin H. Heat and Mass transfer between impinging gas jets and solid surfaces. In: Hartnett JP, Irvine TF, Jr, editors. *Advances in Heat Transfer*, Vol. 13. New York: Academic Press, 1977.
21. International Centre for Diffraction Data. Selected Powder Diffraction Data for Education and Training Search Manual and Data Cards, International Centre for Diffraction Data, USA, Volume 1/Volume 2, 1988.
22. Pierson HO. *Handbook of Refractory Carbides and Nitrides: Properties, Characteristics, Processing, and Applications*. Park Ridge, N.J.: Noyes Publications, 1996.
23. Santos MJ, Silvestre AJ, Conde O. Laser-assisted deposition of r-B4C coatings using ethylene as carbon precursor. *Surf Coat Technol*. 2002;151–152:160–164.
24. Wei B, Vajtai R, Jung YJ, Banhart F, Ramanath G, Ajayan M. Massive icosahedral boron carbide crystals. *J Phys Chem B*. 2002;106: 5807–5809.
25. Niihara K, Nakahira A, Hirai T. The effect of stoichiometry on mechanical properties of boron carbide. *J Am Ceram Soc*. 1984;67: C13–C14.

Manuscript received Nov. 20, 2007, and revision received Feb. 9, 2008.