

Towards the Preparation of Boron Carbide Nanorods by Carbothermal Reaction Method

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ABSTRACT

Nano-sized boron carbide (B_4C) powders have been prepared through a carbothermal reaction process in a conventional high-temperature furnace by using a mixture of boric oxide, amorphous boron powder, and activated carbon black as raw materials. The B_4C products mainly consisted of nanoparticles. In addition, small amounts of B_4C nanorods and nanowhiskers were also found. The yield of rod-like structures was improved by adding a cobalt catalyst in the precursor mixture, and the diameter of the rods was defined by the size of the cobalt particles capped on the rod ends. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and transmission electron microscopy (TEM) were employed to study the crystal phase, morphology, stoichiometry and structure of the prepared nanopowders respectively.

Keywords: nanoparticles, nanorods, boron carbide, synthesis, characterization

1 INTRODUCTION

Boron carbide (B_4C) is an attractive material because of its extreme hardness, low specific weight, high chemical stability and good wear resistance[1-3]. Its hardness comes third after diamond and cubic boron nitride, but with the advantage of being stable at very high temperatures[3,4]. It also has high cross section for neutron capture and excellent high-temperature thermoelectric properties[5]. The combination of these properties consequently makes it an attractive material for numerous applications in micro-electronic, nuclear, military, space and medical applications. With a large amount of extensive research conducted over the past decades[6-10], boron carbide powder can now be prepared by a variety of methods. For example, commercial boron carbide powders can easily be made by carbothermal reduction of boric oxides at high temperatures[10]. But powders made by these methods can only be a few micrometers at the smallest size. The formation of pure nano-sized boron carbide, especially those in processed forms such as nanoparticles, nanowire or nanorods, is still difficult.

Materials at the nano-length scale have attracted great attention because they have unique physical, chemical, and electronic properties, which can be useful for potential high performance applications. Nano-sized boron carbides, especially boron carbide nanowires or whiskers, are expected to be useful as a potential reinforcing phase in ceramic or metal matrix composites and in sliding wear [11]. There is recent research reported on preparing boron carbide nanoparticles by different routes [12-15]. For example, Shi et al discussed a low-temperature method to synthesize boron carbide ultrafine particles (80 nm) through a new metallic Na co-reduction route [12], yet the as-formed boron carbide is associated with metal impurities; Yamad formed fine boron carbide particles (70-300nm) from an amorphous boron/graphite mixture using a shock-wave technique; however, the yield of boron carbide nanoparticles needed further improvement [13]. Lately, Chen et al reported on the synthesis of boron carbide nanoparticles (100 nm) via a reaction of boron with multiwalled carbon nanotubes at 1150 C [14].; obviously, this method could be costly due to the expensive source materials. Furthermore, the formation of boron carbide in other processed forms, such as nanowires and nanorods, is even more difficult. Among recent efforts in generating boron carbide nanowires, there are only a few successful methods developed [16-20], such as plasma-enhanced chemical vapor deposition method[16], alumina templating [17] and inducing heating method[18], carbothermal [19] and microwave heating [20]. Yet, the quantity and quality (e.g. crystallinity, purity and etc.) of the boron carbide nanowires are low.

Therefore, we investigated the synthesis of nano-sized boron carbide with different shapes, such as particles, wires or rods, in a carbothermal reduction by using a mixture of amorphous carbon, boron, and boron oxide as the reactants in a conventional tube furnace reactor. The adding of metal cobalt (Co) in the reaction as the catalyst was studied to facilitate the formation of boron carbide nanorods.

2 EXPERIMENTS

Boron oxide (Alfa Aesar, 99.98%), boron (Alfa Aesar, 99%, -324 mesh, amorphous powder), and carbon (Darco, activated carbon, KB grade) were used as the precursor agents. Carbon powder was baked at 150-200 °C

in vacuum, before weighing. The powders with different ratios of $B/B_2O_3/C$ were mixed for the reaction. Cobalt metal (Fisher Sci. Corp.) powder was used as the catalyst.

Reactions were carried out in a high-temperature tube furnace (Barnstead, F59300CM) with a maximum working temperature of 1700 °C. Dry powders were mixed by roll-milling and put into a covered graphite crucible. The crucible was then placed into the center reaction zone of the tube furnace. The reactor was pre-heated under vacuum at about 150 °C for 1-5 hours. Ultrahigh purity argon was then flushed through the furnace several times before filling the reactor with argon at a constant flow of 200 sccm. The furnace was then heated to 450 °C for 30 minutes. After this period, the temperature was rapidly raised to 1500-1650 °C in about 30 min and was maintained at these temperatures for 1~2 hours before it was turned off and cooled down to room temperature. After the reaction, the as-formed product inside the crucible was collected and analyzed.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis were performed on the as-prepared powders in a Hitachi Scanning Electron Microscope (S4700 FESEM). The powders were prepared for TEM analyses by first dispersing them in ethanol in an ultrasonic bath (Branson 3510). The dispersed powders were then put on holey carbon 200 mesh grids for TEM analyses. TEM analysis was carried out on a JEOL JEM-1200. The powder of the product was applied onto the surface of a plastic Scotch Tape for XRD analyses. XRD was performed at room temperature using a Phillips PW-1729 ($Cu K_{\alpha}$) powder diffractometer.

3 RESULTS AND DISCUSSION

The grayish product obtained from the reaction with a precursor mixture of $B/B_2O_3/C$ was characterized with transmission electron microscopy (TEM). It was found that the product consists of several types of nanostructures of differing aspect ratios, as shown in Figure 1. It can be seen that these nanostructures include nanoparticles (Fig.a, Fig.b, and Fig.c), nano-platelets (Fig.b), nanowires (Fig.c and Fig.f) and nanorods (Fig.d and Fig.e). The qualitative yields of nanoparticles and nano-platelets were high, while the yields of nanowires and nanorods were low as determined from TEM analysis.

In comparison, TEM analysis was also performed on the precursor powders. The reaction temperatures used in our experiments were much lower than the melting temperature of either boron or carbon, which are both above 2000 °C. Meanwhile, the melt temperature for boron oxide is 450 °C, which is much lower than the reaction temperature. Therefore, a comparison was made between the final product and the precursors of boron and carbon powders, not with boron oxide powder. Typical TEM images of raw boron and carbon powders are as shown in Figure 2. Comparison of Figures 1 and 2 shows no obvious correlation between the shape of any reactants and that of

the products. Boron carbide particles in the product are usually facet while particles in boron are usually round shape. In addition, no unreacted amorphous carbon can be seen among the boron carbide nanoparticle products. Since none of the nanostructures in Figure 1 was found in the precursors, it proved that all the structures in the product were indeed formed during the reaction.

The as-prepared sample was also characterized by X-ray diffraction (XRD) analysis. The XRD pattern is indexed as shown in Figure 3, which confirmed the existence of crystalline boron carbide with rhombohedral structure (JCPDS file No. 6-0555) in the final products prepared using $B_2O_3/C/B$ precursor

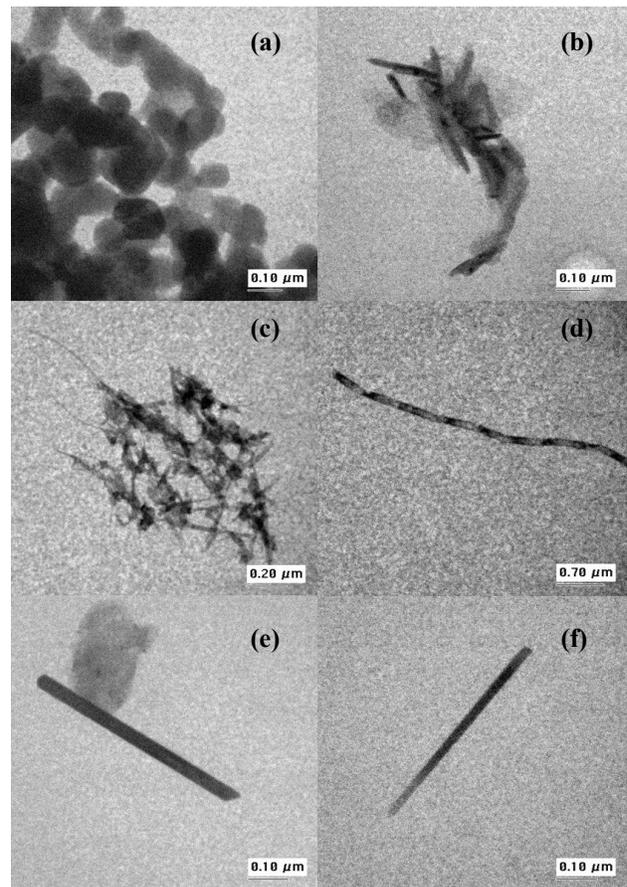


Figure 1: TEM images of the prepared B_4C nanopowders from $B_2O_3/B/C$ precursors: the product consists of several types of nanostructures of differing aspect ratio, including 1) nanoparticles (Fig.a, Fig.b, and Fig.c); 2) nano-platelets (Fig.b); 3) nanowhiskers (Fig.c and Fig.f); 4) nanorods (Fig.d and Fig.e).

Our experiment was performed using an in-situ growth reaction experiment. Although $B/B_2O_3/C$ mixtures were also used as precursors to preparing boron carbide nanowires in a previous report by Ma and et al. [18], their work was carried out in an induction furnace rather than a

simple tube furnace as we used. Because a thermal evaporation process was involved, they postulated that a vapor–solid (VS) mechanism was employed in their reaction.

In addition, several types of boron carbide nanostructures of differing aspect ratio were formed in our product. Therefore, it is possible to have a more complex mechanism involved in our reaction. In addition to a general carbothermal reaction which can take place in the solid or liquid phase and act as the dominant process; other mechanisms such as a vapor-liquid-solid (VLS) mechanism may also be involved.

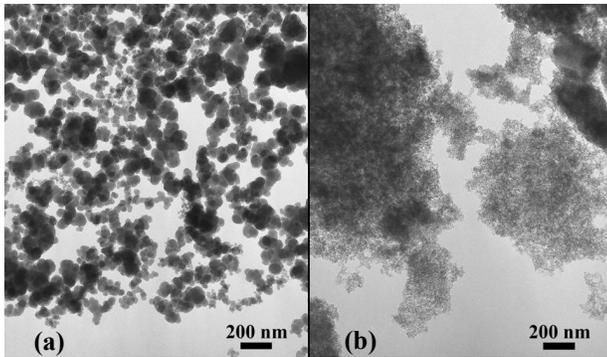


Figure 2: TEM image of raw materials. a) amorphous boron; b) amorphous activated carbon.

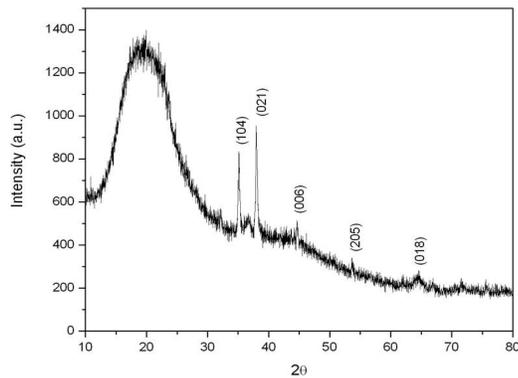


Figure 3: XRD pattern of the prepared B_4C nanopowders. indexed as rhombohedral B_4C , the broad band in lower 2θ range and base line are from the plastic tape.

The high experimental temperatures (over $1500\text{ }^\circ\text{C}$) is above the melting temperature ($450\text{ }^\circ\text{C}$) of B_2O_3 precursor, but below its boiling temperature ($1860\text{ }^\circ\text{C}$). The direct evaporation of boron oxide into vapor is still possible. In addition, other gas-phase species, such as dimeric boron monooxide B_2O_2 vapor, can also be generated during the carbothermal reaction. Thus, as it is reported [19], when

the overall carbothermal reduction of boron oxide at high temperature is $2 B_2O_3 + 7C - B_4C + 6CO$, the same overall reaction can also be observed during carbothermal growth of B_4C whiskers via the VLS mechanism.

We postulate that nanoparticles were produced via a general carbothermal reaction as reported by our group earlier [15] and one-dimensional nanorods and whiskers are formed via other mechanisms, such as VLS and VS, which explains the dominance of the boron carbide nanoparticles and rareness of boron carbide nanorods and nanowires.

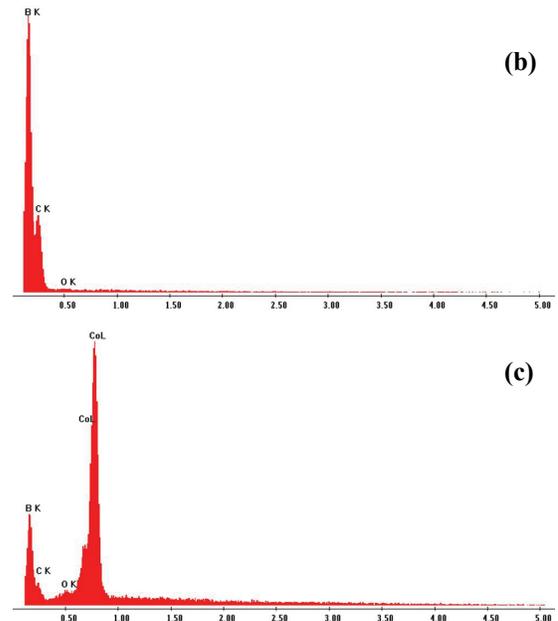
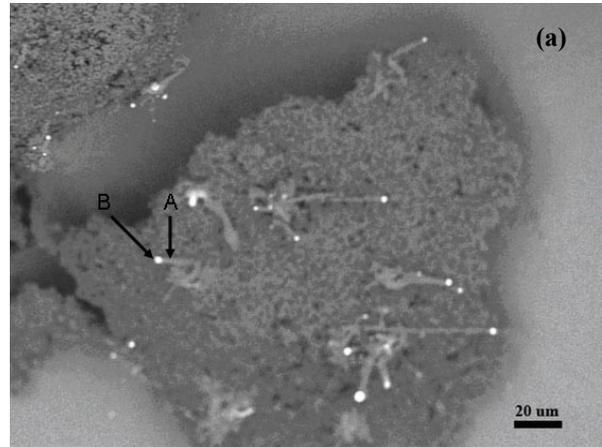


Figure 4: SEM (upper - Fig. a) image and EDX (Bottom - Fig. b and Fig. c) analysis of B_4C product when cobalt powder was added into the reaction mixture. EDX result (Fig. b and and Fig c) were obtained from the middle of a rod (spot A in SEM image Fig. a) and the tip of the rod (spot B) respectively. The results proved that B_4C rods were capped with Co particles.

As VLS growth can be usually promoted by using a metal catalyst which melts in the reaction, we experimented by adding cobalt particles in the precursor mixtures. When cobalt powder was added into the reaction mixture, it was found that more boron carbide rods were formed in the prepared sample. A typical SEM image of the sample is as shown in Figure 4a. It can be seen that the boron carbide rods were of a wide range of sizes with brightly reflecting caps at the ends of the rods. Interestingly, Co particles were usually on the top of the rods and the diameter of the rods varied with the size of Co particles. EDX examination, as shown in Figures 4b and 4c, proved that the capped tips of the nano-rods mainly consisted of cobalt metal. Meanwhile, no cobalt was found in the middle of the nanorods.

The results proved that a VLS mechanism is related to the growth of rod-like structures and cobalt metal particles will act as a catalyst to facilitate the boron carbide rod formation in a carbothermal reaction. The melting temperature of cobalt is 1459 °C. During the high-temperature reaction, the surface of the liquid cobalt metal particles can act as a catalyst to initialize the forming of boron carbide seeds and facilitate them to further grow continuously into rod-like shapes during a VLS process

In addition, it is possible to control the diameter of boron carbide nanorods by controlling the size of the catalytic cobalt particles. Further study of using cobalt particles with controlled size and structure as a catalyst for boron carbide growth is still ongoing.

4 CONCLUSIONS

Nano-sized boron carbide of differing aspect ratios were synthesized in a conventional high temperature furnace reactor. The as-prepared sample contained a large ratio of particles and platelets, but fewer nanowires and nanorods. In addition, the morphologies were difficult to control. By adding cobalt to the reaction mixture, Co-tipped boron carbide nanorods were prepared. This indicates that metal particles can act as catalysts to initialize the forming of boron carbide seeds and facilitate them to further grow continuously into rod shapes during a VLS process.

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REFERENCES

[1] C. Wood, D. Emin, Phys. Rev. B 29, 4582 (1984).

- [2] R. Telle, in: Structure and Properties of Ceramics, Materials Science and Technology, vol. 11, VCH publishers, Weinheim, Germany (1994).
- [3] A. O. Sezer, J. I. Brand, Mat. Sci. Eng., B79, 191-202 (2001).
- [4] A. Weimer, Carbide, Nitride, and Boride Materials Synthesis and Processing, Chapman and Hall, New York, (1997) pp. 7.
- [5] F. Thevenot, J. Eur. Ceram. Soc. 6, 205 (1990).
- [6] M.T. Spohn, Am. Ceram. Soc. Bull. 72, 88 (1993).
- [7] A. Sinha, T. Mahata, B.P. Sharma, J. Nucl. Mater. 301, 165 (2002)
- [8] A.K. Knudsen, in: G.L. Messing, K.S. Mazdiyasi, J.W. McCauley, R.A. Haber (Eds.), Ceramic Powder Science, Advances in Ceramics, Vol. 21, (American Ceramic Society, Westerville, OH, 1987) pp. 237.
- [9] F. Thevenot, in Advanced Ceramics, Key Engineering Materials, Vols. 56 and 57, Ed. C.Ganuly, S.K. Roy, P.R. Roy, (TransTech, Zurich, 1991) pp. 59.
- [10] A.W. Weimer, R.P. Roach, C.N. Haney, W.G. Moore, W. Rafaniello, AIChE Journal, 37, 759-68, (1991).
- [11] P. Larsson, N. Axen, S. Hogmark, Wear 236, 73 (1999).
- [12] L. Shi, Y. Cu, L. Chen, Y. Qian, Z. Yang, J. Ma, Solid State Communications 128, 5-7 (2003).
- [13] K. Yamada, J. Am. Ceram. Soc., 79, 1113 (1996).
- [14] S. Chen, D.Z. Wang, J.Y. Huang, Z.F. Ren, Applied Physics A: Materials Science & Processing 79, 1757 (2004).
- [15] Chang, B. Gersten, S. Szewczyk, J. Adams, Mat. Res. Soc. Symp. Proc., 2005, v848, FF9.28.1-6.
- [16] D. Zhang, D.N. McIlory, Y. Geng and M.G. Norton, Journal of Materials Science Letters 18, 349 (1999).
- [17] M.J. Pender, L. Sneddon, Chem. Matter. 12 280 (2000).
- [18] R. Ma, Y. Bando, Chem. Phys. Lett. 364, 314 (2002)
- [19] M. Carlsson, F.J. Carcia-Garcia, M. Johnsson, Journal of Crystal Growth 236, 466 (2002).
- [20] M.G. Rodriguez, O.V. Kharisova and U. Ortiz-Mendez, Rev. Adv. Mater. Sci. 7, 55 (2004).