Rapid Carbothermal Reduction of Boron Oxide in a Graphite Transport Reactor

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Uniform submicron crystals of B_4C, boron-enriched boron carbide, and B_4C/TiB_2 composite powders have been synthesized continuously by rapid carbothermal reduction at approximately 2,200 K in a 0.14 m ID × 1.68 m long pilot-scale graphite transport reactor. A unique reactor design allowed for continuous feeding of a meltable boron oxide containing precursor, rapid heating rates that completed the carbothermal reduction reaction in seconds, and an expanded cooling that allowed for the precipitation in space of volatile excess boron oxides. Powder morphology resembled that of powder synthesized by laser pyrolysis of gaseous reactants. Rapid heating rates and minimized reaction times at high temperatures promoted nucleation with limited crystal growth. Dense parts fabricated from these powders had fine grains and extreme hardness.

Background

B_4C, boron-enriched boron carbide, and B_4C/TiB_2 composites

Boron carbide (B_4C) is the third hardest material known to man. It is inert to most chemicals, is oxidation and reduction resistant up to approximately 1,400 K, is less than one-third the density of steel, and because of its 78.3 wt. % boron content has a high cross section for neutron absorption.

Major applications for boron carbide relate either to its high hardness or its high neutron absorptivity (B^{10} isotope). Because of its high hardness, it is particularly useful in applications such as armor plating and the production of blasting nozzles, mechanical seal faces, mold and diemaker polishing stones, and cutting and grinding tools. It is also used in the shielding and control of nuclear reactors because of its neutron absorptivity, chemical inertness, and radiation stability.

Boron carbide exists in a broad range of compositions (Allen, 1953; Amberger et al., 1971; Clark and Hoard, 1943; Matkovich, 1976; Ploog, 1972) with reported molar B/C ratios as high as $B_{51}C$. Mechanical and electrical properties of boron carbide depend heavily upon stoichiometry.

Hardness and fracture toughness have been shown (Nihara et al., 1984) to be maximum at essentially the stoichiometric composition molar $B/C = 4$, diminishing rapidly with either carbon-enriched or boron-enriched compositions. Hence, high product quality would dictate molar $B/C = 4$ for mechanical applications.

Stoichiometric boron carbide (molar $B/C = 4$) is a p-type semiconductor having a very large Seebeck coefficient, a thermally activated electrical conductivity (Wood and Emin, 1984a), and a very low thermal conductivity (Wood et al., 1985a,b; Wood and Zoltan, 1984), almost independent of temperature above ambient. On the other hand, boron-enriched boron carbides (<8 wt. % carbon, i.e., $>B_{12.8}C$) may change from p-type to n-type semiconductors. This hopping conductivity has provided much interest in the area of high-temperature thermoelectric power generation for space applications (Wood, 1984a,b; Wood and Emin, 1984b).

There has also been substantial interest in the manufacture of ceramics composites of boron carbide, particularly with titanium diboride (TiB_2). Titanium diboride is not as hard, but is much tougher, with a specific gravity 80% greater than that of B_4C. Recent work (Nishiyama, 1985) has suggested that composites prepared from physical mixtures of B_4C and TiB_2 could be densified to yield parts of exceptional hardness, for

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example, 30% above that of B_4C (harder than cubic boron nitride, the material currently used for superhard tools). Knudsen et al. (1988) have simultaneously synthesized B_4C/TiB_2 composite powders possessing both hardness and toughness greater than that of B_4C alone.

Boron carbide fabricated parts exhibiting a finer grain size are significantly stronger than parts consisting of coarse grains (Osipov, 1982). Since grain size in densified parts is governed by the size of crystallites within the particles from which the parts are fabricated, it is advantageous to fabricate parts from particles comprised of fine, submicron-size crystallites.

In summary, there is substantial interest in developing improved processes for manufacturing stoichiometric (molar $B/C=4$) and boron-enriched (molar $B/C>4$) boron carbide powders composed of submicron crystallites, and in composite B_4C/TiB_2 ceramics having properties improved over those of B_4C alone.

Methods of manufacture

Commercial production of boron carbide is most commonly carried out by the reduction of boron oxide with carbon in a batch electric arc furnace (Lipp, 1965; Scott, 1964). Reaction and cooldown take place over an extended period of time, on the order of days, because of the slow rate of heat conduction that controls the process. The nonuniform process conditions result in a nonuniform chemical composition within the product. The sintered mass of product that results from this process requires physical size reduction in order to achieve a particle size fine enough for densification. Because of the extreme hardness of boron carbide, this size reduction step is extraordinarily difficult and expensive and results in contamination of the product with impurities picked up during milling. Acid leaching of metal impurities is necessary and further complicates the process. The morphology of these products is characterized by fractured surfaces, which are the result of milling. Examples are shown in Figure 1.

Another method for manufacturing boron-containing ceramic powders is by reduction of boron oxide with magnesium metal, the so-called thermite reaction (Gray, 1958; Logan and Walton, 1984). Typically, reactants boron oxide, carbon, and magnesium are intimately mixed, loaded into a container, and the reaction initiated either by heating the entire reaction mixture to a sufficiently high temperature or through the use of electrical ignitors. The thermite reaction is highly exothermic and self-propagating. The ceramic powders produced by the thermite reaction are unsatisfactory for high-purity applications because the powders are contaminated with residual magnesium and even after repeated digestions with hot mineral acids, the magnesium is difficult to remove.

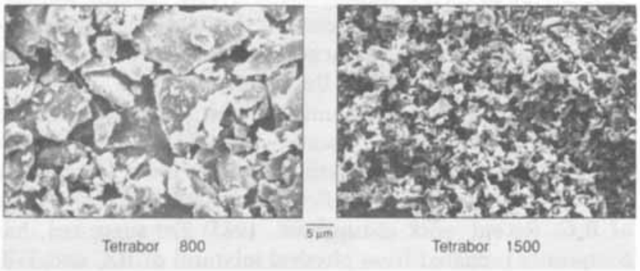

Figure 1. Traditional boron carbide products.

Because of the problems encountered due to slow, nonuniform heating, chemical impurities, and subsequent processing complications, researchers have sought methods of producing high-purity, submicron-size powders directly, so that size reduction and other additional steps can be avoided. One effective method involves the direct synthesis of submicron-size powders from laser-heated or plasma-heated gases.

Knudsen (1987) described the synthesis of ultrafine (34 nm) B_4C powders by the CO_2 laser-driven pyrolysis of $BCl_3/H_2/CH_4$ (C_2H_4) gas mixtures. These uniformly sized, highly pure powders were densified into superior parts having fine microstructure (1 to 1.5 μm grains), which contributed to microhardness greater than that typically reported in the literature for high-quality, dense B_4C.

Boron carbide (MacKinnon and Reuben, 1975) and various submicron-size boron-containing ceramic powders, including titanium diboride (Steiger, 1981), have also been synthesized from radio frequency plasma-heated gases.

In general, the laser or plasma heating of reactant gases is characterized by almost instantaneous and uniform heating rates of reactants, short and uniform reaction times (fractions of a second) with minimal exposure to high temperature, and almost instantaneous and uniform product cooling rates. The net result is submicron, uniformly sized ceramic particles. However, while gas phase synthesized powders possess many of the desirable qualities, they are relatively expensive to produce because of the high cost of the processing equipment and gaseous raw materials (e.g., BCl_3) that they require. Thus, gas-phase routes, while academically intriguing, may not be practical for commercial use.

This paper describes a unique rapid carbothermal reduction process and transport reactor configuration for continuously manufacturing uniform, submicron-size, boron-containing ceramic crystals. This process approaches the uniformity and rapid temperature differentials of the gas-phase laser- and plasma-heated routes, but at a substantially reduced cost.

Thermochemistry and Kinetics of the Carbothermal Reduction Reaction

Chemistry and heat of reaction

Boron carbide can be synthesized by the carbothermal reduction of liquid-phase boron oxide by the overall stoichiometric reaction:

$$7C(s)+2B_2O_3(l)\Rightarrow B_4C(s)+6CO(g) \tag{1}$$

However, it is well known (Rentzepis et al., 1960; Lamoreaux et al., 1987) that gaseous boron suboxides, $B_2O_2(g)$, are synthesized at relatively low temperatures under reducing conditions and provide a gas/solid mechanism through which boron carbide can also be synthesized:

$$C(s)+B_2O_3(l)\Rightarrow B_2O_2(g)+CO(g) \tag{2}$$

$$5C(s)+2B_2O_2(g)\Rightarrow B_4C(s)+4CO(g) \tag{3}$$

Similarly, titanium diboride can be synthesized by carbo-

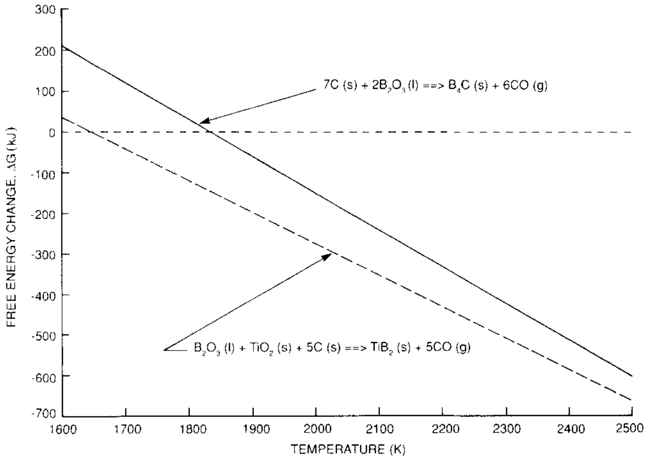

Figure 2. Variation of free energy with temperature for carbothermal reduction reactions.

$P = 0.1$ MPa

thermal reduction according to the overall stoichiometric reaction:

$$5C(s) + B_2O_3(l) + TiO_2(s) \Rightarrow TiB_2(s) + 5CO(g) \qquad (4)$$

Both reactions 1 and 4 are highly endothermic, requiring 1,635 kJ/mol B_4C and 1,259 kJ/mol TiB_2, respectively, at 2,200 K.

Free energy considerations

The variation of free energy with temperature for reactions 1 and 4 at atmospheric pressure is shown in Figure 2. Calculations for these free energy changes have been made using data taken from the JANAF Thermochemical Tables (Chase et al., 1985).

The overall carbothermal reduction reaction to synthesize B_4C, reaction 1, has a positive standard free energy change up to about 1,815 K and so, unless CO produced is removed from the process, a higher temperature is needed to promote reaction at a reasonable rate. In general, reaction 1 is carried out at higher temperatures (Lipp, 1965) where the presence of CO does not inhibit the forward reaction to B_4C.

The overall carbothermal reduction reaction to synthesize TiB_2, reaction 4, is even more thermodynamically favorable than reaction 1 over all temperatures. Hence, any TiO_2 contained in a $C/B_2O_3/TiO_2$ reactant solids feed mixture will result in the synthesis of TiB_2 preferentially to the synthesis of B_4C from C and B_2O_3.

Composite B_4C/TiB_2 powders can be synthesized by simultaneously carrying out carbothermal reduction reactions 1 and 4 by heating mixtures of $C/B_2O_3/TiO_2$ in which the TiO_2 content is less than the stoichiometric quantity specified according to reaction 4. All excess C and B_2O_3 will result in the synthesis of B_4C according to reaction 1.

Thermodynamic equilibrium calculations

The equilibrium product composition for an inorganic system at high temperatures is easily calculated with the FACT interactive computing system (Thompson et al., 1985), which utilizes a free energy minimization routine.

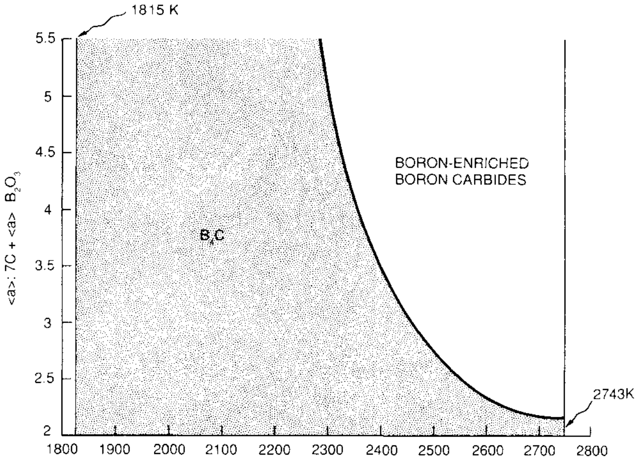

Figure 3. Effect of temperature and feed composition on product composition (free energy minimization)

The effect of temperature and feed composition on product composition for a system of 7 mol C and $\langle a \rangle$ mol B_2O_3, according to reaction 1, was evaluated at atmospheric pressure over the temperature range of interest. The results are summarized in Figure 3. Typically, excess B_2O_3 ($\langle a \rangle > 2$) is utilized (de Castro and Paschoal, 1988) to ensure complete conversion of available C. Any unreacted B_2O_3 is easily solubilized with water as boric acid, H_3BO_3, and washed from the product.

The FACT data base does not include specific boron-enriched phases of boron carbide (i.e., $B_{13}C_2$, $B_{11}C$), however, the formation of a boron-enriched boron carbide product may be assumed when the solid/liquid phase free energy minimization product includes boron, B, as well as B_4C. The boundary between B_4C and boron-enriched boron carbides is shown in Figure 3. No attempt has been made to quantify the boron-enriched boron carbide molar B/C ratio.

It is clear from the thermodynamic results summarized in Figure 3 that B_4C is the stable reaction product for a stoichiometric feed composition ($\langle a \rangle = 2$) over the temperature range of interest. Large excesses of B_2O_3 in the feed result in the formation of boron-enriched boron carbides at temperatures above about 2,300 K. This formation is highly dependent on the feed boron to carbon ratio as well as temperature and is more likely to occur for larger excess boron feed compositions at higher temperatures.

One complicating factor that has not been included in the thermodynamic study is that $B_2O_3(s)$ is highly hygroscopic. Any chemically bound water (as H_3BO_3) will react with C and reduce the amount of feed C available for reaction with B_2O_3. Furthermore, H_3BO_3 has a substantial vapor pressure upon heating and provides a volatile mechanism by which boron can leave the system before reaction, thus affecting the boron to carbon ratio.

In general, one may conclude that B_4C is the stable product for near stoichiometric feed compositions up to its melting point (2,743 K), that boron-enriched boron carbides can be synthesized at temperatures above about 2,300 K in the presence of excess boron, and that the composition of the product is highly dependent upon temperature, the amount of hydrated water in the feed, and the initial molar ratio of C and B_2O_3.

Control of the reactant molar feed B/C ratio and temperature is crucial to the manufacture of stoichiometric B_4C at temperatures above about 2,300 K. This may explain why the commercial electric arc furnace process results in boron carbide products of various stoichiometries. Nonuniform heating rates, nonuniform high temperatures, and the required use of substantial excess boron oxide to compensate for volatile boron losses are typical in the electric arc furnace process (Lipp, 1965).

Reaction kinetics

Suitable times for carrying out reaction 1 have been reported by Smudski (1968) to be between approximately 30 min and 3 h for temperatures between 2,373 and 1,973 K. Various sources of carbon were used including carbohydrates (dextrose, sucrose, and starch), resins (phenolformaldehyde), and polyhydric compounds (glycerine polyvinyl alcohol).

Pikalov (1988) reacted dehydrated boric acid with technical carbon in the 1,770–2,070 K range and found that the reaction was completed in 90 min at 1,870 K and 15 min at 2,070 K.

DeCastro and Paschoal (1988) have found dehydrated boric acid/graphite precursors to be nearly fully converted to B_4C after 15 min reaction time at 1,973 K, provided that at least 125% excess B_2O_3, according to reaction 1, was contained in the precursor.

Rafaniello and Moore (1989) have recently reported much shorter reaction times on the order of seconds to minutes for 400 μm precursor C/B_2O_3 particles being dropped into a heated crucible at temperatures between 2,073 and 2,373 K. Their results indicate that heat transfer resistances are probably rate controlling for the highly endothermic overall reaction 1. Since heat transfer resistances are reduced in the powder drop mode (dispersed, finer particles being heated by thermal radiation rather than heat conduction through a mass), the reaction could be completed in shorter times. Indications are that overall reaction 1 is intrinsically fast once heat transfer resistances are properly accounted for or are removed in the reaction rate studies.

It will be shown in this work that boron carbide can be synthesized within seconds for precursor C/B_2O_3 particles of $d_p < 50$ μm dia. at temperatures $T > 2,100$ K when heat transfer resistances are negligible.

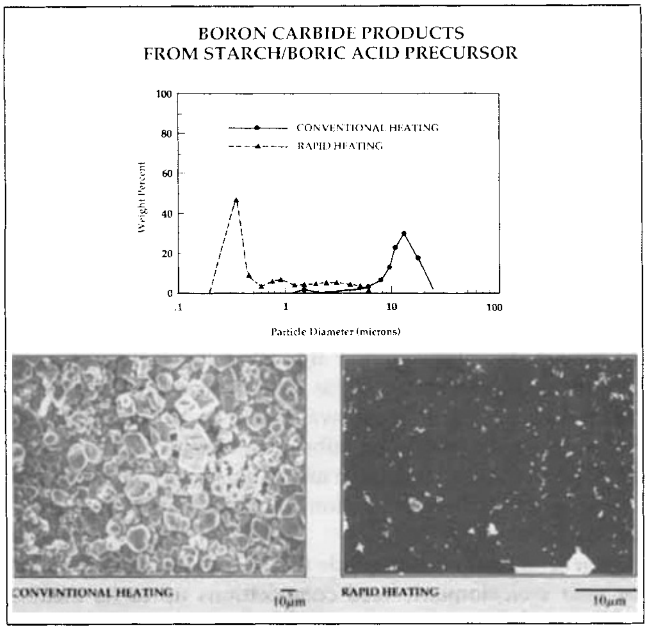

Figure 4. Effect of heating rate on product boron carbide particle size.

Experimental Method

Effect of heating rate on crystal size

It has been found that the rate of heating has a substantial influence on the resulting crystal size of the boron carbide product.

An intimate boron oxide–carbon (calcined corn starch) mixture was prepared as a 0.0762 m ID × 0.254 m long cylinder and was heated in a furnace controlled at 2,023 K for approximately 2 h, cooled to room temperature, and examined for conversion to boron carbide. The outer 0.0254 m of the cylinder was reacted to form boron carbide crystals with a mixture of large (1–20 μm) crystals whereas about 0.0254 m dia. of the inner core of the cylinder remained unreacted. Heat transfer resistances limited heating rates through the cylindrical core such that the predominant crystal size was 10–20 μm, Figures 4 and 5.

The same boron oxide–carbon mixture feed material was ground to less than 2,000 μm and fed continuously into a 1,973 K graphite crucible at a rate that allowed the individual particles to be heated to the surrounding temperature in several seconds, with the result that no large crystals were formed and the product was entirely submicron-size boron carbide crystallites, Figure 5.

Scanning electron photomicrographs, Figures 4 and 5, and Coulter counter particle size analysis, Figure 4, of the boron carbide powders prepared by these techniques clearly indicated that the rate of heating controlled the ultimate crystal size of the product.

Graphite transport reactor

A transport reactor process was developed to continuously

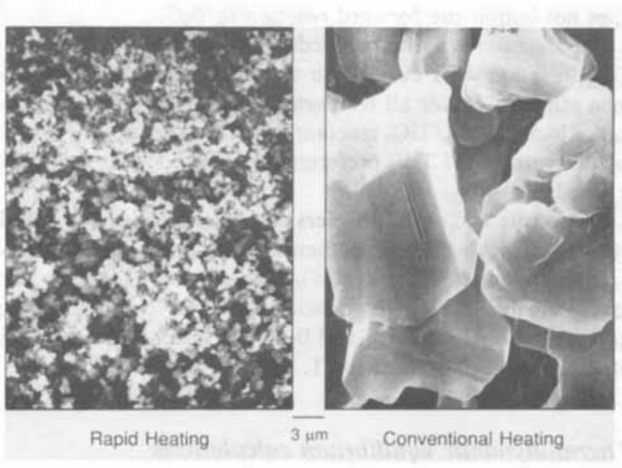

Figure 5. Effect of heating rate on product boron carbide morphology.

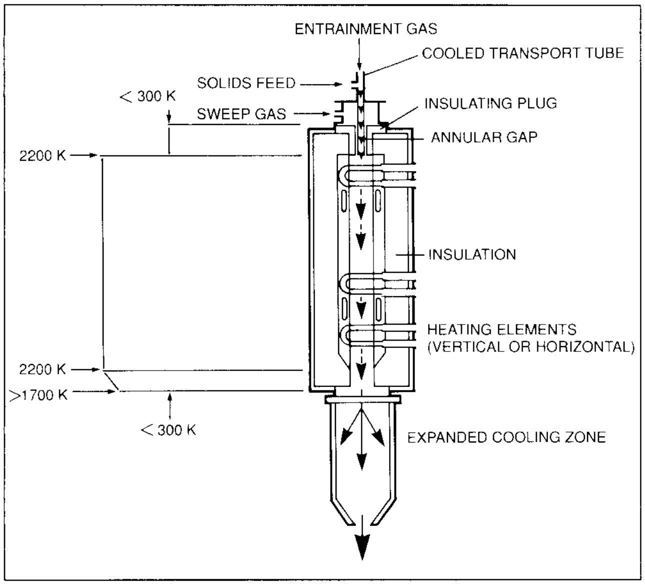

Figure 6. Continuous graphite transport reactor.

carry out the uniform, rapid heating required for synthesizing submicron sized product.

The transport reactor and process temperature profile are shown in Figure 6. The reactor consisted of a solids feed section, a reaction chamber consisting of a 0.14 m ID × 1.68 m long graphite tube heated indirectly by radiation from electrical heating elements surrounding it, and an expanded 0.46 m ID × 1.8 m long jacketed cooling zone.

Temperature demarcations between the solids feed section and the reaction chamber, and then between the reaction chamber and the cooling zone, were extremely sharp to allow for rapid heating of reactant solids in the reaction zone and rapid cooling of products entering the cooling zone. No preheating zone existed in this process.

Solids Feed Section. A cooled reactant transport tube was utilized to continuously feed meltable B_2O_3 containing precursor into the reaction zone, which was operating at a temperature above the melting point of B_2O_3. Boron oxide softens at about 600 K, melts at about 725 K, and in reducing environments yields volatile suboxides—B_2O_2 (g)—at above about 1,550 K (Rentzepis et al., 1960; Lamoreaux et al., 1987). Boric acid formed from moisture pick-up on the surface of boron oxide goes through a melt phase at about 425 to 450 K and forms a liquid metaborate BO·OH. The water-jacketed transport tube was maintained at a temperature of about 300 K and prevented plugging of meltable precursor, which was fed continuously at the inlet of the reaction zone.

Fine reactant powder was entrained through the cooled transport tube with argon entrainment gas. The transport tube exited directly into the graphite reaction chamber. An annular gas flow space existed around the cooled transport tube and allowed argon sweep gas to flow through the annular space and exit concentrically into the reaction chamber around the cooled transport tube. The sweep gas provided a fluid wall between the cooled transport tube and the upper graphite surface of the reaction chamber and eliminated the presence of solid surfaces that would have been at intermediate temperatures within the melting region of B_2O_3.

This feed section design eliminated sticking and plugging and allowed continuous feeding of a fine, meltable precursor powder into the graphite reaction chamber.

Reaction Chamber. The reaction chamber was a 0.14 m ID × 1.68 m long graphite tube that was maintained at a reaction temperature of approximately 2,200 K. The chamber was effectively a blackbody cavity that was heated by radiation from graphite heating elements spaced around it. The graphite heating elements were heated by an AC power source. Temperature was measured with an optical pyrometer focused on the outside surface of the reaction tube through a hole in the furnace insulation. Power to the heating elements was controlled to maintain the desired temperature.

Precursor powder entered the reaction chamber as a dust cloud and was heated almost instantly and uniformly to reaction temperature by thermal radiation from the wall of the reaction chamber. Since the particles were fine, internal conduction heat transfer resistances were negligible and the carbothermal reduction, reaction 1, was driven to completion within seconds by a process hereafter described as rapid carbothermal reduction. The rapid heating rate tended to approach that imposed by plasmas and lasers.

The rapid radiative heating rate was fast enough to allow rapid carbothermal reduction to boron carbide to occur before substantial quantities of volatile reactive components such as boron oxide and suboxides had the opportunity to leave the reactant particles and escape the system. This feature allowed the use of a nearly stoichiometric C/B_2O_3 feed composition, according to reaction 1, in the precursor particles and prevented severe degradation of the reaction tube due to reaction of excess boron oxide with the reaction chamber wall. Other slower heating rate carbothermal processes for synthesizing boron carbide utilized pelletized precursors that contained more than 125% excess B_2O_3 (de Castro and Paschoal, 1988), relative to that required according to reaction 1, in order to ensure complete reaction of the available carbon.

Cooling Zone. The reactor cooling zone was an expanded 0.46 m ID × 1.8 m long jacketed steel pipe that was maintained at a temperature typically less than 300 K. The cooling zone allowed for rapid radiative cooling of the powders leaving the reaction chamber. The expanded configuration helped to eliminate adhesion of significant quantities of unreacted excess boron oxide to the walls of the cooling chamber by permitting recrystallization in space prior to wall contact. The recrystallized boron oxide particles were free flowing. Some of the excess boron oxide also coated the synthesized boron carbide particles exiting the reaction chamber. Continuous operation was maintained because plugging problems were eliminated as any unreacted excess reactant was discouraged from depositing on the walls of the cooling chamber or at the cooling inlet.

Feed precursor preparation

An intimate C/B_2O_3 precursor was prepared from a dried, calcined, and milled cornstarch/boric acid slurry. The precursor preparation method is shown in Figure 7.

Boric acid and cornstarch/water slurries were prepared separately in stainless steel drums. Approximately 0.39 parts boric acid (H_3BO_3, U.S. Borax, powdered Technical Grade) and 0.29 parts cornstarch (Hubinger Co., modified cornstarch, 400L-NF-851) were added to 1 part of water at ambient temperature, respectively, for each slurry. The boric acid/water slurry was

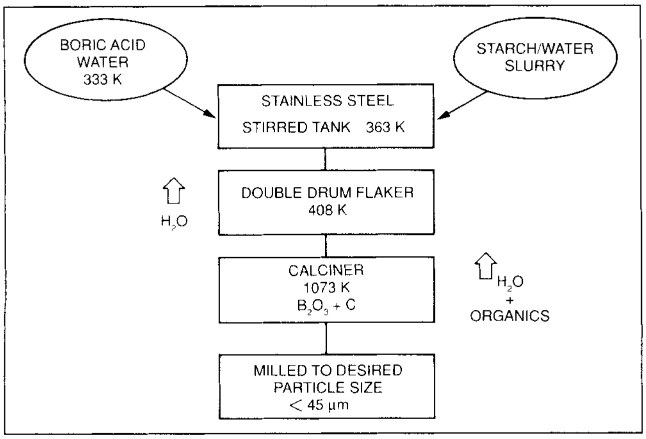

Figure 7. Boron carbide precursor preparation method.

charged to a jacketed, stirred, 0.189 m^3 tank that was heated and maintained at 333 K. The ambient cornstarch/water slurry was added to the heated boric acid slurry. When the heated aqueous cornstarch/boric acid mixture reached 363 K it was pumped to a chrome-plated double drum dryer operating at 430 K. A dried white flake containing about 20 wt. % water was produced at a rate of about 5.9 $kg/m^2 \cdot h$ from the double drum dryer.

The dried white flake was loaded into graphite boats and calcined in a tunnel kiln under flowing nitrogen at 1,073 K. The boats were pushed through a 1.8 m hot zone at the rate of 8.5×10^{-4} m/s. The resulting calcined black flake was an intimate mixture of C/B_2O_3, which was milled and screened to a particle size $d_p < 44$ µm (−325 mesh) for feeding to the transport reactor. The milled precursor particles were homogenous microcontainers of intimately mixed solid reactants.

The composition of the precursor was controlled by the cornstarch/boric acid ratio in the feed tank to the drum dryer. Approximately 0.31 kg carbon resulted from each 1 kg of starch, while the resulting B_2O_3 was approximately what would be expected based upon the water dehydrated from boric acid, H_3BO_3.

For the case of B_4C/TiB_2 composite synthesis, an appropriate amount of TiO_2 (Degussa AG, pigment grade Titandioxid P25) was added to the boric acid solution.

Synthesis of boron carbide

The transport reactor was brought to the desired operating temperature, typically 2,073 K < T < 2,573 K. Milled precursor was loaded into a feed hopper and purged with argon gas to remove air and nitrogen and prevent moisture pick-up. The precursor powder was then fed at a nominal rate of 2×10^{-3} kg/s to the water-cooled transport tube by a screw feeder. Argon entrainment and sweep gases flowed at a combined rate of between 3×10^{-3} and 8.5×10^{-3} kg/s to carry the precursor powder through the cooled transport tube and into the reaction chamber, where complete reaction was achieved within seconds. Residence time within the reaction chamber was controlled by the flow of inert gas, the quantity of CO generated by reaction, temperature, and the cross-sectional area of the reaction chamber. Powder was swept through the reaction chamber by the process gas stream.

Results

Analytical

Precursor powders were analyzed for boron, carbon, and water content. Carbon was determined with a LECO carbon analyzer (LECO Corp., model IR-212 Carbon Determinator) using standard LECO procedures. Water content was determined by thermogravimetric analysis (DuPont TGA model 9900, V2.0B) in nitrogen, using standard TGA procedures. Any weight loss up to 600 K was assumed to be due to free or chemically bound water (as H_3BO_3). For boron analysis, a known amount of precursor sample was heated at 358 K for 6 h in water to promote dissolution of the boric acid. The beaker content was then vacuum filtered to remove carbon. The filtrate was analyzed for boron via inductively coupled argon plasma-optical emission spectrometry (Perkin Elmer Corp., model ICP/6000) using standard ICP/6000 procedures.

Synthesized product powders were analyzed chemically for carbon, oxygen, nitrogen, boron, and trace metallic impurities. Free carbon was determined using an X-ray technique (Beauvy and Angers, 1981). Oxygen and nitrogen values were determined using the LECO TC-136 oxygen and nitrogen system. Free and fixed boron values were determined by a fusion/titration method using an Allied Fisher Scientific model 455 computer-aided titrimeter along with the method described above for the precursor. Crystal phase purity was determined by X-ray diffraction (Rigaku "Miniflex" X-ray diffractometer). Product morphology was identified by scanning electron microscopy (ISI model SS40). Surface area was determined by the BET nitrogen adsorption method using standard manufacturer's procedures (Quantachrome Corp. Monosorb model). Trace metallic impurities were quantified by X-ray fluorescence.

Effect of temperature, feed composition, and residence time

A study was undertaken to determine the minimum excess B_2O_3 needed for completely converting available carbon to B_4C at various temperatures. Precursors containing 5, 9, and 24% adjusted excess B_2O_3 were prepared by adjusting the ratio of starch to boric acid during preparation.

As shown in Figure 8, carbon conversion generally increased with an increase in reaction temperature and excess B_2O_3. Precursors were fed to the cooled transport tube at the rate of 2×10^{-3} kg/s and swept into the reaction chamber with argon gas flowing at the rate of approximately 4.2×10^{-3} kg/s. Residence time within the reaction chamber was less than 2 s. Complete carbon conversion could not be achieved in a single pass through the reaction chamber at temperatures up to 2,273 K for precursors containing 5% adjusted excess B_2O_3. The 9 and 24% excess B_2O_3 precursors were completely converted at 2,273 and 2,173 K, respectively. The general conclusion was that approximately 10% adjusted excess B_2O_3 was necessary to achieve complete carbon conversion in the transport reactor. Adjustment accounted for residual chemically bound water reacting with some of the feed carbon, thus effectively increasing the molar feed B/C ratio for reaction 1.

Fully converted stoichiometric B_4C, Table 1, was achieved for reaction between 2,123 and 2,273 K. Complete carbon conversion required less than 2 s residence time for temperatures greater than 2,173 K and a cumulative 2.2 s at 2,123 K.

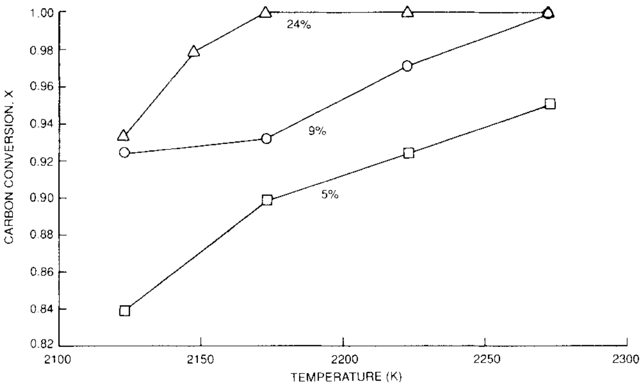

Figure 8. Effect of temperature and excess reactant B_2O_3 on carbon conversion.

Reaction of an adjusted 126% excess B_2O_3 precursor at 2,523 K resulted in a boron-enriched boron carbide product (B/C = 11.2), providing experimental support for the theoretical free energy minimization study, Figure 3.

Powder morphology and chemistry

The rapid carbothermally produced powder had a morphology similar to that produced by a gas phase laser process, Figure 9. Both were equiaxed in crystal structure, with the rapid carbothermally produced powder somewhat larger in the 0.1 μm size range. A comparison with Tetrabor 1500, Figure 10, a fine-grain B_4C powder commercially available from Elektroschmelzwerk Kempten GmbH, indicated a much finer and more uniform crystal size for the rapid carbothermal powder.

Product chemical compositions were similar, Table 2, with the exception of Tetrabor 800 powder, which showed a boron-enriched phase. Product oxygen contents were consistent with surface area; higher surface oxidation levels existed for the higher surface area powders. The relatively low oxygen content of the ultrahigh surface area laser-produced powder was due to this powder being kept under an argon pad (Knudsen, 1987). The iron impurity level of the rapid carbothermally produced powders was comparable to that of the commercial counterparts, but much higher than that of the highly pure gas-derived laser product.

The powder morphology of the rapid carbothermal product was attributable to the nature of the reaction. For temperatures of about 2,200 K, the particle heating rate was estimated to be on the order of about 10^4 to 10^5 K/s. This rapid heating is believed to have resulted in the creation of a large number of nucleation sites, thus yielding submicron crystals. Minimized reaction times at high temperature and comparable initial cooling rates as particles entered the expanded cooling zone probably precluded significant crystal growth by coagulation of colliding particles. Surface area decreased with increased temperatures due to increased crystal growth and agglomeration at higher temperatures. Furthermore, the uniformity of crystal morphology resulted from similar thermal and reactive histories during nucleation and growth. The similarity between the laser and rapid carbothermally produced powders, Figure 9, strongly suggests that significant reaction most likely involved gaseous species, probably B_2O_2(g).

Densification and hardness

The fully characterized powders, Tables 1 and 2, were used in a hot-pressing study to determine the effect of temperature, atmosphere, and load application on powder densification and the resulting part microstructure. Hot-pressing temperatures from 2,173 to 2,473 K were used with 35 MPa pressure applied at room temperature or at the maximum temperature, under vacuum or in argon for 1 h. Parts produced from each powder with the highest density and "best" microstructure (smallest and most uniform grain size) were selected for further testing. The method used to produce these parts is termed the optimum hot-pressing conditions.

While none of the parts had reached full density at 2,173 K, most of the parts were fully dense at 2,373 K. At 2,473 K full density was achieved for the Tetrabor 800 powder, while most other samples exhibited exaggerated grain growth. The optimized hot-pressing conditions are summarized in Table 3.

These parts were tested for hardness using a Vickers diamond indentor (1.0 kg load) according to ASTM E-384. The hardness of boron carbide is known to depend heavily upon stoichiometry (Nihara et al., 1984) with maximum hardness at molar B/C = 4.0. However, while stoichiometry plays a major role in determining the hardness of boron carbide, other factors such as microstructure and additives (TiB_2), or impurities (Fe), have been found to be important.

Hardness results for the rapid carbothermally produced powders are compared in Table 3 to those of the commercially available powders as well as to values reported (Knudsen, 1987) for laser-produced powders. Clearly, the hardness of the rapid carbothermally produced boron carbide powders was equiv-

Table 1. Transport Reactor Performance

Run No.	Precursor Comp., wt. % C	B_2O_3	H_2O	Precursor % Excess B	H_2O Adjusted	Argon Flow, F_g kg/s × 10^3	T K	t s	X %	Product Powder, Fixed B/C
110-45	36.1	60.8	3.1	2	8	6.06	2,123	(0.8	90 (1st)	—
	—	—	—	—	—	3.03	2,123	1.4)	~100 (2nd)	3.94
								2.2		
38-24	33.3	61.7	5.0	12	24	3.03	2,173	1.3	~100	4.04
97-42	33.1	64.8	2.0	18	23	6.74	2,223	0.7	~100	4.03
58-31	35.8	61.3	2.9	3	9	6.06	2,273	0.7	~100	3.98
29-18	23.9	69.1	7.0	80	126	8.42	2,523	0.8	~100	11.20

$F_s = 2 \times 10^{-3}$ kg/s

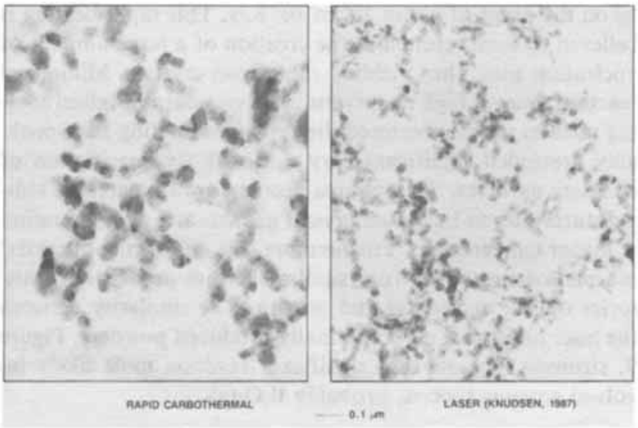

Figure 9. Micrographs of B_4C Powders, 150,000×.
Rapid carbothermal, run 38-24

alent to or higher than that of Tetrabor 1500 and approached closely that of the laser product.

Parts made from the Tetrabor 800 powder had approximately three times the average grain size of Tetrabor 1500 and were not as hard. The larger grain size and boron-enriched stoichiometry contributed to the lower hardness.

The submicron grains of the laser and rapid carbothermally produced powders act to enhance the hardness of the resulting parts. Microstructures are compared in Figure 11. The laser product had the finest grains, followed by the rapid carbothermal and Tetrabor 1500.

A small amount of TiB_2 (2.2 wt. %) increased hardness as expected (Nishiyama, 1985; Knudsen et al., 1988). Titanium diboride crystals were well dispersed within the B_4C as shown in the Ti K-alpha X-ray map, Figure 12, as determined by energy-dispersive X-ray spectroscopy (EDS), where Ti appears white on the gray B_4C background. The discrete black specks were free carbon sites. Boron carbide (B_4C), TiB_2, and free carbon are all shown in the X-ray diffraction pattern of the hot-pressed part, Figure 13. This composite B_4C/TiB_2 part was fabricated from powder synthesized by the simultaneous rapid carbothermal reduction of B_2O_3 and TiO_2 according to overall reactions 1 and 4. The composite powder preparation conditions and characterization are summarized in Table 4.

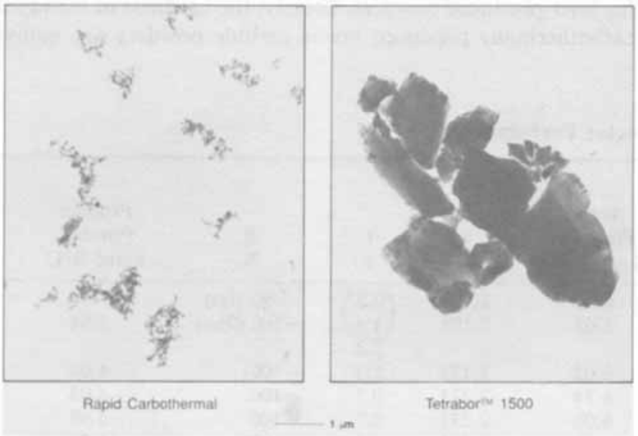

Figure 10. Micrographs of B_4C Powders, 30,000×.
Rapid carbothermal, run 38-24

Table 2. Boron Carbide Powder Comparison

Powder	B wt. %	C wt. %	O wt. %	Fe ppm	Fixed B/C	Surface Area m²/g
Traditional						
Tetrabor 800	78.0	19.6	0.65	530	4.37	3.2
Tetrabor 1500	76.6	20.8	1.82	390	4.04	11.7
Rapid Carbothermal* Run No.						
110-45, 2,123 K	75.1	21.2	2.17	351	3.94	32.0
38-24, 2,173 K	74.6	20.2	1.95	150	4.04	24.4
97-42, 2,223 K	75.7	20.5	2.34	353	4.03	17.7
58-31, 2,273 K	77.2	21.5	0.99	230	3.98	12.5
Laser**	76.8	20.6	0.90	6	4.10	55.4

*Unmilled, water-washed
**Knudsen (1987)

Stoichiometry, microstructure, and additives all play a significant role in determining the hardness of boron carbide parts.

Conclusions

Chemically homogeneous, uniformly sized submicron crystals of boron carbide can be synthesized continuously by rapid carbothermal reduction of boron oxide in a graphite transport reactor. Product stoichiometry can be controlled by temperature and precursor composition, producing either stoichiometric B_4C or boron-enriched boron carbide powders. Large excesses of feed boron oxide combined with reaction temperatures above approximately 2,300 K yield boron-enriched boron carbide powders. A near stoichiometric feed precursor yields B_4C at all temperatures of interest up to the melting point. The addition of TiO_2 to the C/B_2O_3 precursor allows the simultaneous synthesis of composite submicron B_4C/TiB_2 powders.

Rapid heating rates driven by thermal radiation allow the use of near stoichiometric boron feed precursors to completely convert available carbon to B_4C in seconds. Equiaxed product powders with surface areas between 20 and 35 m²/g are much finer than commercially available powders and resemble products made through laser pyrolysis of gaseous reactants. The

Table 3. Densification and Hardness

Powder	Optimum Hot-Pressing Conditions		1 kg VHN* GPa
	Temp., K	Atm.	
Traditional			
Tetrabor 800	2,473	Argon or vacuum	30.0
Tetrabor 1500	2,373	Argon or vacuum	30.6
Rapid Carbothermal			
110-45, 2,123 K	2,373	Argon or vacuum	31.7
38-24, 2,173 K	2,373	Argon or vacuum	31.5
97-42, 2,223 K	2,373	Argon or vacuum	31.5
58-31, 2,273 K	2,373	Argon or vacuum	31.5
112-47, 2,173 K, (2.2 wt. % TiB_2)	2,323	Argon or vacuum	32.9
Laser (Knudsen, 1987)	2,323	Argon	31.9

*Vickers hardness no., fully dense parts

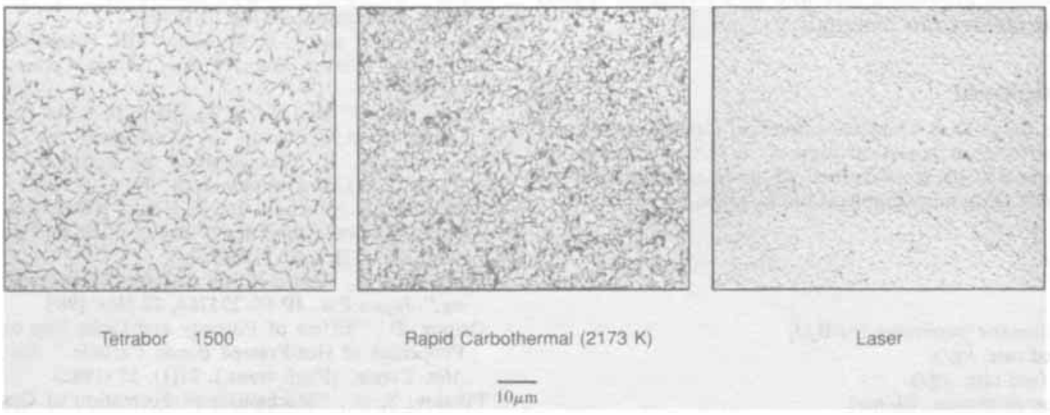

Figure 11. Micrographs of etched, dense, hot-pressed B_4C parts, 1,000×.
Rapid carbothermal, run 38-24

powder morphology and uniformity result from uniform, rapid heating rates and minimized reaction times at high temperatures. The similarity between the laser and rapid carbothermally produced powders, Figure 9, strongly suggests that significant reaction most likely involved gaseous species, probably $B_2O_2(g)$.

These microcrystalline powders can be densified into parts with a very fine microstructure and extreme hardness. Composite B_4C/TiB_2 parts fabricated from simultaneously synthesized B_4C/TiB_2 powders have improved hardness over parts fabricated from B_4C alone.

This unique rapid carbothermal reduction process has a significant cost/performance advantage over traditional boron

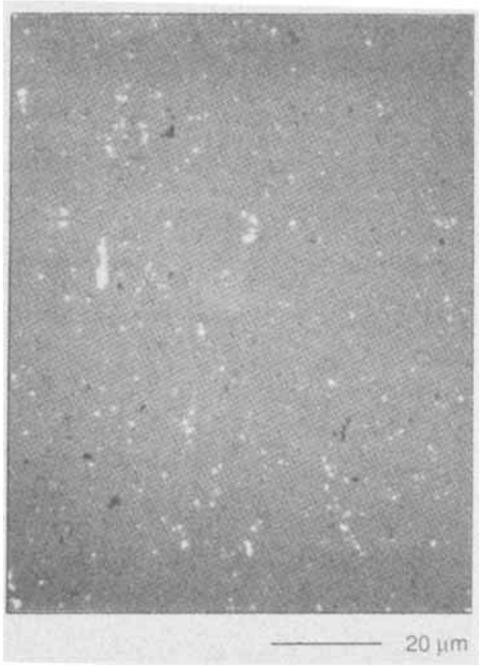

Figure 12. Micrograph of etched, dense, hot-pressed, composite 2.2 wt. % TiB_2/B_4C part, 1,000×.
Run 112-47

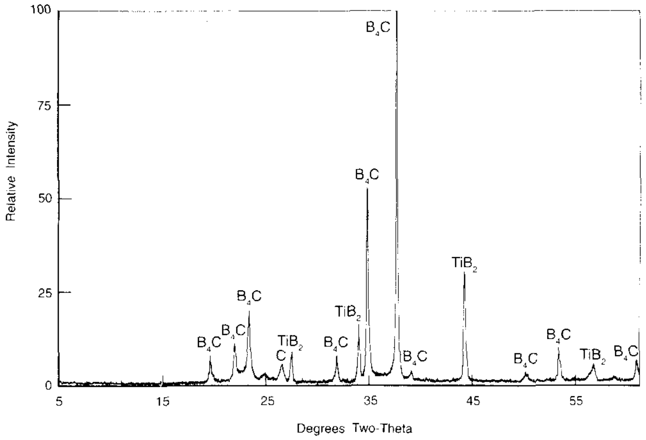

Figure 13. X-ray diffraction pattern of hot-pressed composite 2.2 wt. % TiB_2/B_4C part.
Run 112-47

Table 4. Composite B_4C/TiB_2 Preparation Conditions and Characterization

Slurry Preparation
  70.11 wt. % deionized water
  15.21 wt. % H_3BO_3
  14.30 wt. % corn starch
  0.38 wt. % TiO_2
Calcined Precursor Chemical Analysis
  34.4 wt. % C
  18.6 wt. % B
  1.2 wt. % water
Reactor Operating Conditions
  $T = 2{,}173$ K
  $t = 1.3$ s
  $F_s = 2\times 10^{-3}$ kg/s
Washed Product Analysis
  74.4 wt. % total B
  0.3 wt. % free B
  21.5 wt. % total C
  1.5 wt. % free C
  2.9 wt. % O
  1.5 wt. % Ti (2.2 wt. % TiB_2)
83 ppm Fe
32.8 m^2/g (BET)

carbide processes, producing laserlike powders from readily available, inexpensive raw materials.

Acknowledgment

The authors thank Dow Chemical employees Dave Susnitzky and John Blackson for their analytical support, and Arne Knudsen for supplying a sample of the laser-synthesized boron carbide powder so that comparative photomicrographs could be taken.

Notation

$\langle a \rangle$ = stoichiometric parameter for B_2O_3
F_g = gas feed rate, kg/s
F_s = solids feed rate, kg/s
ΔG = free energy change, kJ/mol
ΔH = enthalpy change, kJ/mol
P = pressure, MPa
t = time, s
T = temperature, K
X = % carbon conversion, see Table 1

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Manuscript received Dec. 18, 1990, and revision received Mar. 21, 1991.