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# Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 4:

Benzyl Alcohol to Calcium Sulfate

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## Boron Carbide, Boron Nitride, and Metal Borides

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1. Boron Carbide .....	295	2.1. Properties .....	300
1.1. Crystal Structure .....	295	2.2. Production .....	301
1.2. The Boron-Carbon System .....	296	2.3. Uses .....	302
1.3. Physical Properties .....	296	3. Metal Borides .....	303
1.4. Chemical Properties .....	297	3.1. Properties .....	303
1.5. Production .....	297	3.2. Production .....	305
1.6. Uses .....	298	3.3. Uses .....	306
1.7. Economic Aspects .....	300	4. References .....	306
2. Boron Nitride .....	300		

### 1. Boron Carbide

Boron carbide [12069-32-8] belongs to the important group of nonmetallic hard materials, which includes alumina, silicon carbide, and diamond [1]. Although it was first prepared over a century ago, in 1883, by JOLY [2], the formula  $B_4C$  was assigned only in 1934 [3]. Today a homogeneity range from  $B_{4.0}C$  to  $B_{10.4}C$  has been established. The composition of commercial boron carbide is usually close to a boron:carbon stoichiometry of 4:1, the stoichiometric limit on the high-carbon side.

Boron carbide is an exceedingly hard material, inferior in hardness only to diamond and cubic boron nitride. In addition, it has a high melting point, high mechanical strength combined with low density, and high neutron cross section, and is a semiconductor. General information about boron carbide is available in the reviews of LIPP [4] and THEVENOT et al. [5], [6].

#### 1.1. Crystal Structure

Structurally, boron carbide can be considered a prototype of the so-called interstitial compounds of  $\alpha$ -rhombohedral boron [7], which include  $B_{12}C_3$  [12075-36-4] ( $= B_4C$ ),  $B_{12}C_2Al$  [8],  $B_{12}S$ ,  $B_{12}O_2$ ,  $B_{12}As_2$ ,  $B_{12}P_2$ , and  $B_{3-4}Si$  [9]. The crystal structure for these materials consists

of icosahedra that occupy the points of a rhombohedron, plus a chain of atoms that runs along the  $c$  axis of the rhombohedron. For the most part, boron atoms occupy the points of the icosahedra. The second constituent — C, Al, O — in general occurs on the chain (Fig. 1). (There is no chain at all in  $\alpha$ -rhombohedral boron.) The rigid framework of polyatomic units of closely bonded atoms is reflected in the refractory nature and great hardness.

For compositions close to  $B_{12}C_3$ , the lattice parameters are  $a_H = 0.5607$  nm and  $c_H = 1.2095$  nm [10]. However, the details of the boron carbide structure [11], [12] are not firmly established. According to a recent investigation [13] the sequence C-B-C can be assumed for the chain. In addition to these two carbon atoms per unit cell, carbon

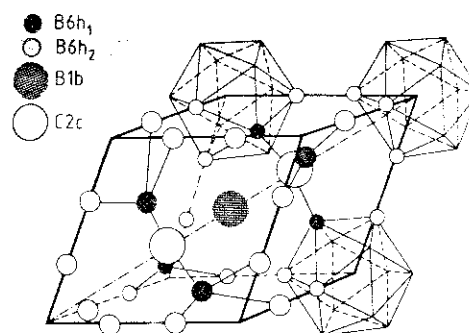


Figure 1. The structure of boron carbide for the stoichiometry  $B_{13}C_2$

likely replaces boron at the boron sites in the icosahedra. With 15 atoms per unit cell ( $B_{12}C_3$ ) and 20 mol% C, boron carbide can be reformulated as  $(B_{11}C)CBC$  to show this effect.

On the boron-rich side the extension of the homogeneity range to 8.7 mol% C, the ratio B:C = 10.4, has been reported by BOUCHACOURT, THEVENOT [14], who propose the structural formula  $B_{12-2}C_n(C/B_{2n}C_{1-2}/C)$  and  $n = 15.33$  atoms per unit cell for  $B_{10.4}C$ . The density of boron carbide at the boron-rich end is 2.465 g/cm<sup>3</sup>; the volume of the unit cell, only 2.5% larger than  $B_4C$ , corresponding to the lattice parameters  $a_H = 0.5651$  nm and  $c_H = 1.2196$  nm.

## 1.2. The Boron-Carbon System

Although numerous studies are available, not all parts of the B-C system have yet been fully elucidated.

SAMSONOV, SHURAVLOV, et al. [15], [16] reported the compounds  $B_{13}C_2$  and  $B_{12}C_3$ , both with a large homogeneity range, in addition to the carbon-rich  $BC_2$  and the boron-rich  $B_{12}C$  phases. In the diagram of DOLLOFF [17], rhombohedral  $B_{13}C_2$  and  $B_{12}C_3$  phases are combined with a wide range of solid solubility of only one carbide phase,  $B_{4-2}C$ , which is stable only below 1800°C. ELLIOT [18] reported the solid solubility of boron carbide from  $\approx 8$  to 20 mol% C over the temperature range from room temperature to the melting point of 2450°C. The  $B_4C$ -C eutectic temperature was reported to be 2375°C, at 29.0 mol% carbon (see Fig. 2). Recent measurements by KIEFFER et al. [19] support this broad range of solid solubility. In addition to the compounds given in these publications,  $B_{25}C$  [20],  $B_6C$  [21], and  $B_{13}C_3$  [22] have been reported recently. These are likely low-temperature phases, which are often observed in chemical vapor deposition. THEVENOT, BOUCHACOURT [5], [14] recently postulated a peritectic transformation of the  $\beta$ -rhombohedral boron-carbon mixed crystal, giving homogeneity range limits of  $B_{10.4}C$

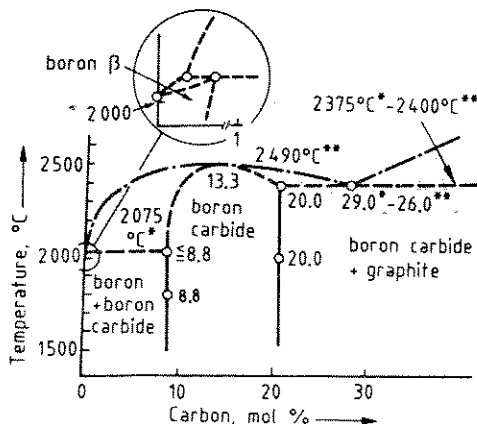


Figure 2. The boron-carbon system  
\* R. P. Elliot [18] \*\* — R. Kieffer et al. [19]  
— M. Bouchacourt, F. Thevenot [10]

(8.8 mol% C) and  $B_{4.0}C$  (20.0 mol% C). Their x-ray diffraction studies indicated a discontinuity in the lattice parameters at the composition  $B_{6.5}C$ . According to the phase diagram reported in 1983 by BEAUVY [23], the carbon-rich limiting composition corresponds to  $B_{3.63}C$ , i.e., " $B_{11}C_3$ " with 21.6 mol% C. Consequently the limit  $B_{4.0}C$  has not been firmly established.

## 1.3. Physical Properties

The purest  $B_4C$  crystals yet obtained by the electrothermic production process are deep black and shiny, a contrast to SiC crystals, which in their purest form are transparent and colorless. The crystals melt congruently at  $\approx 2450^\circ C$ ; the liquid boils above  $3500^\circ C$ . The density of  $B_4C$  having the natural isotopic composition is 2.52 g/cm<sup>3</sup>;  $^{10}B_4C$  is less dense, 2.37 g/cm<sup>3</sup>.

The Knoop microhardness number HK-0.1, i.e., the hardness measured with a load of 0.1 kp ( $\approx 0.98$  N), is  $\approx 3000$  [24] (2000 for  $\alpha$ - $Al_2O_3$ , 2600 for SiC and elemental boron, 4700 for cubic BN, and 7000-8000 for diamond). Therefore, except for diamond, the hardest known materials all contain boron. Table 1 presents some mechanical properties of hot-pressed  $B_4C$  and pressureless-sintered  $B_4C$  doped with 1 or 3 wt% carbon [25]. The fracture mode of these materials is almost 100% transgranular. Boron carbide must be considered to be a refractory material, since hardness and strength do not degrade up to  $1500^\circ C$  in an inert atmosphere [4].

The average coefficient of thermal expansion is  $4.6 \times 10^{-6} K^{-1}$  over the range  $25-800^\circ C$ , i.e., almost identical with that for pure SiC ceramic.

Table 1. Mechanical properties of hot-pressed and sintered boron carbide materials [25]

Property	Units	S- $B_4C$ *	
		1% C	3% C
Carbon content			
$C_{total}$ **	wt%	21.7	22.5
Porosity	%	< 0.5	< 2
Bulk density	g/cm <sup>3</sup>	2.51	2.44
Mean grain size	$\mu m$	5	8
Flexural strength	MPa	480	351
(4-point bend)		$\pm 40$	$\pm 40$
Young's modulus	GPa	441	390
Shear modulus	GPa	188	166
Poisson's ratio	—	0.17	0.17
Fracture toughness	MPa $\cdot m^{1/2}$	3.6	3.3
( $K_{IC}$ , SENB)		$\pm 0.3$	$\pm 0.2$

\* HP = hot-pressed, S = sintered

\*\* The amount of free carbon is estimated from the equation  $C_{free} = 1.28 C_{total} - 28$

The coefficient of thermal expansion is

$$\alpha = 3.016 \times 10^{-6} +$$

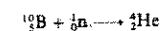
Thermal conductivity is

$$\frac{t}{\lambda} = \frac{C}{W m^{-1} K^{-1}}$$

However,  $B_4C$  shock [26].

Boron carbide is a semiconductor with a band gap of 0.8 eV. The electrical resistivity of the same material is  $10^8 \Omega \cdot cm$  at room temperature [4]. Boron carbide is a ceramic material with high thermal conductivity and high electrical conductivity. The Hall effect of boron carbide is of the same order of magnitude as that of a metal-insulator transition  $B_4C$ .

The nuclear properties of boron are such that it is a neutron absorber in most types of nuclear reactors. The cross section for thermal neutrons is  $384$  barns for  $^{10}B$  and  $0.0048$  barns for  $^{11}B$ . The  $(n, \alpha)$  reaction



produces helium and active neutrons. Boron carbide is used in neutron absorbers and in the secondary neutron absorber in the neutron moderation. The entire neutron flux is sufficient for thermal, inter

## 1.4. Chemical

Boron carbide is a refractory compound. It is insoluble in aqueous alkaline solutions.

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S-B <sub>4</sub> C*	
1% C	3% C
22.5	24.8
< 2	< 2
2.44	2.46
8	7
351	353
± 40	± 30
390	372
166	158
0.17	0.17
3.3	3.2
± 0.2	± 0.2

from the equa-

The coefficient of thermal expansion as a function of temperature ( $t$  in °C) is

$$\alpha = 3.016 \times 10^{-6} + 4.30 \times 10^{-9}t - 9.18 \times 10^{-13}t^2$$

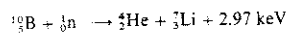
Thermal conductivity decreases with temperature:

$t, ^\circ C$	25	200	400	600	800
$\lambda, W m^{-1} K^{-1}$	35	28	23	19	16

However, B<sub>4</sub>C has low resistance to thermal shock [26].

Boron carbide is a high-temperature  $p$ -type semiconductor. The width of the forbidden band is 0.8 eV. The electrical conductivity depends on the B:C ratio and impurity content. The specific electrical resistance of B<sub>4</sub>C is 0.1–10  $\Omega \cdot cm$ , i.e., of the same magnitude as that of SiC and graphite [4], [27]. Boron carbide has a negative temperature coefficient of resistivity, similar to other ceramic materials. Boron carbide is notable for its high thermoelectric power, which increases with temperature [5]. Electronic properties, i.e., electrical conductivity, thermoelectric power, and the Hall effect, were recently measured as a function of B:C ratio by WERHEIT et al. [13]. A metal-insulator transition occurs at the composition B<sub>4</sub>C.

The nuclear properties of boron carbide are such that it is a very effective neutron absorber in most types of reactors [4]. The effectiveness of boron as a neutron absorber is due to the large cross section of the <sup>10</sup>B isotope ( $\approx 4000$  b). The natural abundance of <sup>10</sup>B is  $19.9 \pm 0.3$  mol%. The (n,  $\alpha$ ) reaction



produces helium plus lithium — and no radioactive nuclei. (In contrast, cadmium or the lanthanides do produce radioisotopes.) In addition, the secondary gamma radiation is so small that it can be ignored. The cross section is a linear function of the neutron energy and follows a  $1/v$  relation. The cross sections of boron over the entire neutron energy spectrum, 0.01–1000 eV, are sufficiently large to make boron effective in thermal, intermediate, and fast reactors.

#### 1.4. Chemical Properties

Boron carbide is one of the most stable compounds. It is not dissolved by mineral acids or aqueous alkali; however, it is decomposed slowly

by mixed hydrofluoric-sulfuric acid or hydrofluoric-nitric acid. One technique of refining B<sub>4</sub>C from free carbon and boron is based on the differing oxidation rates of the parent elements and boron carbide. The boron carbide powder is heated in a mixture of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> [28].

Molten alkali decomposes boron carbide to give borates. Boron carbide reacts with many metal oxides at elevated temperature to give carbon monoxide and metal borides. Boron carbide reacts with many metals that form carbides or borides at 1000 °C, i.e., iron, nickel, titanium, and zirconium. Aluminum [8] and silicon [29] form substitutional compounds with boron carbide. Boron carbide withstands metallic sodium fairly well at 500 °C [30] but is slowly etched by hydrogen at 1200 °C. At that temperature it does not interact with sulfur, phosphorus, or nitrogen. Above 1800 °C it reacts with nitrogen to give boron nitride. Elemental carbon can be dissolved in B<sub>4</sub>C at the B<sub>4</sub>C-C eutectic temperature of about 2400 °C, precipitating again on cooling [17].

Chlorine attacks B<sub>4</sub>C at about 600 °C and bromine attacks it at 800 °C and above. These reactions can be used to prepare boron halides. Boron carbide can be melted without decomposition in an atmosphere of carbon monoxide, but it reacts in the temperature range 600–750 °C with CO<sub>2</sub> to form B<sub>2</sub>O<sub>3</sub> and CO. Oxidation in air starts at 500 °C and is severe at 800–1000 °C. However, the oxidative damage depends to a great extent on the surface area of the object, powder being attacked more severely than bulk samples.

Detailed descriptions of chemical, mass spectrometric, and spectrochemical analysis of boron carbide have been issued by the American Society for Testing and Materials (ASTM) [31].

#### 1.5. Production

**Powder.** The most common method for large-scale production of boron carbide is *carbothermic reduction* of boric oxide:

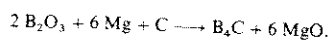


The process is so strongly endothermic, 1812 kJ/mol or 9.1 kWh/kg, that it is usually carried out at 1500–2500 °C in an electric furnace. Either arc furnaces or resistance furnaces, analogous to Acheson furnaces for SiC, are used

[4]. The starting material is an intimate mixture of boric oxide and carbon, e.g., petroleum coke or graphite. Large quantities of carbon monoxide, 2.3 m<sup>3</sup>/kg, are generated, and boron can be lost by evaporation of B<sub>2</sub>O<sub>3</sub> at the high temperatures. In the electrothermic process used by ESK, a subsidiary of Wacker Chemie, the product is cooled, and the unreacted outer-zone material is removed to leave a fused coarse-grained boron carbide of high purity: B plus C ≥ 99 wt%, total metal impurity ≤ 0.2 wt%, N plus O ≤ 0.3 wt%, B:C mole ratio of 4.0–4.3. This boron carbide is obtained in the form of regular blocks, which are broken up and milled to produce the B<sub>4</sub>C grain size appropriate for final use.

If the carbothermic reduction is carried out below the melting point of B<sub>4</sub>C, e.g., at 1600–1800 °C, in a vented graphite tube furnace starting from a dehydrated mixture of H<sub>3</sub>BO<sub>3</sub>, acetylene black or sugar, and ethylene glycol, very fine-grained (0.5–5 μm), stoichiometric B<sub>4</sub>C powders are produced [32], although productivity is low.

Boron carbide powders are produced directly (no need of the expensive comminution) by magnesiothermic reduction of boric oxide in the presence of carbon at 1000–1800 °C:



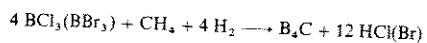
This reaction is strongly exothermic. It is carried out either directly by point ignition (thermite process) or in a carbon tube furnace under hydrogen [33]. The product is washed free of magnesium oxide and unreacted magnesium metal with hydrochloric or sulfuric acid and can be further purified by heating under vacuum at 1800 °C. Since the MgO acts as a grain growth inhibitor, ultrafine boron carbide particles on the order of 0.1–1.5 μm are obtained.

There are other methods of powder preparation:

- 1) synthesis from the elements  
(4 + x)B + C → B<sub>4+x</sub>C
- 2) reduction of boron trichloride by hydrogen in the presence of carbon



- 3) chemical vapor deposition [34]



However, these methods are generally used only on the laboratory scale for preparing high-purity boron carbide crystals or coatings [4].

**Dense Shapes.** Self-bonded [35] boron carbide shapes having 100% theoretical density, small final grain size, and high mechanical strength can be produced by *hot pressing* [36]. This is accomplished by placing a loose powder or a compact preform in a graphite die and applying uniaxial pressure of 10–30 MPa at a temperature exceeding 2000 °C for 5–10 min. Inert or reducing atmospheres are necessary to protect B<sub>4</sub>C and the graphite from oxidation. Increasing the boron content to the composition B<sub>13</sub>C<sub>2</sub> has been found to facilitate sintering by reducing the necessary temperatures and to almost double the strength [37]. However, for boron-rich B<sub>4+x</sub>C compositions, expensive boron nitride-lined graphite molds must be used, to avoid carburization resulting in formation of carbon-rich B<sub>4</sub>C [38].

In 1977, ESK developed a process for *pressureless sintering* of boron carbide, a process now used in everyday production [39]. The key observation, that carbon additives are extremely effective in inducing densification of B<sub>4</sub>C, was also made by HENNEY, JONES [40] and SUZUKI et al. [41] almost simultaneously. The properties of sintered B<sub>4</sub>C can be improved further by post-sintering, i.e., post-densifying by hot isostatic pressing without cladding [42]. Pressureless sintering and post-sintering were recently developed to produce new B<sub>4</sub>C–SiC *composite materials*. These combine the good thermal shock and oxidation resistance of silicon carbide with the hardness and low density of boron carbide [43]. In this way a maximum strength of 550 MPa (4-point bend) was achieved for a composite of 59 wt% SiC–37 wt% B<sub>4</sub>C–4 wt% C. This composite can be used in oxidizing atmospheres up to 1200 °C. (Also see → Powder Metallurgy).

## 1.6. Uses

The uses of boron carbide are described in [4], [6], [26], [27], [44].

**Uses Based on Hardness.** The major industrial use of boron carbide is as abrasive grit or powder. Commercial grits are available in particle sizes from 1 μm to 10 000 μm and predominantly used as polishing, lapping, and grinding media for hard materials, especially cemented tungsten carbide and fine ceramics. Water and commercial oils serve as lubricant and coolant. Available as a substitute for loose

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powders is  $B_4C$  paste, which can withstand temperatures up to 350 °C.

The second category is wear-resistant engineering components made of dense, sintered shapes. Boron carbide sand-blasting nozzles are now the most common form of such a component. These nozzles are characterized by minimum wear, even with corundum or silicon carbide grit. Sintered- $B_4C$  wheel dressing sticks are used to produce new cutting edges on surface grains of grinding wheels with minimum wear. So-called hand laps are used to render the cutting edges of cemented carbide tools keen and smooth. Mortars and pestles of boron carbide are suitable for grinding hard materials without contamination from the grinding equipment.

Ultrahard substances are nonductile. This factor, together with a density of only 2.5 g/cm<sup>3</sup>, is fully exploited in the use of dense  $B_4C$  as ceramic plates against armor-piercing bullets of caliber up to the thickness of the plates [44]. Light-weight ceramic tiles have been used extensively for the protection of helicopters; monolithic breastplates, for the protection of personnel. Hot pressings made from a finer grade of boron carbide are used in air bearings of inertial navigation equipment.

**Uses in Nuclear Technology** [26], [45]. Boron carbide is both cheaper and easier to fabricate than the element boron itself. As a result it has found almost exclusive usage as a control rod material, neutron poison, and a neutron shielding material. The bulk density of vibro-packed  $B_4C$  powder, better the sintered density of self-bonded boron carbide pellets, or the  $^{10}B:^{11}B$  ratio can be varied to adapt absorber efficiency to the specific conditions in thermal (BWR, PWR), high-temperature (HTR), and fast breeder reactors (FBR).

A  $^{10}B$ -enriched boron carbide, e.g., corresponding to  $\leq 92$  mol%  $^{10}B$ , is commercially available; thus, the nuclear worth of an absorbing element can be increased nearly 4.5-fold by substituting enriched for natural material, without a change in dimensions. The helium formed during reactor exposure is partially retained within the solid  $B_4C$  as micropores, but the fraction released ( $\leq 50\%$ ) must be accommodated by some aspect of control assembly design, such as a plenum within an individual pin or a reliable pressure relief vent. The He and Li atoms, because of their relatively large size, cause some radial swelling ( $\leq 10\%$ ) of the  $B_4C$  pellets.

In a typical thermal reactor the operating temperature of the absorber is below 500 °C, and low-density ( $\approx 75\%$  of theoretical density)  $B_4C$  pellet columns clad in metal sheets have proved adequate for large-scale commercial use. In gas-cooled reactors, boronated graphite containing about 40 wt% B meets the high-worth control rod requirements. Ceramic-based dispersions, i.e., combinations of relatively small amounts of  $B_4C$  in an inert matrix, exhibit smaller macroscopic neutron absorption cross sections but swell less and release less gas. So-called burnable poison rods, which are consumed at the same rate as the fuel, are commonly designed in this fashion. Examples are  $Al_2O_3-3$  vol%  $B_4C$  for water-cooled reactors and boronated graphite ( $\approx 6$  wt%  $B_4C$ ) for gas-cooled reactors.

$^{10}B$ -enriched  $B_4C$  has been chosen as the absorber for fast-breeder reactor control material. A potential alternative for future fast breeder generations is  $^{10}B$ -enriched europium hexaboride, which has better engineering properties and which loses its absorption reactivity because of  $^{10}B$  burnup about 40% slower than  $B_4C$  [46]. Carbon-bonded boron carbide plates (Tetrabor) [47] provide for the closest possible arrangement of spent fuel elements in high density intermediate storage pools. Sizes range up to 500 mm in length and down to 2 mm in thickness. These shield plates with  $> 50$  vol%  $B_4C$  usually contain more absorber material than aluminum-bonded  $B_4C$  (Boral) and silicone-bonded  $B_4C$  plates (ESK-Elastosorb). Doors, windows, or walls in laboratories where radioactive matter is investigated are screened with  $B_4C$  plates. Their low density of  $\approx 1.6$  g/cm<sup>3</sup> makes them excellent for lining containers for nuclear fuel or any matter radiating neutrons.

**Chemical Uses.** Boron carbide powder is used to introduce boron into the surface layer of steels and other ferrous materials [27], [48]. This takes place by diffusion of boron into the surface layer, resulting in the formation of a thin (10–1000  $\mu$ m) but hard, wear-resistant layer of iron boride,  $Fe_2B$ . Vickers hardness numbers of 2400 HV-0.1, corresponding to tungsten carbide or  $\alpha-Al_2O_3$ , were measured on the surface of high-alloyed tool steels. The surfaces of cemented carbides (WC–Co, WC–TiC–TaC–Co/Ni/Fe, and Ferrotic) and stellite alloys can even be hardened further by boron [49]. According to the EKabor powder packing method

$B_4C$ -SiC powder mixtures with added sodium tetrafluoroborate activator are used.

Its high boron content makes  $B_4C$  useful as a raw material for the production of other boron compounds, including the boron halides and metal borides [4]. The exceptionally high heat of combustion of  $B_4C$  makes powders with a mean particle size of  $2\ \mu\text{m}$  useful energy carriers in solid rocket propellants [4].

**Other Uses.** The thermoelectric properties of  $B_{13}C_2$  [50] are such that  $B_{13}C_2$  could be an interesting material for high-temperature thermoelectric conversion. Thermoelements made of the couple  $B_4C$ -C can be used for temperature measurements up to  $2300^\circ\text{C}$  [51].

### 1.7. Economic Aspects

ESK is the world's largest producer of boron carbide. The granular and sintered  $B_4C$  products of this company are sold commercially under the trademark Tetrabor. The price of  $B_4C$  is \$ 15-75 per kg, depending on grit size. Annual production in the non-communist countries is about 500 t, small compared to a SiC production of 500 000 t.

## 2. Boron Nitride

The elements boron and nitrogen, both neighboring carbon in the periodic table, form the 1:1 compound BN [10043-11-5], which has allotropes isostructural to the allotropes of carbon:

- 1) Alpha-BN, hexagonal modification with a layered structure similar to graphite, sometimes called white graphite
- 2) Beta-BN, high-pressure diamondlike modification, cubic zinc blende structure
- 3) Gamma-BN, dense hexagonal modification, wurtzite structure

More detailed reviews of the properties, preparation, and uses of the various BN modifications are given in [52]-[54].

### 2.1. Properties

**Alpha-BN.** The most common form of boron nitride is the graphitelike hexagonal, used increasingly because of its unique combination

of properties: low density,  $2.27\ \text{g/cm}^3$ ; high-temperature stability,  $mp$  near  $3000^\circ\text{C}$ ; chemical inertness, especially its resistance to acids and molten metals and its stability in air up to  $1000^\circ\text{C}$  and in inert gases like  $N_2$ , Co, and Ar up to  $2700^\circ\text{C}$ ; stability to thermal shock; workability of hot-pressed shapes; extremely low electrical conductivity, which makes it an excellent insulator; and high thermal conductivity.

In *thermal conductivity* BN ranks with stainless steel at cryogenic temperatures and with beryllium oxide, BeO, at higher temperature. Above  $700^\circ\text{C}$  the thermal conductivity of  $\alpha$ -BN exceeds that of BeO. Boron nitride has a dielectric constant of 4, one half that of  $\alpha$ - $Al_2O_3$ , which also has high dielectric strength. It is a lubricant over a wide range of temperatures; its low coefficient of friction is retained up to  $900^\circ\text{C}$ , whereas other solid high-temperature lubricants, e.g., graphite and molybdenum disulfide, burn away well below  $900^\circ\text{C}$  [55].

Because of its *stability* at high temperature and inertness towards carbon and carbon monoxide up to  $1800^\circ\text{C}$ , it is used as a refractory ceramic. In this function it is superior to the nitride ceramics  $Si_3N_4$  and AlN and the oxide ceramics MgO, CaO, and  $ZrO_2$ . It is not wet by and thus is stable against attack by molten glass, molten silicon, boron, nonoxidizing slags, molten salts such as borax and cryolite, and reactive molten metals, including aluminum, iron, copper, and zinc. Because it sinters poorly, dense shapes of  $\alpha$ -BN are produced exclusively by hot-pressing. Typical properties of axial and isostatic hot-pressed BN are summarized in Table 2.

Most chemical and physical properties of axial hot-pressed BN shapes depend on the nature and amount of densification additives ( $\leq 5\ \text{wt}\%$   $B_2O_3$  or metal borates) [53]. In addition, the coefficient of expansion and thermal conductivity as well as the flexural strength and Young's modulus are *anisotropic*; they vary with the direction of hot-pressing. In this respect, BN is similar to graphite. However, isostatic hot-pressing (HIP) of canned BN powder, a recent development, produces pure isotropic  $\alpha$ -BN shapes of theoretical density. Such shapes possess superior thermal and mechanical properties (see Table 2) [56].

**Beta-BN.** The cubic form of boron nitride,  $\beta$ -BN, the commercial Borazon, resembles diamond in crystal structure and other properties. Pure  $\beta$ -BN is colorless and a good electrical insu-

Table 2. Physical

Property

Sintered density,  
Flexural strength  
(4-point bend)

Young's modulu

Thermal conduct  
 $W\ m^{-1}\ K^{-1}$ Coefficient of lin  
expansion,  $K^{-1}$ Electrical resistiv  
 $\Omega\cdot\text{cm}$ 

Dielectric consta

\* HP = hot-press  
mechanical and  
tropic — they dif  
parallel (||) to th  
same propertieslator. Doping  
C, or P turns  
other properti  
ness.The the  
 $3.48\ \text{g/cm}^3$ .  
HK-0.1 is  $\approx$   
 $> 7000$  for di  
air up to  $1400^\circ\text{C}$   
only  $800^\circ\text{C}$  —  
abrasive.**Gamma-BN**  
which is meta  
atures where  
close to cubic  
BN transfor

### 2.2. Produc

Hexagona  
time by BA  
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curiosity until  
when hot-pre  
the first time