

production of continuous boron filaments, the manufacture of dye stuffs and in high-energy propellants. No other practical route exists for the production of non-oxide compounds for the stable oxides, except through the carbide intermediate. B₄C also is used in some reaction schemes to produce refractory metallic borides.

Other applications include the use of fine B₄C powder as the generally accepted sintering aid for densification of SiC. Recently, the thermoelectric properties of B₄C have been used in making high-temperature thermocouples.

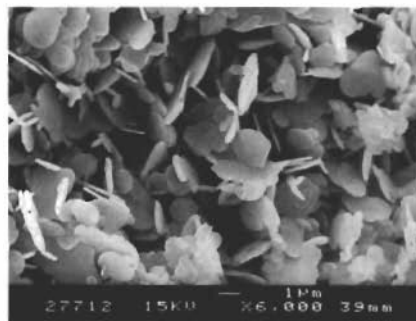
The unique combination of low specific gravity, high elastic modulus and high hardness of B₄C has led to development of B₄C-containing metal-matrix composites and cermets, which are used for wear parts and armor components. The ceramic armor is used for protection against a variety of ballistic threats. These applications are especially important in aircraft, where weight is a primary consideration.

—Submitted by Mary T. Spohn, Advanced Refractory Technologies Inc., Buffalo, N.Y. ■

Boron Nitride

Hexagonal boron nitride (α-BN) is a white, talc-like powder that has a graphitelike sheet structure. Therefore, it is often referred to as white graphite. In contrast to graphite, it has localized π-electrons that are responsible for its high electrical resistivity and white color. Furthermore, boron nitride is a high-temperature solid lubricant, good thermal conductor and good dielectric. It is chemically inert and not wetted by many metallic and silicate melts. Boron nitride is stable in air up to 1000°C, under vacuum up to 1400°C and can be used to 2400°C in a nitrogen-gas atmosphere.

Boron nitride is available as a powder with BN concentrations ranging from as low as 92% for refractory purposes to >98.5% for ceramic applications. High-purity grades are >99.5% BN. Boric oxide

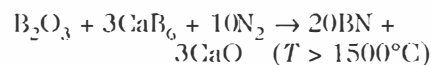
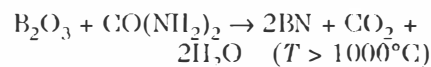
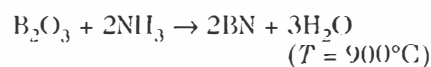


SEM micrograph (secondary electron image) illustrating the platelike particles of a ceramic-grade boron nitride powder.

(B₂O₃), carbon, oxygen (forming amorphous boron oxynitride) and metallic impurities may be present.

Boron nitride does not occur in nature and was first prepared in 1842 by reacting molten boric acid with potassium cyanide. However, commercial production was initiated in the 1950s.

Three synthesis routes are used today. Boric oxide, borax, boric acid or calcium hexaboride may be the source of boron, which forms boron nitride in the presence of ammonia (by using an inert filler), an organic nitrogen-containing compound (e.g., urea) or nitrogen gas, according to one of the following reactions:



The resulting boron nitride is well crystallized in the hexagonal structure,

showing platelets with a dimension of 1–10 μm and a thickness of 0.1–0.5 μm. Purification may be done by reheating the product to temperatures >1500°C to evaporate the remaining boric oxide.

No statistical figures are available on the production levels of boron nitride, but a reliable estimate is about 220 metric tons in 1993 for the western world, one-third of which was produced in each the United States, Europe and Japan. Although boron nitride is produced in the Commonwealth of Independent States (CIS, formerly the Soviet Union), no information can be obtained from there.

The principal producers include Advanced Ceramics Corp. (formerly Union Carbide/Praxair Advanced Ceramics) and Carborundum Co. in the United States; Boride Ceramics & Composites Ltd. in the United Kingdom; Elektroschmelzwerk Kempten GmbH and H. C. Starck GmbH & Co. KG in Germany; and Denki Kagaku Kogyo, Kawasaki Steel Corp., Shin-Etsu Chemical Co. Ltd. and Showa Denko KK in Japan.

The costs of boron nitride powder for lots of 100 kg are about \$70–\$80/kg for refractory grades and \$100–\$120/kg for ceramic grades. High-purity and tailor-made grades may be purchased at prices ranging from about \$200–\$400/kg, depending on quality and size of order.

Large quantities of boron nitride powder are used for the production of titanium diboride/boron nitride intermetallic composites, such as evaporator crucibles and boats for vacuum metallization of plastics and glass. Considerable amounts are used for refractory purposes

Commercially Available Boron Nitride Powders

Component	Composition (%)		
	Refractory grades	Ceramic grades	High-purity grades
BN	92–96	>98.5	>99.5
B ₂ O ₃	5–7	0.1	<0.03
Oxygen*	5	0.5–1.5	0.3
Carbon	0.1	0.1	0.1
Metallic impurities	0.2	0.2	>0.01

*Includes oxygen content of B₂O₃.

Boron Nitride Powder 1993 Estimated Production

Supplier	Amount (metric tons)*
United States	
Advanced Ceramics Corp.	~60
Carborundum Co.	12-15
Total	70-75
Europe	
Boride Ceramics & Composites	10-15
Elektroschmelzwerk Kempten	40-50
H.C. Starck	40-50
Total	80-90
Japan	
Denki Kagaku Kogyo	30-50
Kawasaki Steel Corp.	5-10
Shin-Etsu Chemical Co.	NA
Showa Denko KK	NA
Total	60-80
World Production†	~220

*NA is data not available. †Excluding Commonwealth of Independent States (formerly the Soviet Union).

Boron Nitride Powder 1993 Estimated Consumption

Use	Consumption (metric tons)*
TiB ₂ /BN composites	60-70
Refractory applications	20-30
Break rings	20-30
Cubic boron nitride	15-20
HIPed shapes	15-25
Paints/coatings/lubricating agents	25-35
Electronic applications	NA

*NA is data not available.

and the production of break rings for horizontal continuous steel casting. Dense shapes of hexagonal boron nitride are made by hot isostatic pressing (HIPing) of powders using boron oxide as a sintering agent; this consumes 15-25 metric tons/year of boron nitride powder. The resulting shapes are soft and easily machined to desired sizes.

Hexagonal boron nitride is also the source of cubic boron nitride (β -BN, a diamond-like modification with zinc blende structure). 15-20 metric tons/year are used for this conversion; however, the output is only 5-10% cubic boron nitride.

An increasing amount of boron nitride is used in paints and coatings that act as release and lubrication agents for light-metal casting, and glass and other forming processes—such as superplastic forming of titanium sheets for aerospace and defense applications. The paints are dispersions of boron nitride in a carrier (water or alcohol)—often blended with refractory binders—that can be applied similar to household paints. Certain formulations are available in aerosols for easier application. Such coatings are produced by Advanced Ceramic Corp., Carborundum Co. and ZYP Coatings Inc. in the United States and by Elektroschmelzwerk Kempten GmbH and Büro für angewandte Mineralogie in Germany.

Because of its good thermal conductivity, high dielectric strength and nontoxic nature, boron nitride is used as an alternative to beryllia in electronic applications for heat transfer between semiconductor chips and their substrates.

Latest developments show applications of boron nitride in cosmetics because of its good lubrication properties.

Boron nitride-producing companies are encouraged to submit more precise data on production and use for next year's Annual Minerals Review.

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Calcium Aluminate Cements

Calcium aluminate (CA) cements are manufactured hydraulic binders. They are commercially prepared by melting or sintering various bauxites or aluminas with limestone into clinker form, which is then ground to cement.

The most important strength-generating mineral phase present in CA cements is monocalcium aluminate ($\text{CaO} \cdot \text{Al}_2\text{O}_3$), which combines chemically with water to form several hydrate phases when the cement is used. Other lime-alumina phases also are present in varying amounts, and they

influence the overall properties of the cement.

CA cements develop strength quickly once setting has begun. They reach strength levels in 24 h which are not generally achieved by portland cements for 28 days.

These cements have properties that make them useful in a wide variety of applications. However, during the past few decades, most CA cements have been used in the refractories industry. They retain a relatively strong structure as they are heated, making them good refractory binders in high-temperature castables and gunning mixes.

Also, CA cements are more resistant to chemical attack than portland cements and, thereby, find use in concretes designed to resist acids, sea water, sewage, industrial wastes and other hostile fluids.

CA cements can be batched with portland cements, water and other materials to make quick-setting mixes. These are useful for patching, machine grouting, post setting and other applications where rapid strength gain is more important than optimizing the overall final strength.

CA cements containing the lowest amount of alumina and the highest amounts of primary impurities (Fe_2O_3 and SiO_2) are the least expensive. Higher alumina content cements can be made from bauxites containing lower levels of Fe_2O_3 and SiO_2 . The color and specific physical properties of these cements depend on the impurity levels of the bauxites chosen, the manufacturing process and other materials which may be used in production. Colors may range from near black or dark brown to beige or light gray.

Cements of higher refractory performance can be manufactured, but processed alumina must be used to minimize impurity content. The most expensive, highest quality bauxites found in nature contain about 5% or 6% Fe_2O_3 and SiO_2 total, but to increase refractory performance over bauxite-