

contract. Applications include control rod pellets, shut down balls and burnable poisons for commercial nuclear power facilities, and for hold down as required in high-density storage of spent nuclear fuel.

The unique combination of B_4C 's low specific gravity, high elastic modulus and high hardness has led to development of B_4C -containing metal-matrix composites and cermets, which are used for wear parts and armor components. The resultant ceramic armor is used for protection against a variety of ballistic threats. These applications are especially important where weight is a primary consideration—aircraft and increasingly popular lightweight, maneuverable land vehicles, which are more prevalent in skirmish battles.

Recently, B_4C 's thermoelectric properties have been used in making high-temperature thermocouples and thyristors.

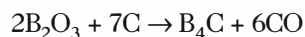
B_4C , CAS No. 12069-32-8, is the third hardest material known, relative to diamond and cubic boron nitride, and is currently the hardest material produced in tonnage quantities. It is often grouped with other nonmetallic hard materials, such as alumina, silicon carbide and diamond. Over 100 years ago, Wohler produced B_4C as a secondary product in the production of metal borides. Joly (1833) and Moissan synthesized B_4C in a purer form and identified boron carbide compounds of different compositions. Phase compositions were first investigated in 1934 and the formula B_4C assigned.

Although boron carbide is chemically represented as B_4C , it actually exhibits a range of compositions from B_4C to $B_{10.5}C$. Localized phases of varying composition may exist in a material of a given overall composition. The representation B_4C does not therefore imply an exact formula. The typical commercial material has a composition that closely approaches B_4C and the related formula weight of 55.26 and density of 2.52 g/cm³. The atomic structure cannot have fewer than four boron atoms per carbon atom, but boron carbide frequently

contains a quantity of free, uncombined carbons. This explains why commercial boron carbide may contain less than the theoretical 78.3% boron by weight.

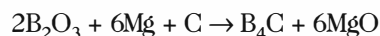
B_4C powders can be formed by a variety of reactions, including the carbon reduction of any of several boron-oxygen compounds, such as boric oxide (B_2O_3), boric acid (H_3BO_3), borax ($Na_2B_4O_7 \cdot 10H_2O$) and boracite ($Mg_7Cl_2B_{16}O_{30}$). It also can be produced by the direct combination of the elements. Coatings, filaments and powders can be made by the reaction of several vapor species, including boron halides (BCl_3 and BBr_3), borane (BH_3) or diborane (B_2H_6), with methane, chloroform or other carbon sources, as well as by the decomposition of organoboranes.

Most commercial B_4C is produced in arc furnaces. A mixture of boric oxide and carbon is fed into a furnace with a water-cooled shell. An electric arc is maintained between graphite electrodes inside the furnace. The synthesis reaction is strongly endothermic and is accompanied by the release of large volumes of carbon monoxide (2.3 m³/kg). Venting and disposal of the carbon monoxide gas constitutes a major process design consideration. The reaction is



Whereas a stoichiometric reaction mix contains a boric oxide to carbon ratio of about 1.66, in production this ratio can be 2.7 or higher.

Magnesiothermal reduction of boric oxide in the presence of carbon also yields B_4C . This strongly exothermic reaction is



The removal of MgO and unreacted magnesium via HCl or H_2SO_4 is a necessity and a significant problem with this approach.

Crude B_4C obtained from these methods is subsequently crushed, milled and may then be leached with acid to remove metallic impurities, to yield a fine powder. Different particle size grades are produced for use in a variety of applications.

There are several manufacturers of B_4C . Standard material is produced by Elektroschmelzwerk Kempton GmbH in Germany, Washington Mills Electro Minerals Co. and Advanced Refractory Technologies Inc. in the United States and Denka Corp. in Japan. Additional suppliers of B_4C include H. C. Starck in Germany, Electro Abrasives Corp. and Advanced Ceramics Corp. in the United States and Mudanjiang Abrasive 2 Factory in China (the country's largest producer). There also are some Russian and other Chinese sources. Enriched forms of B_4C are produced by Eagle-Picher Industries Inc. in the United States.

The typical cost of standard B_4C powder ranges from \$25/kg to \$225/kg, depending on the quality, grade and purchase volume of the material. The world market for B_4C is estimated to be 500–700 metric tons/year, representing around \$40–\$50 million/year in sales.

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Advanced Refractory Technologies Inc.

Boron Nitride

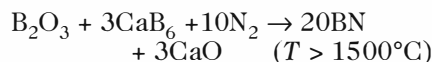
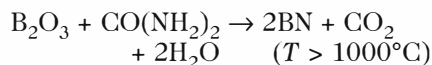
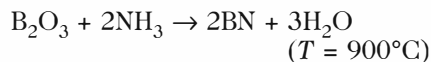
Hexagonal boron nitride (α -BN) often is called white graphite, because it has a graphite-like hexagonal layer structure. In contrast to graphite, however, BN is white and has a high electrical resistance. The reason for these differences is the absence of the delocalized π bonds in the BN structure.

BN is a ceramic material with outstanding chemical, thermal and electrical properties. It can be used as a high-temperature solid lubricant, is stable at high temperatures and is not wetted by many metallic melts, such as aluminum and magnesium. BN shows good thermal shock resistance, high thermal conductivity and low dielectric constant. Therefore, it is a nontoxic substitute for beryllia in certain electronic applications.

BN does not occur in nature. It was first prepared in 1842 by reacting molten boric acid with potassium cyanide. In the 1950s,

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commercial production was initiated by Union Carbide and Carborundum Co. Three general reactions are used for the synthesis of α -BN:



These processes yield refractory grades with concentrations of 92%–95% BN and 5%–7% B_2O_3 . The glassy B_2O_3 cannot be converted to BN. The B_2O_3 is removed by evaporation in a second step by reheating the product to temperatures $>1500^\circ\text{C}$. The remaining ceramic-grade product has BN concentrations $>98.5\%$.

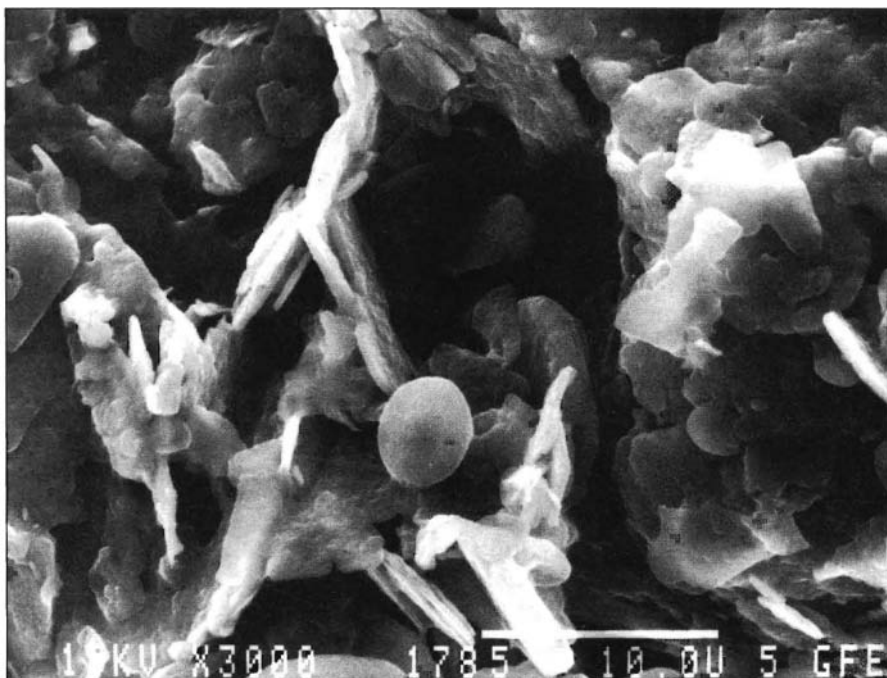
BN production figures are not included in statistical reports. Estimates, however, show production of 220–250 metric tons in 1994 for the western world. Companies involved include Advanced Ceramics Corp. and Carborundum Co. in the United States; Boride Ceramics & Composites Ltd. in the United Kingdom; 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.

Costs of BN powders are about \$70–\$80/kg for refractory grades and \$100–\$120/kg for ceramic grades, with little or no increase expected for the near future.

1994 BN Powder Estimated Consumption

Use	Consumption (metric tons)*
TiB ₂ /BN composites	60–70
Refractory applications	20–35
Break rings	20–30
β -BN	15–20
HIPed shapes	15–25
Paints/coatings/lubricating agents	35–45
Electronic applications	NA

*NA is data not available.



SEM micrograph (secondary-electron image) illustrating the platelike particles of a refractory-grade BN powder and a sphere of molten B_2O_3 (center) that was not converted to BN during synthesis.

High-purity grades can be purchased at \$200–\$400/kg, depending on quality and size of order.

BN powders are used for the production of TiB₂/BN intermetallic composites used as evaporator boats for vacuum metallization of plastics and glass. Dense shapes, e.g., crucibles and break rings for horizontal continuous steel casting, are made by hot isostatic pressing, using B_2O_3 as a sintering agent. α -BN also is the starting material for the synthesis of cubic boron nitride (β -BN), a dense, diamond-like modification, with zinc blende structure. β -BN is the second hardest material known.

The extremely good high-temperature lubrication and nonwetting properties of BN are used in coatings

in the production of aluminum and magnesium castings as well as glass-forming and superplastic forming of titanium sheets for aerospace and defense applications.

These paints and lubricating coatings are suspensions of BN in a carrier (mainly water for safety and environmental considerations), often blended with binders and rheological additives. Some formulations are available as aerosols. BN coatings are produced by Advanced Ceramic Corp. and ZYP Coatings Inc. in the United States and by Büro für Angewandte Mineralogie and Elektroschmelzwerk Kempten GmbH in Germany.

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Büro für angewandte Mineralogie

Commercially Available Ceramic-Grade BN Powders

Component	Composition by supplier (%)			
	A*	B*	C	D
Boron	42.2	43–44	43	42.5
Nitrogen	55.8	54–55	54.5	55.5
Oxygen†	0.5	1.5	1.5	0.5–1.0
Carbon	0.2	NA	0.1	0.1
B_2O_3	NA	0.1	0.1	0.15
Metallic impurities	0.1	0.2	0.2	0.1

*NA is data not available. †Includes oxygen content of B_2O_3 .

Commercially Available Refractory-Grade BN Powders

Component	Composition by supplier (%)			
	A*	B*	C	D
Boron	41.5	42–45	41.5	41.5
Nitrogen	53.5	50.5–53.4	51.5	52.0
Oxygen†	3.5	5.0	7	5
Carbon	0.4	NA	0.1	0.2
B ₂ O ₃	NA	1.0	7	5
Metallic impurities	0.1	0.2	0.2	0.1

*NA is data not available. †Includes oxygen content of B₂O₃.

Calcium Aluminate Cements

Calcium aluminate (CA) cements are commercially manufactured hydraulic binders. They are different from portland cements. Portland cements are calcium silicates and are manufactured from limestones and clays or shales. CA cements are made from limestones and bauxites or processed aluminas. CA cements withstand more severe conditions than portland cements in terms of high temperatures and chemically hostile environments.

CA cements are manufactured by sintering or by fusing. The fused or sintered clinker is ground to cement fineness in ball mills and is sold either in packages or in bulk containers.

Several mineral phases are created during manufacturing, the most important of which is monocalcium aluminate (CaO·Al₂O₃). The other mineral phases that may be present contain varying lime-to-alumina ratios, and are important to the overall properties of the cement.

Most of the phases present in CA cement hydrate when mixed with water to form various crystal structures. CA cements usually do not have extremely short working times (pot life), but, under certain conditions, a retarder or other set modifier can be recommended by the manufacturer.

CA cements develop strength quickly once the setting has begun. CA cements typically develop as much strength in 24 h as portland cements develop in 28 days. This property, as well as the thermal, mechanical and chemical stability of CA cements, makes

these binders suitable to many industrial applications.

CA cements can be produced in a variety of grades. The least expensive CA cements contain ~40% alumina, 37% lime and the balance in iron oxide, silica and other minor constituents. Other grades of CA cements contain increasing amounts of alumina, with decreasing amounts of iron and silica. Generally, as the amount of alumina increases, the price of the cement also increases. At high temperatures, iron becomes detrimental in reducing atmospheres, and the iron content in CA cements must be restricted. High-performance CA cements are made from processed aluminas and pure limestone.

High-purity CA cements are available that have iron contents of <0.5% and silica contents of <1%, and they may be interground with pure alumina to further limit total impurities. These cements are used in the most severe temperature applications that the lime-alumina system can withstand, and are the most expensive of the CA cements.

The color of CA cement varies. Low-purity CA cements are typically dark-brown or black. As the amount of iron decreases, the cement becomes lighter. High-purity cements are bright-white. The intermediate purity cements vary from brown and gray to light-tan or light-gray. CA cements produced by fusing tend to be black or gray, whereas those made by sintering tend to be brown or tan.

Historically, most CA cements were used in refractory applications, especially those related to

steel production. However, as the steel industry has sought to lower costs during the past two decades, refractory use has decreased significantly. This has lowered the use of CA cements in some industry segments, and has limited the overall use of CA cements in traditional high-temperature applications.

Because of the maturity of the refractory products market, CA cements are being increasingly used in chemical-resistant applications and other areas that utilize their properties. Such applications include concretes for handling acids, bases, sewage, industrial wastewater, sea water and other hostile fluids. CA cements, when mixed with portland cements and/or other materials, can be used to formulate quick-setting mixes. These mixes are used as grouts, water plug mixes, machine-anchoring mixes and patching compounds. In these cases, rapid strength gain is more important than final overall strength.

CA cements are not often chosen for structural applications. Besides cost considerations, CA cements are subject to conversion. Conversion is a series of complex hydraulic reactions that can weaken the concrete over time. Conversion is not an obvious cracking of the concrete (such as a shrinkage crack), but a change in the crystal structure at the molecular level.

Users of CA cements who anticipate heavy structural loading of the placement are urged to contact the manufacturers of the cements for recommendations on avoiding or managing conversion.

Because CA cements are manufactured products, information regarding costs, capacities, and production capabilities is generally considered proprietary.

Environmental and exposure concerns in the manufacture and use of CA cements are minimal, because they are not known to be hazardous, toxic or carcinogenic. Common-sense rules for handling dusty materials and powders should be observed. Users should