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Boron Nitride Powder A Review

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The chemical combination of boron and nitrogen does not occur in nature. This article discusses the properties, manufacture and applications for one of the key advanced ceramics in modern technology.

The chemical combination of boron and nitrogen must be synthesized from other natural or refined raw materials. The first synthesis was made in 1842 by W. H. Balmain using the action of molten boric acid on potassium cyanide. Unfortunately, the new compound was unstable and it was not until the mid 1950s and early 1960s that researchers were able to create more stable material in the form of powders and hot-pressed shapes. New processing technology has made boron nitride an economically affordable advanced material which is now used in various forms in a multitude of applications.

Boron and nitrogen are adjacent to carbon in the periodic table of elements. In combination B and N have many similarities to carbon. Both carbon (C) and boron nitride (BN) have hexagonal (graphitic) and cubic (diamond) crystal structures. Hexagonal boron nitride or (h)BN is a soft lubricious material while cubic boron nitride (c)BN (or CBN) is second only to diamond in hardness and is commonly used as an abrasive. The most notable differences between C and BN are color and electrical properties. Graphitic carbon is black and electrically conductive while (h)BN is white and electrically insulating. These properties and other unique performance characteristics are the reason why BN is valuable in many applications. The important material characteristics are listed in Table 1.



Figure 1
Typical (h)BN powder. Flat platey crystals about 10µm.

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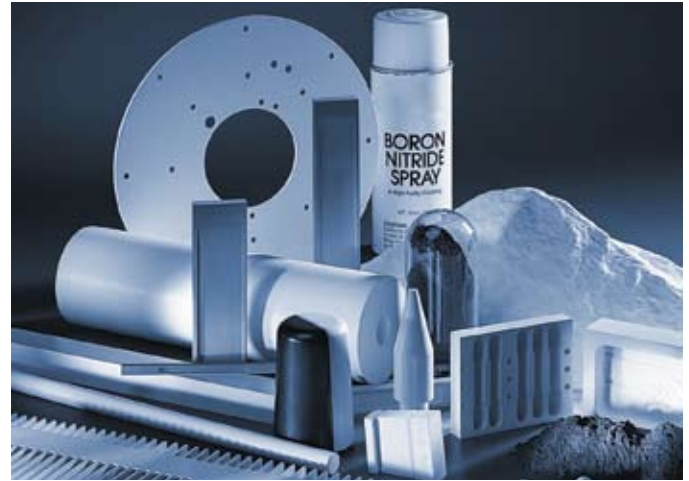


Figure 2
(h)BN comes as powder, hot-pressed shapes, and pyrolytic shapes.

Cubic Boron Nitride

Cubic boron nitride, (c)BN, is synthesized from (h)BN at high temperature and pressure. Powdered hexagonal boron nitride is heated to approximately 1500°C at a pressure in excess of 60 kilobars in the presence of a solvent/catalyst. This process changes the atomic structure from hexagonal to cubic—the same as that of diamond. The density of cubic boron nitride (3.49g/cc) is close to that of diamond. In fact, diamond is the only substance harder than CBN. Because diamond is harder, it is the super abrasive of choice for many applications, but CBN has several unique characteristics that have contributed to its use in a variety of industries. One important fact about cubic boron nitride is that, unlike diamond, it does not react with ferrous alloys. CBN is gaining rapid acceptance in the grinding and shaping of tool steel, high nickel and high cobalt super alloys, ferrous materials with a hardness greater than 50Rc and parts that require tight tolerances and fine surfaces.

There are several other advantages that cubic boron nitride has over competing materials. It is stable in air at temperatures up to 1400°C, while diamond starts to decompose at 800°C. It also shares the superior thermal conductivity characteristic of hexagonal boron nitride, thus conducting heat rapidly away from the workpiece. CBN is also chemically inert, exhibits extreme toughness (resistance to fracture) and can be produced in a variety of uniform grain sizes. In addition, properties such as thermal conductivity and toughness may be altered through process adjustments to fit specific applications.

Table 1

Comparison of hexagonal and cubic boron nitride.

(h)BN	(c)BN
Soft	Hard
Lubricating	Abrasive
Electrically insulating	Thermally conductive
Thermally conductive	Oxidation resistant
High temperature resistant Inert	Non-reactive with ferrous alloys

The initial cost of CBN is more than offset by its cost-effective performance. Momentive Performance Materials reported that the use of cubic boron nitride wheels reduced sharpening times for tool steel hobs by 80 percent when compared to the alumina wheels used previously.

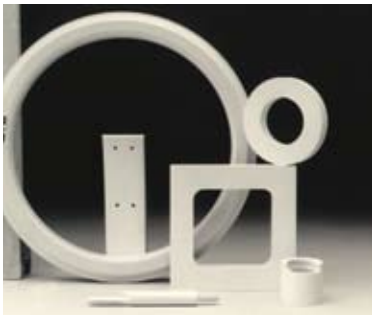


Figure 3
Hot-pressed (h)BN for use in a variety of applications.

Hexagonal Boron Nitride

Hexagonal boron nitride is available in a variety of forms:

- Powders
- Dispersion of powder in liquid for use as a coating
- Hot-pressed shapes
- Pyrolytic shapes (CVD-Chemically Vapor Deposited, that is, synthesized at high temperature in vacuum)

Powders

In its powdered form, hexagonal boron nitride is a naturally lubricious material and it is often called white graphite. Boron nitride is an electrical insulator and exhibits excellent resistance to oxidation, performs exceptionally well at high temperatures (up to 3000°C) and is resistant to corrosive attack.

Ceramics and Intermetallic Composites Are Incorporating Boron Nitride in Their Formulations to Enhance Performance Characteristics

(h)BN Powder as an Additive

The primary use of (h)BN is as an additive to a variety of other advanced materials. As an additive, boron nitride:

- Improves thermal shock resistance
- Improves machinability
- Reduces friction
- Improves release quality
- Enhances electrical properties
- Improves thermal conductivity

Applications for boron nitride powder are expanding rapidly. Its high temperature performance and lubricity make it an ideal additive to metal composite friction materials used in high-performance aircraft brakes. The increased speed and closer packaging of semiconductor devices created a need for effectively transferring thermal energy away from devices while also acting as an electrical insulator. This need is filled by elastomers and thermoplastics containing boron nitride.



Figure 5
A pyrolytic boron nitride and pyrolytic graphite ceramic resistance reacting element.

Ceramics and intermetallic composites are incorporating boron nitride in their formulations to enhance performance characteristics. A partial list includes:

SiC/BN	TiB ₂ /BN
Si ₃ N ₄ /BN	AlN/BN
ZrO ₂ /BN	Al ₂ O ₃ /BN

Boron nitride adds key performance characteristics to intermetallic composites such as TiB₂/BN for use in vacuum brazing operations. The addition of BN allows these composites to be chemically and thermally stable in vacuum and in the presence of corrosive metal vapors. It improves the machinability characteristics of the material and permits the conductivity and resistivity characteristics of the material to be adjusted.

Si₃N₄/BN

While certain grades of silicon nitride alone lack the thermal stress resistance necessary for use in critical turbine engine components, the addition of boron nitride creates a continuous-matrix dispersed-phase composite with markedly improved thermal stress resistance and greater flexural strength than Si₃N₄ alone.

Al₂O₃/BN

The combination of boron nitride and alumina results in a refractory material that, for many applications, is superior to both alumina and hot-pressed boron nitride. This composite combines the hardness, abrasion resistance and chemical stability of alumina with the inertness, thermal shock resistance and machinability of boron nitride.

Dispersions

BN powder may be dispersed in water-based or solvent-based systems to form a sprayable or paintable coating. These types of coatings can be used to impart the desirable features of (h)BN to a on almost any surface. These economical



Figure 4
Water-based coating used to protect graphite from oxidation.

products are used in molten metal and metal forming operations as a lubricant and release agent. They are also valuable processing materials for glass, plastic, rubber and ceramics.

Hot-Pressed BN

Hot-pressed BN is compacted at temperatures up to 2000°C and pressures up to 14MPa. B₂O₃ is introduced to help form a dense, strong engineering material that is remarkably easy to machine.

Several grades of hot-pressed boron nitride are available which differ in the type and amount of binder present. Standard grades, such as Momentive Performance Materials' grade HBN, have 2-5 per cent B₂O₃ which can hydrate when exposed to moisture or high humidity. This can result in limited thermal shock resistance. Other grades have a calcium addition which combines with the B₂O₃ to form a higher melting point glass binder which is less hygroscopic and gives improved performance at high temperatures (up to 1200°C). There is a high purity grade HBC from which the B₂O₃ binder has been removed. The process yields a diffusion bonded ceramic that actually increases in strength with increasing temperature. This grade HBC is commonly used at temperatures over 2000°C.

In addition to sharing the performance characteristics of powdered hexagonal boron nitride from which it is made—chemically inert, high thermal shock resistance, high electrical resistance, high thermal conductivity, excellent corrosion resistance, low loss tangent and low dielectric constant—HPBN adds some strengths of its own. It is not wetted by most molten metals including aluminum, antimony, bismuth, cadmium, copper, germanium, indium, iron, silicon, steel and tin. It does not react with halide salts and many other chemicals. Because HPBN is relatively soft, it is easily machined. This is unusual among ceramics used in electronics applications and reduces the need for precision surfaces to maximize contact area.

Applications for HPBN

The unique combination of thermal and electrical characteristics found in hot-pressed boron nitride, coupled with its machinability, have caught the attention of design

engineers in a variety of industries. A sampling of today's uses includes:

- As a boron source in p-type diffusion furnaces
- As a heat sink in transistor packages
- As a substrate
- As an interface and nozzle material for manufacture of amorphous alloys
- As a break ring in horizontal continuous casting of steel
- As a mold for casting carbon steel, low alloy steels and stainless steel
- As insulators and source holders for ion implant systems
- As insulators for vacuum furnaces
- As glass-forming tools and refractories
- As windows in aerospace re-entry vehicles
- As microwave windows for high frequency satellite applications
- As an ablative material for aerospace applications
- As plasma rings
- As electrical insulating spacers for tungsten resistance heaters
- As refractory wall liners and crucibles in a variety of hot metal applications

Pyrolytic BN-Anisotropic Performance

The final form of boron nitride that is having a major impact on modern technology is pyrolytic boron nitride (PBN). This material is even higher in purity and features many of the same performance advantages of powdered and hot-pressed BN plus a unique anisotropic orientation.

PBN is manufactured by reacting ammonia with a boron halogenide at temperatures of approximately 2000°C. The resulting BN vapor is deposited on graphite substrates or mandrels and can either be removed from the mandrel or left as a coating for the graphite. This production technique gives pyrolytic boron nitride a very high degree of crystal orientation with the hexagonal layer lattice always parallel to the surface of the substrate. This orientation approaches 1000:1 and gives PBN the highly anisotropic characteristics typical of single crystals. These characteristics are especially important when PBN is used as a crucible material. The thermal conductivity around the wall is about 40 times as

Table 2

Comparative properties of (h)BN grade HBR and some other ceramics used in electronics.

	Boron nitride(1)	Aluminum oxide	Beryllium oxide	Aluminum nitride
Hardness (KNOOP) Kg/mm ²	205	2000	1200	1200
Theoretical density g/cc	2.27	3.98	3.01	3.26
Dielectric strength KV/mm	35	9	10.5	14
Dielectric constant	4.2	9.7	6.7	10
Volume resistivity Ω-cm	1 x 10 ¹³	1 x 10 ¹⁴	1 x 10 ¹⁴	1 x 10 ¹¹
Loss tangent at 1MHz	0.0004	0.0003	0.0004	0.0005
Thermal conductivity at RT W/m/°K	55	33	251	117
Coefficient of thermal expansion n/in/°C x 10 ⁻⁶	1.2	7.1	8.1	4.1
(1) Grade HBR Hot-Pressed BN				

great as it is through the thickness. This results in exceptionally even heat distribution required by many leading-edge processes.

Other important performance characteristics of PBN include:

- High tensile strength that actually increases as it is heated
- High thermal shock resistance
- Thermal conductivity that increases in the thickness direction as temperature increases
- Thermal conductivity in the planar direction that does not change as temperature increases
- The highest dielectric strength of any available material
- Inert to almost all reagents at room temperature and to a large number of reagents, metals and compounds at temperatures in excess of 2000°C.

Pyrolytic boron nitride first appeared commercially as helix support rods in traveling wave tubes. The advantages inherent in its anisotropic characteristics were quickly recognized by electronics engineers and scientists. PBN was soon being used for aluminum evaporation crucibles, for molecular beam epitaxy crucibles and furnace hardware, and for coatings on graphite for epitaxy boats and susceptors. Because pyrolytic boron nitride is compatible with group III-V and II-VI elements and compounds, it is finding rapid acceptance in the form of boats and crucibles for their purification, compounding and single crystal growth.

PBN is being seen as a replacement for quartz crystals in the growth of gallium arsenide, indium phosphide and gallium phosphide. Although more expensive than quartz, crucibles of pyrolytic boron nitride offer several advantages that reduce the final production costs. Compound materials held in PBN crucibles are grown into high quality, single crystal ingots at 1300°C, a temperature at which quartz decomposes and introduces silicon into the melt. PBN crucibles also increase crystal yield and provide a useful service life 10 to 20 times longer than quartz.

For more information contact Momenive Performance Materials to discuss your boron nitride requirements.

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The Future for PBN

The properties of PBN coupled with its anisotropic nature make it suitable for use in many emerging technologies. One use is in a new type of heater which will find applications across a wide spectrum of industries. This concept uses PBN as an insulating substrate and pyrolytic graphite (PG) as a resistance heater. In combination, these two materials provide several advantages that cannot be found anywhere else:

- Operating temperatures up to 2000°C
- Thermal gradients custom tailored to the application
- Excellent performance in ultra-high vacuum
- Quick response because of low thermal mass
- High operating efficiency
- Exceptional corrosion resistance
- Elimination of the need for induction power supplies
- Wide range of resistance values
- Durability

Currently, PBN/PG heaters are being manufactured in both plate and tubular configurations.

Summary

While a wide variety of applications for boron nitride have been considered in this article, this unique material is only just beginning to realize its potential in the technology of today. High volume production techniques have made boron nitride readily available and new technologies have created demands for its unique performance characteristics. Boron nitride is filling an important role as one of the key advanced ceramics for modern technology.

