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REFRACTORY BORON COMPOUNDS

Borides have metallic characteristics such as high electrical conductivity and positive coefficients of electrical resistivity. Many of them, particularly the borides of metals of Groups 4 (IVB), 5 (VB), and 6 (VIB), the MB_6 compounds of Groups 2(II) and 13(III), and the borides of aluminum and silicon, have high melting points, great hardness, low coefficients of thermal expansion, and good chemical stability.

Borides are inert toward nonoxidizing acids; however, a few, such as Be_2B and MgB_2, react with aqueous acids to form boron hydrides. Most borides dissolve in oxidizing acids such as nitric or hot sulfuric acid and they are also readily attacked by hot alkaline salt melts or fused alkali peroxides, forming the more stable borates. In dry air, where a protective oxide film can be preserved, borides are relatively resistant to oxidation. For example, the borides of vanadium, niobium, tantalum, molybdenum, and tungsten do not oxidize appreciably in air up to temperatures of 1000–1200°C. Zirconium and titanium borides are fairly resistant up to 1400°C. Engineering and other properties of refractory metal borides have been summarized (1).

Table 1 lists many metal borides and their observed melting points. Most metals form more than one boride phase and borides often form a continuous series of solid solutions with one another at elevated temperatures; thus close composition control is necessary to achieve particular properties. The relatively small size of boron atoms facilitates diffusion.

The structures of borides range from the isolated boron atoms in the M_2B borides through single chains in MB borides, double chains (M_3B_4), two-dimensional hexagonal nets (MB_2), cross-linked nets (MB_4), and interconnected B_6 octahedra (MB_6), to cages of 24 boron atoms surrounding the central metal atom in the MB_{12} borides (3, 4). The three-dimensional frameworks of the boron-rich borides provide stable lattices through which the metal atoms may migrate at high temperatures, ca 1600°C; damaged surfaces may thereby be rejuvenated. These stable lattices also improve the chemical stability of such borides.

1. Preparation

The simplest method of preparation is a combination of the elements at a suitable temperature, usually in the range of 1100–2000°C. On a commercial scale, borides are prepared by the reduction of mixtures of metallic and boron oxides using aluminum, magnesium, carbon, boron, or boron carbide, followed by purification. Borides can also be synthesized by vapor-phase reaction or electrolysis.

To produce wear-resistant or hardened surfaces, thin layers of borides can be prepared on metal surfaces by reaction and diffusion (see Metal surface treatments). Boride powders can be formed into monolithic shapes by cold pressing and sintering, or by hot pressing.

1.1. Uses

In spite of unique properties, there are few commercial applications for monolithic shapes of borides. They are used for resistance-heated boats (with boron nitride), for aluminum evaporation, and for sliding electrical

Table 1. Metal Borides[a]

Molecular formula	Boride	CAS Registry Number	Mp[b], °C	Molecular formula	Boride	CAS Registry Number	Mp[b], °C
AlB_2	aluminum diboride	[12041-50-8]	975, d	NdB_6	neodiymium hexaboride	[12008-23-0]	2540
AlB_{12}	aluminum boride (1:12)	[12041-54-2]	2070	NiB	nickel boride	[12007-00-0]	1080
BaB_6	barium hexaboride	[12046-08-1]	2070	Ni_2B	dinickel boride	[12007-01-1]	1230
BeB_2	beryllium diboride	[12228-40-9]	>1970	Ni_2B_2	dinickel diboride	[12007-00-0]	1160
BeB_6	beryllium hexaboride	[12228-40-9]	2070	Ni_3B	trinickel boride	[12007-02-2]	1155
Be_2B	diberyllium boride	[12536-51-5]	1520	Pd_3B	tripalladium boride	[12429-53-7]	820, d
Be_5B	pentaberyllium boride	[12536-53-7]	1160	Pd_5B_2	pentapalladium diboride	[11130-91-9]	870, d
CaB_6	calcium hexaboride	[12007-99-7]	2235	ReB_2	rhenium diboride	[12355-99-6]	2400
CeB	cerium boride	[12045-00-0]		RuB	ruthenium boride	[12523-59-0]	1600
CeB_4	cerium tetraboride	[12007-52-2]	2380, d	RuB_2	ruthenium diboride	[12360-00-8]	1600, d
CeB_6	cerium hexaboride	[12008-02-5]	550	Ru_2B_3	dirutherium triboride	[12356-00-2]	1600
CoB	cobalt boride	[12006-77-8]	1460	ScB_2	scandium diboride	[12007-34-0]	2250
Co_2B	dicobalt boride	[12045-01-1]	1285	ScB_6	scandium hexaboride	[12785-49-8]	
Co_3B	tricobalt boride	[12006-78-9]	1125, d	SiB_4	silicon tetraboride	[12007-81-7]	1870, d
CrB	chromium boride	[12006-79-0]	2060	SiB_6	silicon hexaboride	[12008-30-9]	1980, d
CrB_2	chromium diboride	[12007-16-8]	2130	SmB_4	samarium tetraboride	[12007-82-8]	
Cr_2B	dichromium boride	[12006-80-3]	1875	SmB_6	samarium hexaboride	[12008-29-6]	2540
Cr_3B_2	trichromium diboride	[12045-40-8]	1960	SrB_6	strontium hexaboride	[12046-08-1]	2235
Cr_3B_4	trichromium tetraboride	[12045-71-5]	1920	TaB	tantalum boride	[12007-07-7]	2040
Cr_4B	tetrachromium boride	[12006-81-4]	1680	TaB_2	tantalum diboride	[12007-35-1]	3100
FeB	iron boride	[12006-84-7]	≈1550	Ta_2B	ditantalum boride	[12045-26-0]	1900
Fe_2B	diiron boride	[12006-86-9]	1390	Ta_3B_4	tritantalum tetraboride	[12045-92-0]	2650
				Ta_3B_2	tritantalum diboride	[12045-92-0]	2450
GdB_4	gadolinium tetraboride	[12007-54-4]		ThB_4	thorium tetraboride	[12007-83-9]	2500
GdB_6	gadolinium hexaboride	[12008-06-9]	2100	ThB_6	thorium hexaboride	[12229-63-9]	2195
HfB	hafnium boride	[12228-27-2]	2100, d	TiB	titanium boride	[12007-08-8]	2600
HfB_2	hafnium diboride	[12007-23-7]	3250	TiB_2	titanium diboride	[12045-63-5]	2900 ± 50
LaB_4	lanthanum tetraboride	[12007-73-7]	1800	Ti_2B	dititanium boride	[12305-68-9]	2200
LaB_6	lanthanum hexaboride	[12008-21-8]	2150	Ti_2B_5	dititanium pentaboride	[12447-59-5]	2670
MgB_2	magnesium diboride	[12007-25-9]	800, d	UB_2	uranium diboride	[12007-36-2]	2385
MgB_6	magnesium hexaboride	[12008-22-9]	1100, d	UB_4	uranium tetraboride	[12007-84-0]	2495
MgB_{12}	magnesium boride (1:12)	[12230-32-9]	1300, d	UB_6	uranium hexaboride		2235
MnB	manganese boride	[12045-15-7]	1890	VB	vanadium boride	[12045-27-1]	2250
MnB_2	manganese diboride	[12228-50-1]	1900	VB_2	vanadium diboride	[12007-77-3]	2450
MnB_4	manganese tetraboride	[12271-96-4]	2160	V_2B_3	divanadium triboride	[12313-74-5]	2300
Mn_2B	dimanganese boride	[12045-16-8]	1580	V_3B_2	trivanadium diboride	[12421-53-3]	2060
Mn_3B_4	trimanganese tetraboride	[12229-02-6]	1750, d	WB	tungsten boride	[12007-09-9]	2660
Mn_4B	tetramanganese boride	[12260-22-9]	1285, d	W_2B	ditungsten boride	[12007-10-2]	2670
MoB	molybdenum boride	[12006-98-3]	600	W_2B_5	ditungsten pentaboride	[12007-98-6]	2365
MoB_2	molybdenum diboride	[12007-27-1]	2300, d	YB_2	yttrium diboride	[12429-58-2]	2100
Mo_2B	dimolybdenum boride	[12006-99-4]	2280	YB_4	yttrium tetraboride	[12045-95-3]	2800
Mo_2B_2	dimolybdenum diboride	[12006-98-3]	2066	YB_6	yttrium hexaboride	[12008-32-1]	2600, d
Mo_2B_5	dimolybdenum pentaboride	[12007-97-5]	2100	YB_{12}	yttrium boride (1:12)	[12046-90-1]	2200, d
NbB	niobium boride	[12045-19-1]	2270	ZrB	zirconium boride	[12045-28-2]	2800
NbB_2	niobium diboride	[12007-29-3]	2900	ZrB_2	zirconium diboride	[12045-64-6]	3040
				ZrB_{12}	zirconium boride (1:12)	[12046-91-2]	2250, d

[a] Ref. 2.

[b] d = Decomposes.

contacts. There are a number of potential uses in the control and handling of molten metals and slags where corrosion and erosion resistance are important. Titanium diboride and zirconium diboride are potential cathodes for the aluminum Hall cells (see Aluminum and aluminum alloys). Lanthanum hexaboride and cerium hexaboride are particularly useful as cathodes in electronic devices because of their high thermal emissivities, low work functions, and resistance to poisoning.

2. Boron Carbide

Boron and carbon form one compound, boron carbide [12069-32-8], B_4C, although excess boron may dissolve in boron carbide, and a small amount of boron may dissolve in graphite (5). Usually excess carbon appears as graphite, except for the special case of boron diffused into diamonds at high pressures and temperatures, eg, 5 GPa (50 kbar) and 1500°C, where boron may occupy both interstitial and substitutional positions in the diamond lattice, a property utilized in synthetic diamonds (see Carbon, diamond, synthetic).

2.1. Properties

Boron carbide has a rhombohedral structure consisting of an array of nearly regular icosahedra, each having twelve boron atoms at the vertices and three carbon atoms in a linear chain outside the icosahedra (3, 4, 6, 7). Thus a descriptive chemical formula would be $B_{12}C_3$ [12075-36-4]. Each boron atom is bonded to five others in the icosahedron as well as either to a carbon atom or to a boron atom in an adjacent icosahedron. The structure is similar to that of rhombohedral boron (see Boron, elemental). The theoretical density for $B_{12}C_3$ is 2.52 g/mL. The rigid framework of relatively closely bonded atoms corresponds to a high melting point, about 2400°C, appreciable electrical conductivity, great hardness, about 27 GPa (270 kbar) on the Knoop scale (diamond indenters), and a high compressive strength. Brittleness limits its useful tensile strength to about 150 MPa (1.5 kbar) at 950°C; this, in combination with a moderate coefficient of thermal expansion, makes boron carbide sensitive to thermal shock. It is noticeably oxidized in air at 800–1000°C, and is a semiconductor having a room temperature resistivity of $0.001-0.1\ \Omega\cdot\mathrm{m}\cdot$

Boron carbide is resistant to most acids but is rapidly attacked by molten alkalies. It may be melted without decomposition in an atmosphere of carbon monoxide, but is slowly etched by hydrogen at 1200°C. It withstands metallic sodium fairly well at 500°C and steam at 300°C (8).

2.2. Preparation

Boron carbide is most commonly produced by the reduction of boric oxide with carbon in an electric furnace between 1400 and 2300°C. In the presence of carbon, magnesium reduces boric oxide to boron carbide at 1400–1800°C. The reaction is best carried out in a hydrogen atmosphere in a carbon tube furnace. By-product magnesium compounds are removed by acid treatment.

In general, the purified boron carbide is ultimately obtained as a granular solid that subsequently may be molded or bonded into useful shapes. To achieve high density and strength, it is hot pressed at 1800–2400°C in graphite molds.

2.3. Uses

Applications for boron carbide relate either to its hardness or its high neutron absorptivity (^{10}B isotope). Hot-pressed boron carbide finds use as wear parts, sandblast nozzles, seals, and ceramic armor plates; but in spite of its hardness, it finds little use as an abrasive. However, this property makes it particularly useful for dressing grinding wheels.

Boron carbide is used in the shielding and control of nuclear reactors (qv) because of its neutron absorptivity, chemical inertness, and radiation stability. For this application it may be molded, bonded, or the granular material may be packed by vibration.

3. Boron Nitride

Boron and nitrogen form one compound, boron nitride [10043-11-5], BN, which may exist in a hexagonal, graphitelike form, hBN, having a layered structure and planar 6-membered rings of alternating boron and nitrogen atoms (3, 9). On alternate sheets boron atoms are directly over nitrogen atoms. A rhombohedral form, rBN, is similar in density and structure, but the layers of sheets are stacked in groups of three instead of two as in hBN (10). A denser cubic form having a zinc-blende lattice (cBN) also exists in addition to an equally dense form having a wurtzite lattice (wBN). The latter two forms are, like diamond, thermodynamically stable only at high pressures but persist at normal pressures and temperatures because of the slowness of the transition.

3.1. Properties

Under nitrogen pressure hexagonal boron nitride melts at about 3000°C but sublimes at about 2500°C at atmospheric pressure. Despite the high melting point, the substance is mechanically weak because of the relatively easy sliding of the sheets of rings past one another (3). The theoretical density is 2.27 g/mL and the resistivity is about $10^5\ \Omega\cdot\text{cm}\cdot$

Hexagonal boron nitride is relatively stable in oxygen or chlorine up to 700°C, probably because of a protective surface layer of boric oxide. It is attacked by steam at 900°C, and rapidly by hot alkali or fused alkali carbonates. It is attacked slowly by many acids as well as alcohols (to form borate esters), acetone, and carbon tetrachloride. It is not wetted by most molten metals or many molten glasses.

The cubic and wurtzitic forms have similar chemical properties (11), but their reaction rates tend to be slower because of the denser structure. The dense forms expand to the graphite forms above ca 1700°C.

The cubic form resembles diamond in its crystal structure and is almost as hard. The theoretical density is 3.48 g/mL. It is colorless and a good electrical insulator when pure; traces of impurities add color and make it semiconducting, eg, a few ppm of Be make it blue and p-type whereas small amounts of S, Si, or CN favor yellow, n-type crystals. It is possible to make p–n junctions by growing n-type material on p-type seed crystals (12). If this is done carefully in an alkaline-earth nitride bath using a temperature difference technique, as with large diamond crystals (see Diamond, synthetic), the resulting diodes are several mm in size and emit blue light when forward-biased (13, 14).

3.2. Preparation

Hexagonal boron nitride can be prepared by heating boric oxide with ammonia, or by heating boric oxide, boric acid, or its salts with ammonium chloride, alkali cyanides, or calcium cyanamide at atmospheric pressure. Elemental nitrogen does not react with boric oxide even in the presence of carbon, though it does react with elemental boron at high temperatures. Boron nitride obtained from the reaction of boron trichloride or boron trifluoride with ammonia is easily purified.

Rhombohedral boron nitride can be prepared by heating a mixture of $NaBH_4$ and NH_4Cl rapidly to 750–1000°C (15). The presence of NaCl appears to favor the rhombohedral form.

The cubic zinc blende form of boron nitride is usually prepared from the hexagonal or rhombohedral form at high (4–6 GPa (40–60 kbar)) pressures and temperatures (1400–1700°C). The reaction is accelerated by lithium or alkaline-earth nitrides or amides, which are the best catalysts, and form intermediate liquid compounds with BN, which are molten under synthesis conditions (11, 16). Many other substances can aid the transformation. At higher pressures (6–13 GPa) the cubic or wurtzitic forms are obtained without catalysts (17).

The wurtzite form differs only slightly from the cubic form, but it is not quite as stable. It is most easily obtained by static or dynamic compression of hBN or rBN at high pressures (17). In the presence of a liquid catalyst at high pressures, the wurtzite form changes rapidly to the cubic form. The change occurs more slowly without a catalyst above 6 GPa (60 kbar) (18).

Many attempts have been made to synthesize cubic BN at low pressures by some sort of chemical vapor deposition process in analogy with the low pressure deposition of diamond from methane in the presence of H atoms (see Diamond, synthetic). However, the amounts of cubic BN produced in this fashion in 1991 were miniscule, and were at best thin layers only a few dozen atoms thick (12).

3.3. Uses

Hot-pressed hBN is useful for high temperature electric or thermal insulation, vessels, etc, especially in inert or reducing atmospheres, and for special materials such as III-V semiconductors (qv). Its low thermal expansion makes it resistant to thermal shock. The powder can be used as a mold release agent or as thermal insulation. Boron nitride is also available in fiber form (19). BN deposited pyrolytically on refractory substrates at 1200–1800°C has a turbostratic structure and low porosity; it has greater chemical resistance and is impervious to helium.

The greatest use of cubic boron nitride is as an abrasive under the name Borazon, in the form of small crystals, 1–500 μm in size. Usually these crystals are incorporated in abrasive wheels and used to grind hard ferrous and nickel-based alloys, ranging from high speed steel tools and chilled cast-iron to gas turbine parts. The extreme hardness of the crystals and their resistance to attack by air and hot metal make the wheels very durable, and close tolerances can be maintained on the workpieces.

The cubic BN crystals may also be bonded into strong bodies that make excellent cutting tools for hard iron and nickel-based alloys. Such tools produce red-hot chips and permit the wider use of tough, high temperature alloys which would otherwise be prohibitively difficult to shape (12, 20, 21) (see Abrasives).

4. Economic Aspects

In 1990 the sales value of most borides was less than a million dollars per year, with the most important being the rare-earth hexaborides, used for electronic cathodes.The sales value of boron carbide is also small compared with other hard materials and abrasives. The sales of the soft forms of boron nitride, at prices in the range $15–100/kg, run to a few million dollars per year in the United States. The Norton Co. and Carborundum Co. are significant producers of hBN and boron carbide. The sales of the cubic form of boron nitride amount to over several dozen million dollars per year, worldwide, on account of its great popularity as an industrial abrasive in many industries and its high value ($15,000/kg). A large machine-tool industry based on this abrasive has sprung up. The General Electric Co. is the principal producer in the United States, but production in Japan and Russia is comparable.

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