

Boron Ferroalloys

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Chapter Outline

17.1 Properties of Boron and Its Compounds	449	17.3.1 Boron Alloys Types	453
17.2 Boron Sources and Its Reduction	452	17.3.2 Ferroboron Technology	453
17.3 Technology of Boron Alloys	453	17.3.3 Technology of Other Boron Alloys	456
		References	457

17.1 PROPERTIES OF BORON AND ITS COMPOUNDS

Boron is the lightest nonmetallic element on the periodic table after hydrogen and helium. Its serial number is 5, its atomic weight is 10.811, its melting point is 2074°C, and its boiling point is ~3658°C. This makes boron at the same time one of the most refractory elements, compatible with carbon. Boron belongs to group III of the period table (its outer electronic shell configuration is $2s^2 2p^1$), normally appearing in the oxidation state +3. Several allotropic modifications of boron are known, of which α -B and β -B (the most stable) are rhombohedral, γ -B is orthorhombic, and T-phase is tetragonal. The last two modifications are formed at high pressures and temperatures but remain stable after release into ambient conditions.

Natural boron consists of two stable isotopes of ^{10}B (19.57%) and ^{11}B (80.43%). The cross section of the thermal neutron capture for ^{10}B is very high ($3 \cdot 10^{-25} \text{ m}^2$) in comparison with ^{11}B ($4 \cdot 10^{-32} \text{ m}^2$).

Boron is a typical microalloying element—even small additions in steel have a great influence on the mechanical properties (Davis, 2001). This in many cases saves expensive and scarce alloying elements as well as mineral and energy resources. Boron is added to steels for its unique ability to increase hardenability when present in concentrations of around 0.001% to 0.004%, so very small amounts of boron in combination with carbon and manganese might be an effective substitute for more traditional alloying elements. In stainless steels,

boron is used to improve their creep properties or for the nuclear industry, where enhanced neutron absorption is required (a very high neutron capturing cross section has already been achieved for steels $<1\%$ B). It is also used for high-strength low-alloy (HSLA) and other structural steels. Ferroboron may be added also to avoid the interstitial nitrogen effect and to improve the steel's formability. It is normally added in preliminarily deoxidized (by aluminum) steel, which provides a high uptake of boron (70%) with its stable content (0.002% to 0.0025% B).

With iron, boron forms thermodynamically stable borides Fe_2B , FeB , and FeB_2 (Fig. 17.1). Dissolution of boron in liquid iron is highly exothermic.

In the system B-C, the stable carbide is B_4C , which has a wide concentration homogeneity range and a high melting point $\sim 2450^\circ\text{C}$ (Fig. 17.2).

Boron and silicon form stable boron silicides SiB_3 , SiB_6 , and SiB_{14} . Silicide SiB_6 melts incongruently at 1850°C (Fig. 17.3).

Boron also forms stable borides with many metals. In the system B-Al, known borides are AlB_2 , AlB_{10} , and AlB_{12} . Aluminide AlB_2 melts incongruently at $\sim 960^\circ\text{C}$, and AlB_{12} melts congruently at $\sim 2150^\circ\text{C}$. Compound AlB_{10} exists in a narrow temperature range of 1660° to 1850°C (Fig. 17.4).

With oxygen, boron produces a number of oxides with different boron/oxygen ratios: B_7O , B_6O , B_2O , B_4O_3 , BO_2 , B_4O_5 , and B_2O_3 , the last one being the most stable. The melting point of B_2O_3 is 450°C , and it is well known to form glassy phases upon cooling, which is used for the production of borosilicate glasses. Boron oxide reacts with water, generating weak boric acid H_3BO_3 .

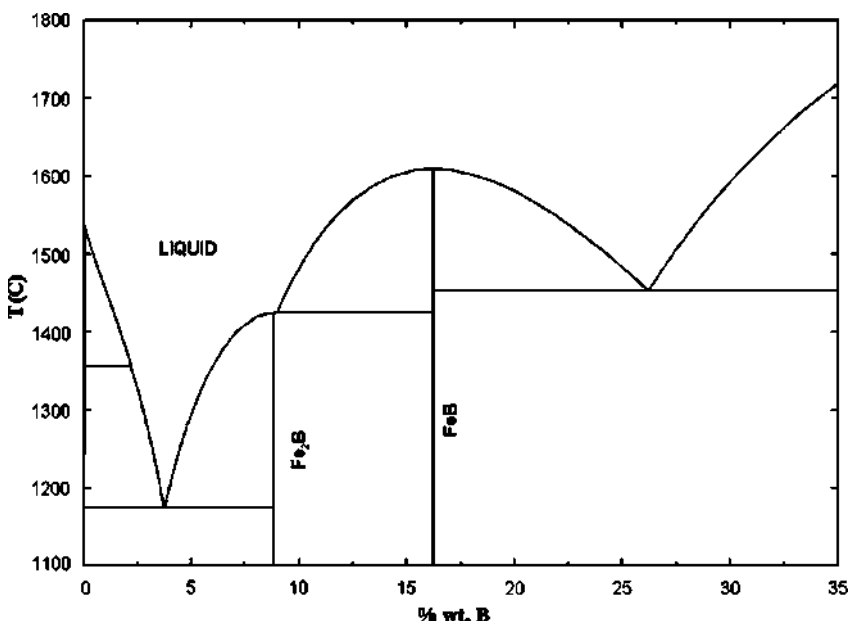


FIGURE 17.1 Equilibrium diagram of the system Fe-B (FeB_2 compound not shown).

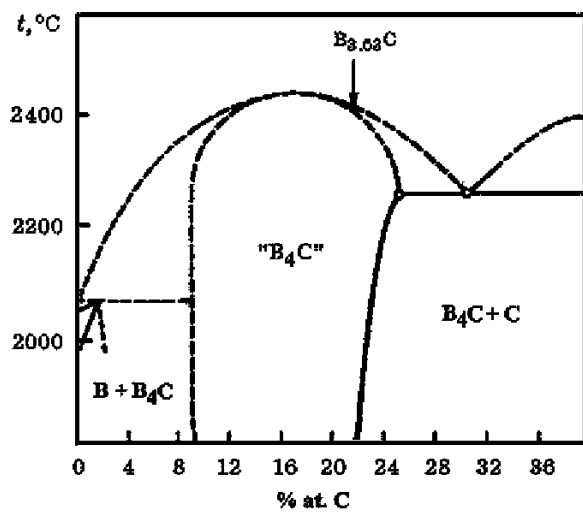


FIGURE 17.2 Diagram of the equilibrium state of the system B-C.

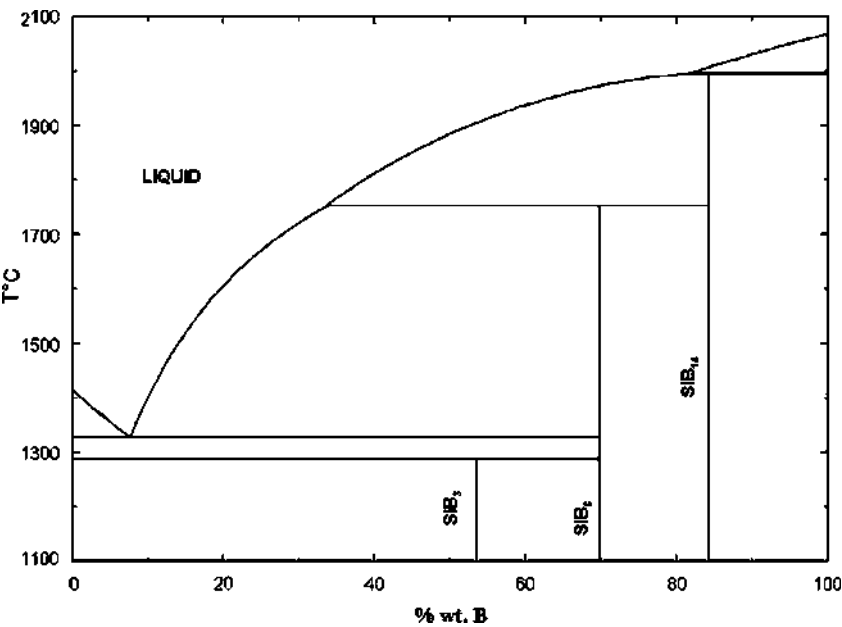


FIGURE 17.3 Diagram of the equilibrium state of the system B-Si.

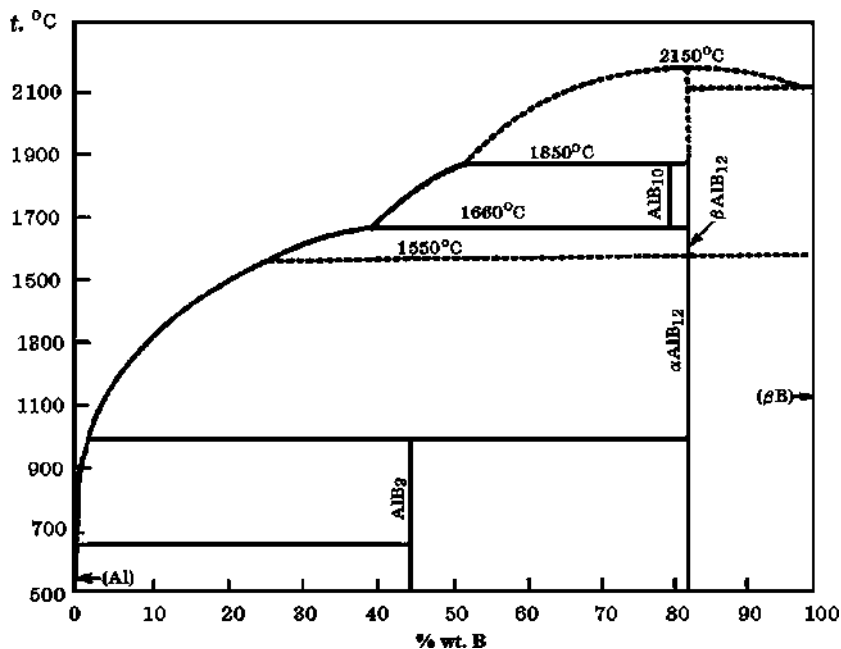


FIGURE 17.4 Diagram of the equilibrium state of the system B-Al.

17.2 BORON SOURCES AND ITS REDUCTION

The main minerals of boron are boracite $(\text{Mg,Fe,Mn})_3[\text{ClB}_2\text{O}_3]$, ascharite $\text{Mg}_2[\text{B}_2\text{O}_5] \cdot \text{H}_2\text{O}$, colemanite $\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3]$, kernite $\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2] \cdot 3\text{H}_2\text{O}$, ulexite $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$, and probably the most well-known, borax $\text{Na}_2[\text{B}_4\text{O}_7(\text{OH})_4] \cdot 8\text{H}_2\text{O}$. More than a hundred minerals with boron are known, but not all have commercial potential (Garrett, 1998). As an example, borate ore has the following composition (Gasik et al., 2009), % wt.: 8 to 8.5 B_2O_3 , <13 SiO_2 , 15 to 25 CaO , 10 to 30 MgO , 2 to 5 FeO , 2 to 6 Na_2O , 2 to 3 C , 5 to 10 S , and ≤ 0.01 P . From such ores several grades of concentrates are recovered (Table 17.1).

These concentrates are suitable for the smelting of some of boron ferroalloys such as ferroboral (FeBAl) and ferrosilicoboral (FeSiBAl). For more boron-rich master alloys, technical quality grade boron anhydrite or more pure raw materials are used (Gasik et al., 2009).

Boron might be reduced from its oxide form by carbon, silicon or aluminum. In the case of carbon reduction, the formation of boron carbide (B_4C) is preferred thermodynamically, so in the presence of iron this FeB alloy has <10% to 20% B and <2% to 4% C.

Silicon reduction is not thermodynamically favorable and not used in practice, as the maximum boron content in the alloy does not exceed 4% B.

TABLE 17.1 Chemical Composition, max. % wt., of Boron Concentrates

Concentrate Type	B ₂ O ₃	CaO	MgO	SiO ₂	Fe ₂ O ₃	Na ₂ O	H ₂ O
Boric anhydrite (B ₂ O ₃)	>95	—	—	—	0.0065	—	3–5
Calcium diborate (CaO·B ₂ O ₃ ·2H ₂ O)	>38	35.6	1	2	0.04	0.1	22
Boric acid (H ₃ BO ₃)	>99.5	—	—	0.8	0.0065	—	—
Sodium octaborate (Na ₂ B ₈ O ₁₃)	>74	—	—	1	—	23	—

Thus, aluminum is the only choice for the processing of boron ferroalloys and master alloys where carbon content should be minimized.

17.3 TECHNOLOGY OF BORON ALLOYS

17.3.1 Boron Alloys Types

The composition of commercial boron alloys is shown in [Table 17.2](#) (Gasik et al., 2009). Ferroboron is the most common addition agent in steelmaking. However, as ferroboron does not have protective elements (with a higher affinity to oxygen and nitrogen than boron), it might only be added to deoxidized steel.

Boron master alloys (see [Table 17.2](#)) are more efficient in terms of application and results stability, but with the drawback of higher costs.

17.3.2 Ferroboron Technology

Ferroboron is processed in electric furnaces by reduction of either aluminum or carbon. For the aluminum reduction process, the main part of the charge is composed of borate ore (see [Table 17.1](#)) and secondary aluminum chips. Iron-termite mix (exothermic mixture) has secondary iron oxides and aluminum chips, and the ignition mix consists of all three components (calcined borate ore, iron oxides, and aluminum) ([Table 17.3](#)). Ignition mix for the initiation of the process is about 6% to 7% of the total charge, whereas the iron-rich mixture is 20% to 27% of the total charge depending on the ferroboron grade required.

The furnace with a power of ~1 MVA is lined with magnesite bricks and the hearth is movable (installed on the truck), which means it can roll in and out under the electrodes. The melting process can be divided into three periods: the formation of a melt, oxides reduction, and processing of the slag with iron-rich

TABLE 17.2 Chemical Composition, % wt. of Ferroboron and Special Boron Master Alloys (maximal allowable, except for boron)*

Grade	B	Si	Al	C	S	P	Cu	Other
Ferroboron								
FeB20	20	2	3	0.05	0.01	0.015	0.05	
FeB17	17	3–4	5	0.2	0.02	0.03	0.1	
FeB17A	17	4	0.5	4				
FeB10	10	5–15	8–12					
FeB6	6	5–12	6–12					
Master Alloys								
Ferroboral (FeBAI)	6	10	10					
Ferrosilicoboral (FeSiBAI)	10	15	15					
Nickelboron (NiB)	11	2	9	0.1	0.01			Ni
Chromeboron (CrB)	8	2	2	0.1	0.01			Cr
Ferrochromeboron (FeCrB)	15	3	5	0.4	0.02			Cr
Greyenal	1	6	15	0.2	0.06	0.06		Ti 10, Zr 1.5

*The balance elements are Fe, Ni, or Fe + Cr depending on the alloy type. Empty cells: content not specially regulated.

TABLE 17.3 Composition of the Charge for Ferroboron Smelting with Aluminum Reduction (% wt.)

Component of the Charge	Ignition	Main	Iron-Rich Precipitant
Borate ore	11.6	81.9	13.3
Iron oxide	58.1	—	64
Aluminum powder	18.6	18.1	22.7
Iron chips	11.6	—	—

TABLE 17.4 Material Balance of FeB Smelting with Reduction of Boric Anhydride by Aluminum

Input Stream	kg	Output Stream	kg
Boric anhydride (93% B_2O_3)	1200	FeB (21.8% B)	1095
Iron ore (90% Fe_2O_3)	1400	Tapped slag (9.4% B_2O_3)	1200
Aluminum (99.2% Al)	1167	Furnace slag (10.6% B_2O_3)	1858
Lime (88% CaO)	340	Bottom slag (12.7% B_2O_3)	167
Magnesite bricks use	265	Dust in gas ducts (28% B_2O_3)	30
Total	4372	Total	4350

precipitant. The ignition mix is loaded first and heated with an electric arc. Upon reaction and melting of the ignition mix, half of the main charge is loaded and melted; after that half of the iron-rich precipitant is added and the furnace is switched off until the slag is tapped out. Then the second half of the main charge is added with the second part of the precipitant mixture (Gasik et al., 2009). The temperature of the melt is supported at about 1750° to 1780°C . After the smelting has been completed, the rest of the slag is tapped but the metal is left in the hearth to cool down. Tapped slag has (% wt.) 6 to 10 B_2O_3 , <2 SiO_2 , 10 to 14 CaO, 3 to 7 MgO, 2 to 4 FeO, and 65 to 73 Al_2O_3 . The boron extraction yield in this process is 60% to 65%. The material and heat balances of ferroboron smelting by aluminum reduction are shown in Tables 17.4 and 17.5, respectively.

TABLE 17.5 Heat and Energy Balance of FeB Smelting

Energy Input	%	Energy Output	%
Chemical exothermic reactions	60	Slag latent heat	49.2
Electric energy	21.3	FeB latent heat	16.7
Metal and slag formation reactions	9.7	Anhydride dehydration	0.5
		Furnace accumulated heat	24.2
		Heat radiative losses	8.4
Total	100	Total	100

It is also possible to smelt FeB with both slag and alloy tapping, which enables better utilization of latent and accumulated heat and reduces the consumption of refractories.

Reduction by carbon might be used when there are no high restrictions to carbon content in ferroboron (Gasik et al., 1995). With this method, 10% to 20% B and 4% to 6% C alloy could be produced. The technology is based on the use of recycled, secondary, and lower-grade boron materials such as captured B_2O_3 dust, recycled boron carbide, iron mill scale (Fe_3O_4), and petroleum coke as reductant. Here carbon from petrocok and carbon from B_4C reduce iron and form iron borides in parallel with carbon reduction of B_2O_3 . A lower temperature of reduction is ensured by the exothermic effect of iron borides formation.

17.3.3 Technology of Other Boron Alloys

Among the master alloys (see Table 17.2), ferroboral (FeBAI) is produced in a manner similar to that used to produce ferroboron utilizing aluminum reduction. The process attains better performance if fused borate ore is used instead of raw B_2O_3 sources, also achieving a complete breakdown of sulfates and carbonates.

Nickelboron (NiB) contains 11% to 18% B, but the base metal is nickel, not iron. NiB alloy could be made either in a smelting hearth or in an electric furnace. In the first case, the charge for NiB smelting is shown in Table 17.6. The main difference from FeB technology is that the precipitant in this case is based on NiO and aluminum.

Nickelboron is smelted in a hearth with MgO lining, starting from a partial melting of boric acid and aluminum under the electrodes. Upon melting of the ore part of the charge, and after 5 to 10 min of soaking, the reduction part of the charge is loaded. The duration of the melting of ore charge and the reducing part of the charge at 600 kW power is 45 to 60 min. After that, the precipitant

TABLE 17.6 Composition of the Charge for Nickelboron Smelting with Aluminum Reduction (% wt.)

Component of the Charge	Reduction Charge	Main Charge	Precipitant
Calcined borate ore (<3% SiO_2)	8.8	83.6	—
Boric acid (52%–55% B_2O_3)	44.7	—	—
Nickel oxide (NiO)	28.2	—	74.1
Aluminum powder	18.3	16.4	18.5
Lime	—	—	7.4

part is loaded; the furnace is kept on for the next 20 min and then switched off. The alloy is extracted from the furnace after about 20 h.

Chromium–boron (CrB) alloys are processed with the same technology, where NiO is replaced by chromium oxide. The boron extraction yield is ~70%, and the chromium yield is ~86% (Gasik et al., 2009).

In special steels and alloy, boron is often added in other master alloys such as the “greynal” type (see Table 17.2). For the smelting process, the metal part of the charge is composed of FeAl, FeSi, and titanium scrap. The exothermic part of the charge is composed of iron ore, lime, and aluminum powder, of which about half goes toward reduction and the other half is used for greynal alloying.

Smelting of greynal is carried out in a melting hearth lined with MgO bricks. The metal part of the charge is preheated to 400°C and loaded on the hearth. Then the whole exothermic mixture is loaded and the charge is ignited from the top. The rate reaction propagation through the charge is very high—it takes only 4 minutes to produce 1 ton of the alloy. The resulting liquid melt settles down on the hearth, where it reacts and dissolves the metal part of the charge. Limiting the thickness of greynal ingot to <100 mm is recommended in order to avoid elements liquation.

The production of 1 t of greynal requires about 440 kg FeB (calculated as for 5% B), 150 kg FeSiZr (with ~40% Zr), 150 kg of titanium scrap, 630 kg of aluminum powder, 1000 kg iron ore, and 150 kg of lime. The yield of boron in this process is ~88%, titanium ~99.5%, zirconium 100%, and aluminum 92%. Such high yield numbers are due to a minimal reduction of these elements, as most are added to the charge in the form of already reduced ferroalloys.

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