

The Optimization of Parameters for the Carbothermic Production of Ferroboron

O. YÜCEL, O. ADDEMİR, and A. TEKİN

Technical University of Istanbul, Maslak-Istanbul, Turkey

Ferroboron containing 10 to 20 per cent boron (by mass) is used as a master alloy in the production of Metglass 2605 S-2 type transformer sheets and other boron-containing magnetic materials. The core losses of transformers produced from these sheets are approximately one-third those for the conventional ordinary grain-oriented silicon sheet.

In the work described, a mixture of boric acid, iron oxide, charcoal, and wood-chips was smelted in a submerged-arc d.c. electric furnace at a power rate of 100 kVA in the production of ferroboron. The furnace was lined with alumina and graphite. The temperature profiles, power consumption, and electrode spacing were controlled by a computer, which was also used for the acquisition of data.

At a fixed $\text{H}_3\text{BO}_3/\text{Fe}_2\text{O}_3$ ratio, charcoal additions were used as a parameter in an investigation of boron recovery in the alloy. It was found that, for H_3BO_3 -to- Fe_2O_3 ratios of 0,44 to 1,12, boron recoveries of 70 to 80 per cent can be achieved. The boron concentration in the alloy was found to be 17 per cent, and the energy consumption was 44,15 kWh per kilogram of boron.

Introduction

Ferroboron is a master alloy used in the manufacture of metallic glass and magnetic materials, and in the alloying of steel. For decades, ferroboron has been utilized to increase the mechanical properties of steels. Recently, owing to improvements in the magnetic properties of transformer sheets, ferroboron has become important to the electrical sector. The replacement of conventional silicon steels by ferroboron has resulted in a reduction of one-third in the core losses of transformers, making a big impact on energy conservation¹⁻⁴.

Since elemental boron is an expensive chemical, boron is usually introduced into alloys in the form of cheaper compounds such as H_3BO_3 , B_2O_3 , etc.⁵.

There are two main processes for the production of ferroboron: aluminothermic and carbothermic methods.

In conventional aluminothermic processing during the reduction of a mixture of boron oxide and iron oxide with aluminium, 1 to 6 per cent aluminium is left in the alloy^{6,7}. The presence of aluminium prevents the use of this product in the production of metallic glass.

The carbothermic method of ferroboron production yields a better product, which satisfies the impurity limits set by the metallic-glass industry. There are six different carbothermic processes listed in the literature.

Allied Corporation's process includes preheating and pre-reduction in an arc furnace. The reagents used are boric acid, iron (or iron oxide), coal, and sugar, all of which are introduced at set ratios in a continuous operation. It is reported⁸ that the product contains 13,6 to 15,4 per cent boron and 0,3 per cent carbon, with a boron yield in the alloy of 68 to 86 per cent.

In a study⁹ conducted by Mitsui Mining & Smelting Co., an alloy containing 10,5 per cent boron was produced, with a boron yield of 76 to 82 per cent and an energy consumption of 44 kWh per kilogram of boron.

Seki and Hiromoto¹⁰ introduced 90 per cent of the stoichiometric carbon and produced an alloy containing 16,5 to 21,4 per cent boron. However, there was difficulty in the production of ferroboron in that an unsmelted deposit formed under the electrode.

Hamada^{3,11} and his co-workers carried out their ferroboron studies in a vertical-shaft furnace. Boron oxide and boric acid were reduced in the presence of carbon, the aim being the direct utilization of the alloy in the production of metallic glass. The product obtained contained 3 per cent boron, 3 per cent silicon, and 3 per cent carbon. To avoid decarburization, an alloy containing 10 per cent boron, 11 to 13 per cent silicon, and 0,3 per cent carbon was produced. This alloy was introduced into liquid steel for the production of metallic glass.

Hahn and his co-workers^{9,12} developed another method of carbothermic reduction in an electric submerged-arc furnace. In that study, a mixture of wood chips, charcoal, boric acid, and iron oxide was reduced to produce an alloy containing 18 to 20 per cent boron and 0,02 per cent carbon. The process had a boron conversion rate of 95 per cent and an energy consumption of 35,5 kWh per kilogram of boron.

In that study, ferroboron alloy was produced from boric acid, hematite, charcoal, and wood chips. The mixture was smelted in a 100 kVA monophasic arc furnace. The process was optimized, with the charge composition, applied voltage and current, energy and electrode consumption, and physical conditions of the furnace as parameters.

Theory

The reduction of Fe_2O_3 and B_2O_3 in the presence of carbon is shown in Figure 1. It is obvious from the diagram that the reduction sequence with solid carbon includes Fe_2O_3 , Fe_3O_4 , FeO , B_2O_3 (g), and B_2O_3 (l). Iron is reduced prior to boron, and the reduction of gaseous boron starts at 1650 K. The liquid-phase reduction starts at 1900 K. Under these conditions, PB_2O_3 was at a pressure of 10 mm Hg. For this reason, it can be concluded that the reduction of boric oxide with solid carbon takes place preferentially in the gaseous phase. As shown in Figure 2, the affinity of boron for iron is higher than its affinity for carbon. Consequently, at a high iron concentration, the possibility of the formation of ferroboron is higher than the possible formation of boron carbide.

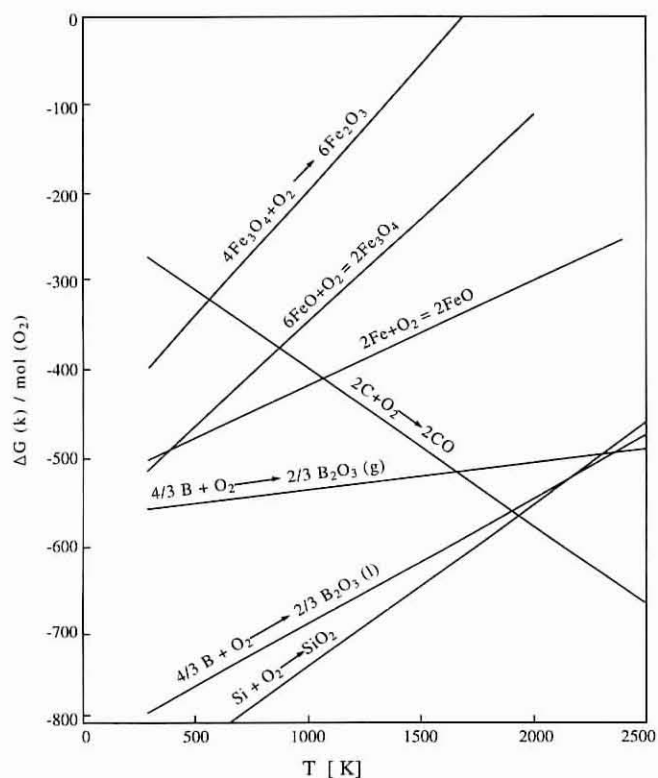


FIGURE 1. Change in the free energy of reactions¹³

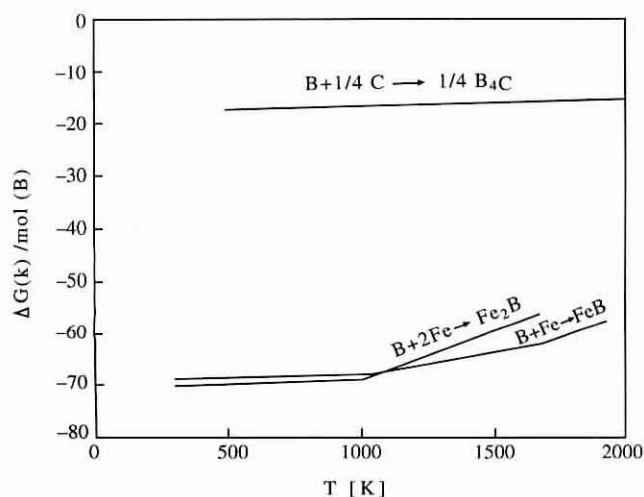


FIGURE 2. Change in free energy of reactions¹³ for boron carbide and ferroboron

Experimental

Raw materials

The boron, carbon, and silicon contents of the raw materials used in the present study are shown in Table I. The boric acid used was 99,5 per cent pure and contained Fe, Si, Mg, Ca, and Na as impurities. The hematite was pigment-grade, which contained Si, Co, Ni, Cu, and Mn as impurities. The particle sizes of the charcoal and wood chips were 1 to 3 mm and 5 to 15 mm respectively.

TABLE I
ANALYSES OF RAW MATERIALS IN WT %

Material	B	Fe	SiO ₂	C	Ash	Volatile matter	Moisture
Boric acid	17,1	0,1	0,1	—	—	—	—
Iron oxide	—	68,7	1,4	—	—	—	—
Charcoal	—	—	*	63,7	3,6	32,7	†
Woodchips	—	—	—	7,2	0,1	81,7	11,0

* The ash contains 43,0% SiO₂

† On a dry basis

Experimental Apparatus

The laboratory-type monophasic resistant arc furnace has a 40 kg charge capacity (Figure 3). The smelting process was conducted with a d.c. power supply of 100 kVA. The temperature profile was monitored by the use of four thermocouples located in the furnace lining. The inner surface of the furnace was lined with graphite and, to provide the necessary heat insulation, refractory bricks were used as a backing for the graphite. The voltage and current readings were fed to a computer-control system for the acquisition of data that were used in the control of the position of the upper electrode (Figure 4).

Experimental Procedure

The charcoal and wood chips in the selected ratios of H_3BO_3 and Fe_2O_3 were mixed in a rotary mixer for 2 hours, and 100 kg of the mixture was fed to the open heated arc. After 1 to 2 hours from the start of the experimental run, the

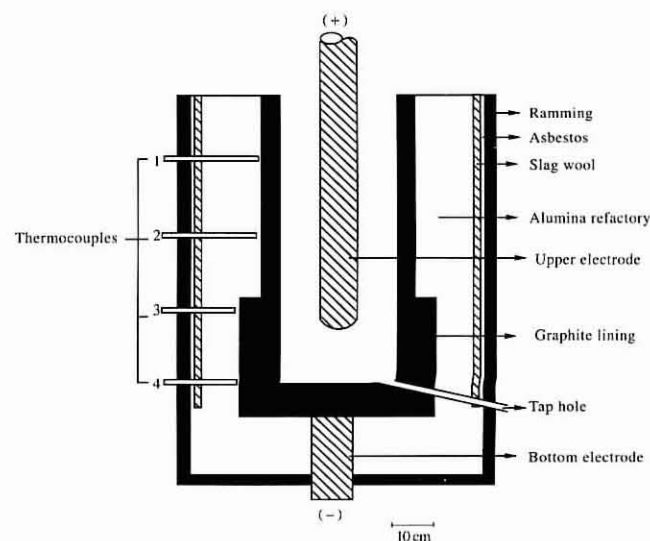


FIGURE 3. Cross-section of the 100 kVA d.c. electric-arc furnace

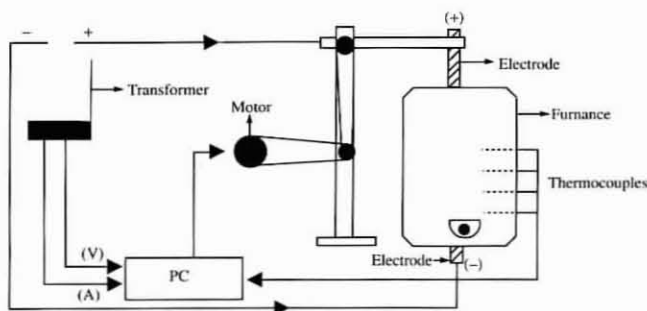


FIGURE 4. Schematic view of the experimental set-up

liquid metal was removed from the tap-hole at the bottom and the arc was stopped. The furnace was left to cool for inspection. In the experimental evaluation, the metal and boron that remained in the unmelted deposit were taken into consideration. The energy consumption was also evaluated accordingly. The changes in the electrodes such as consumption, erosion, shape, and dimension were carefully inspected and quantified.

Results and Discussion

Effect of Charcoal Addition

Two H_3BO_3 -to- Fe_2O_3 ratios were used: 0,44 and 1,12. These ratios changed the content of carbon in the furnace. Generally, the addition of the increased amount of charcoal increased the concentration of boron and silicon in the alloy. The effect of charcoal addition on the concentrations of boron and silicon are shown in Figure 5.

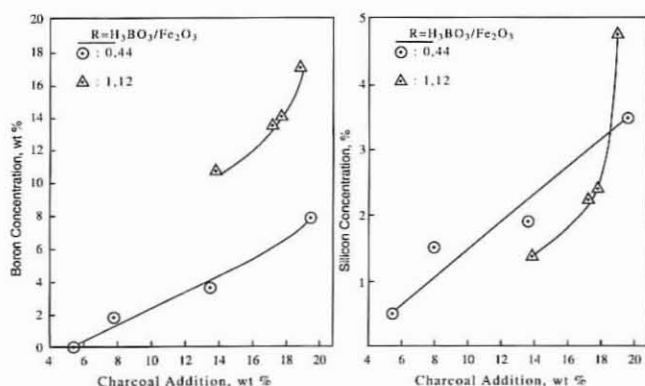


FIGURE 5. The effect of charcoal addition on the concentrations of boron and silicon

The silicon arising from the coal and hematite is not detrimental if the production of Metglass 2605 S2 is required. Even if other coloured metals are present in the alloy, the use of steel in the production of Metglass 2605 S2 dilutes the undesirable effects.

The carbon content of the alloy decreased with increasing boron concentration and, for an alloy containing 17,1 per cent boron, the carbon content decreased to 0,1 per cent.

Energy Consumption

The energy consumption per kilogram of boron in the alloy is shown in Figure 6. The production of ferroboron alloys containing 10 to 20 per cent boron consumed an extra 15,5

kWh per kilogram of boron. This means that, for every unit of boron, nearly 1,55 kWh of energy per kilogram of boron was consumed. On the other hand, for alloys containing less than 10 per cent boron (for example 4 to 10 per cent boron), the energy consumption was 13,5 kWh per kilogram of boron for every unit of boron. It is obvious that the production of high-grade boron alloys is more economical from an energy point of view.

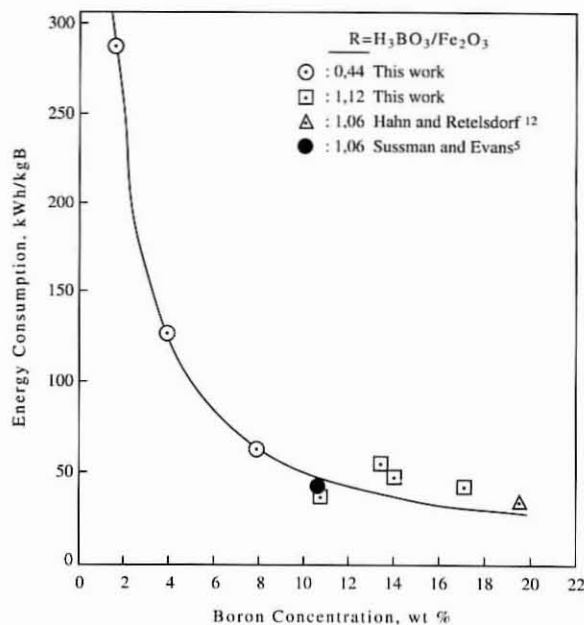


FIGURE 6. Relationship between boron concentration and energy consumption

Processes in the Arc Furnace

Variation in voltage and current

Curves of voltage-versus-time and current-versus-time for a typical experiment are shown in Figure 7. Similar curves were obtained in all the experiments. During the first 30 per cent of the experiments, the voltage fluctuated between 1600 and 1750 A. This system was short-circuited at 8 V and 1850 A. The choice of initial voltage was critical. If the voltage was less than 20 V, the arc was lost owing to a short-circuit. For this reason, the electrode spacing was adjusted to ensure the arc and to keep the voltage above 20 V. Excessive increase of the voltage caused the power consumption to increase and burn the charge. The experiments indicated that 20 to 30 V was a satisfactory experimental condition.

Electrode movement and consumption

The movement of the electrodes was controlled during the experiments by the use of a photocell. It was observed that electrodes were under the influence of two processes: electrode erosion and the accumulation of metals at the bottom and in the unmelted deposit. The change in the rates of electrode erosion and weight loss with the amount of charcoal added is shown in Table II. The erosion of the electrode was not from the sides as expected, but from the bottom. For this reason, the charged reagents were observed to be relatively unreactive during their contact with the sides of the electrode, and most of the reaction took place at the tip of the electrode.

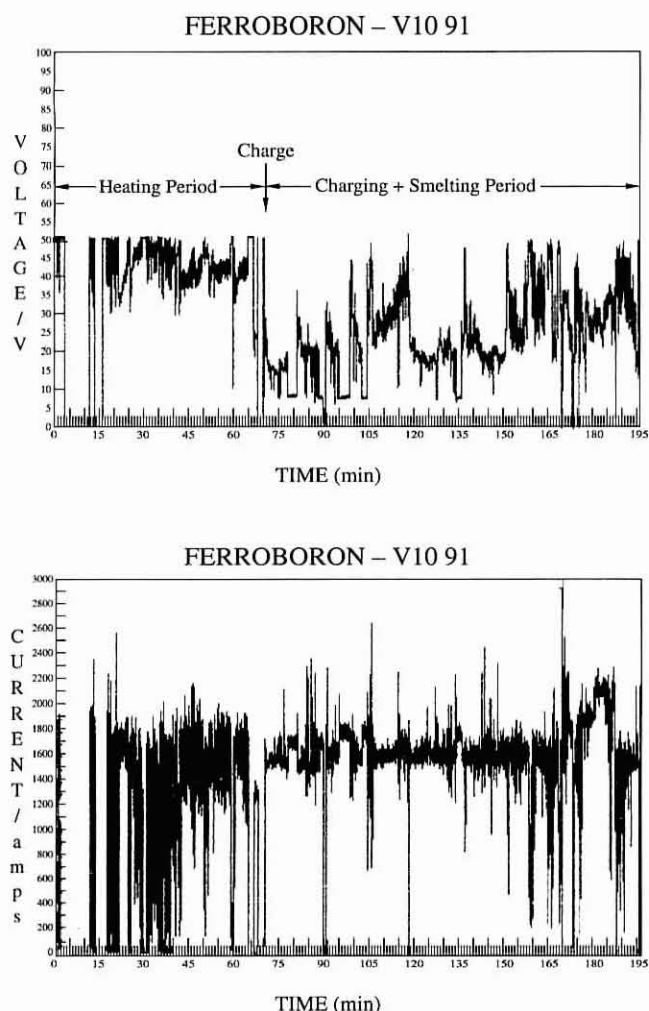


FIGURE 7. The time dependence of voltage and current

TABLE II
ELECTRODE CONSUMPTION

$R = \frac{H_3BO_3}{Fe_2O_3}$	Charcoal added wt %	Electrode consumption	
		g/kg of FeB	cm/h
0,44	5,41	—	12,8
	7,87	134,2	6,1
	13,47	127,7	6,3
	19,54	64,3	3,4
1,12	13,84	92,4	5,2
	17,24	135,4	6,0
	17,69	131,7	6,7
	18,89	102,2	4,1

When the ratio of the charcoal was below 18 per cent and the erosion rate was greater than the accumulation rate of the molten liquid under the electrode, the electrode movement was towards the bottom. In contrast, when the charcoal ratio was higher than 18 per cent, the movement was observed to be upwards.

Processes at the bottom of the electrode

An unmelted deposit was observed to form when an excessive amount of carbon was present during the production of high-boron ferrobaboron. The unmelted deposit at the bottom of the furnace and the sintered surrounding material were analysed by X-ray techniques, and were found to have completely different mineral structures.

The carbon content of the unmelted deposit, contrary to Seki's findings¹⁰, was found to be less than 9 per cent and was in the form of graphite. It was observed that the deposit contained ferrobaboron as well as a sintered phase. The surrounding layers of deposit were composed of alpha iron and boron compounds, which were in an amorphous form. The phases were formed by the reduction of B_2O_3 under the electrode and reaction with the downward-flowing iron to form ferrobaboron, which accumulated at the bottom of the furnace.

Conclusions

Thermodynamic calculations indicate it likely that the reduction of boron oxide takes place in the gaseous phase. In the presence of liquid iron, the reduced boron is more likely to react with iron than with carbon. Therefore, the formation of ferrobaboron is favoured over that of boron carbide.

For an H_3BO_3 -to- Fe_2O_3 ratio of 1,12, the addition of 18,9 per cent charcoal resulted in a boron concentration in the alloy of 17,1 per cent.

Above a concentration of 10 per cent boron, the energy consumption is relatively smaller (35 to 50 kWh per kilogram of boron) than for lower concentrations of boron. Therefore, it is more economical to produce a higher-grade boron alloy than a lower-grade one.

Short-circuiting occurs at 8 V and 1850 A under the conditions used in the tests described. It was realized that 20 V is critical, being the voltage at which the arc is discontinued as a result of short-circuiting.

Erosion takes place from the bottom of the electrode and its extent is highly dependent on the charcoal content of the mixture. Under optimum conditions, the electrode erosion rate is 4 cm/h and the consumption 100 g per kilogram of ferrobaboron.

For a charcoal content of more than 18 per cent in the charge mixture, an unmelted deposit formed under the electrode. X-ray analysis of the deposit indicated the formation of graphite.

The boron recovery was found to vary between 70 and 80 per cent for the optimum conditions used in this study.

Acknowledgments

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