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MECHANISM OF FERROBORON FORMATION IN A DC ELECTRIC ARC FURNACE

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ABSTRACT

Ferroboron, containing 10-20 % boron (by weight), is used as a master alloy in the production of transformer sheets and other boron containing magnetic materials. This manuscript describes the mechanism of ferroboron formation during carbothermic production process. A mixture of boric acid, iron oxide, charcoal and woodchips was smelted in a submerged dc arc furnace at a power of 100 kVA. At fixed H_3BO_3/Fe_2O_3 ratio, charcoal addition was used as a parameter in an investigation of ferroboron formation mechanism. Ferroboron formation was found to take place at the arc zone via the reduction of iron and boron from the shallow ironborate slag. However, it was also observed that, use of excess amount of charcoal causes the formation of an unmelted deposit that prevents metal bath formation in the furnace hearth.

INTRODUCTION

Ferroboron is used as a master alloy in the manufacture of metallic glasses, magnetic materials and steels [1-4].

There are mainly two processes for production of ferroboron, these are metalothermic and carbothermic reaction methods. In conventional aluminothermic process, during the reduction of a mixture of boron oxide and iron oxide with aluminum , 1 to 6 % aluminum is left in the alloy [5]. The presence of aluminum prevents the use of this product in the production of metallic glass. The carbothermic method of ferroboron production yields a better product that satisfies the impurity limits set by the metallic glass industry [6,7]. It was also determined, by Yücel et al [8], that the impurities in ferroboron such as Mn, Cu, Ni, Cr and Co come from the iron ore but impurities like Si and Al mostly come from the ash of the selected coal. Additionally, carbon content was observed to decrease with increasing boron content.

The carbothermic ferroboron production is made in a small electric arc furnace [1] and the energy consumption, kWh/kg B, decreases with increasing boron content in ferroboron; i.e., in 3 % B containing ferroboron production the energy consumption is 360 kWh/kg B and in 18 % B containing ferroboron production the energy consumption is 35 kWh/kg B [6].

Mechanism of ferroboron formation is not well understood in electric arc melting process. It has been observed by Seki et al [9] that unmelted carbon and carbide rich deposit forms below the arc zone in a submerged electrode arc melting process. It was proposed, that in the ferroboron production process, an unmelted deposit is necessary to occur initially in order to accumulate ferroboron droplets at the bottom of the furnace.

In this study, ferroboron alloy was produced from a mixture of boric acid, hematite, charcoal, and wood chips. The vapour pressure of B_2O_3 is very high (10 mm-Hg) at 1900°K which is the melting and tapping temperature of ferroboron. Thus, in order to avoid boron evaporation, a deep arc furnace was used in the experiments, which allowed boron to condensate in the upper (cooler) zone of the furnace. Thermodynamic calculation showed that at a high iron concentration, the possibility of the formation of ferroboron is higher than the possible formation of boroncarbide [6]. The mixture was smelted in a 100 kVA, single-phase arc furnace. The process was studied to define the mechanism of ferroboron formation in the furnace.

EXPERIMENTAL

Raw Materials

The purity of boric acid was 99.5 %, containing Fe (0.1 %), SiO_2 (0.1%), Mg, Ca and Na as impurities. The chemical composition of hematite is given in Table 1. Chemical analysis of charcoal and woodchips, with particle sizes of 1 to 3 mm and 5 to 15 mm respectively, are shown in Table 2. The ash analysis of charcoal is given in Table 3.

TABLE 1. Chemical Analysis and Surface Area of Hematite.

Surface Area [m^2/g]	Weight Percent						
	SiO_2	Al_2O_3	Mn	Cu	Cr	Ni	Co
6.80	1.13	0.36	0.27	0.11	0.03	0.04	0.03

Experimental Set-up

The laboratory type 100 kVA DC arc furnace used in this work was graphite lined and with 40 kg charge capacity. The diameter of the furnace was 30 cm and 80 cm depth. The temperature profile was monitored by the use of thermocouples located in the

furnace lining.The voltage and current readings were measured by a data recording unit. During the tapping of ferroboron, temperature measurements were done by using of an optical pyrometer.

TABLE 2. Chemical Analysis of Charcoal and Woodchips (wt %).

Reductant	C_{fix}	Ash	Volatiles	Moisture	Sulphur
Charcoal	74.07	1.79	17.39	6.61	0.14
Woodchips	10.41	0.39	77.40	11.80	-

TABLE 3. Chemical Composition of Ash (wt %).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
51.90	17.30	19.80	5.80	3.60

Experimental Procedure

Charcoal, woodchips and selected ratios of H_3BO_3 and Fe_2O_3 were mixed in a rotary mixer and 100 to 150 kg of these mixtures were fed to the open arc heated furnace. After 1 to 2 hours of the experimental run, the liquid metal was tapped and the arc stopped. The furnace was left to cool for inspection. After cooling, the samples were taken from sinter sectors in the furnace (Figure 1). These samples were analyzed with wet chemical methods and x-ray diffraction (Rigaku, $Cu_{K\alpha}$); this was also the case for the ferroboron samples.

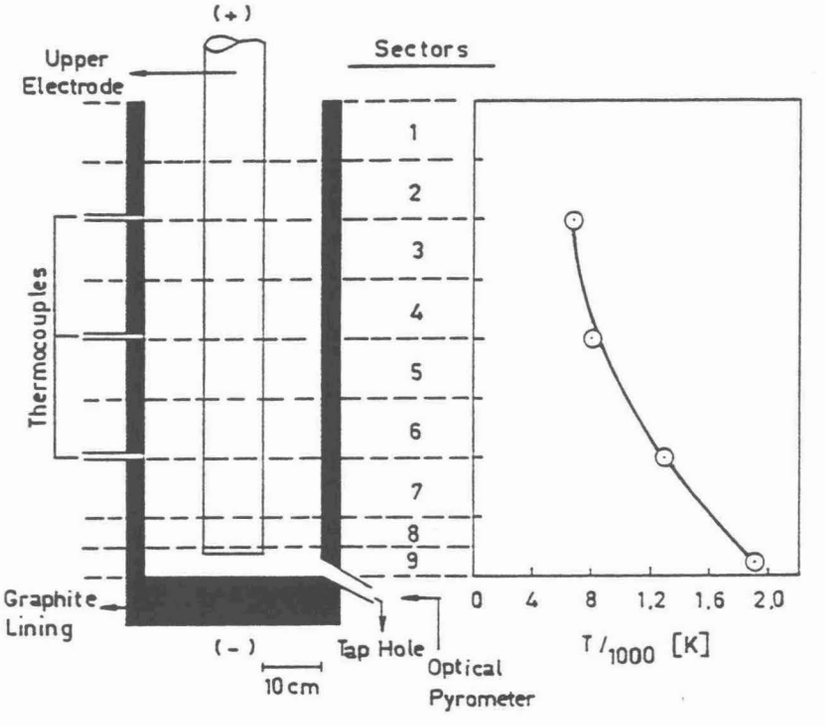


FIG 1. Sectors in the furnace from which samples were taken and their temperatures.

RESULTS AND DISCUSSION

Effect of Charge Composition

H_3BO_3/Fe_2O_3 ratios of 0.44 and 1.12 were selected for the experiments. The amount of charcoal addition was restricted to 5-25 % of charge by weight.

At H_3BO_3/Fe_2O_3 ratio of 0.44 and charcoal additive at 12.35 %, boron concentration in ferroboron went up to 9.90 % (Figure 2). Unfortunately, addition of higher quantities of charcoal to charge drastically reduced charge resistance which in turn created problems during metal tapping. The decrease of the reductant in the charge caused increase in the amount of slag, the latter contained 14 % boron. Because of insufficient amount of reductants for the reaction, the boron concentration in ferroboron was reduced to about 1.55 %. Thus, the electrical energy was consumed for the smelting of slag instead of metal reduction.

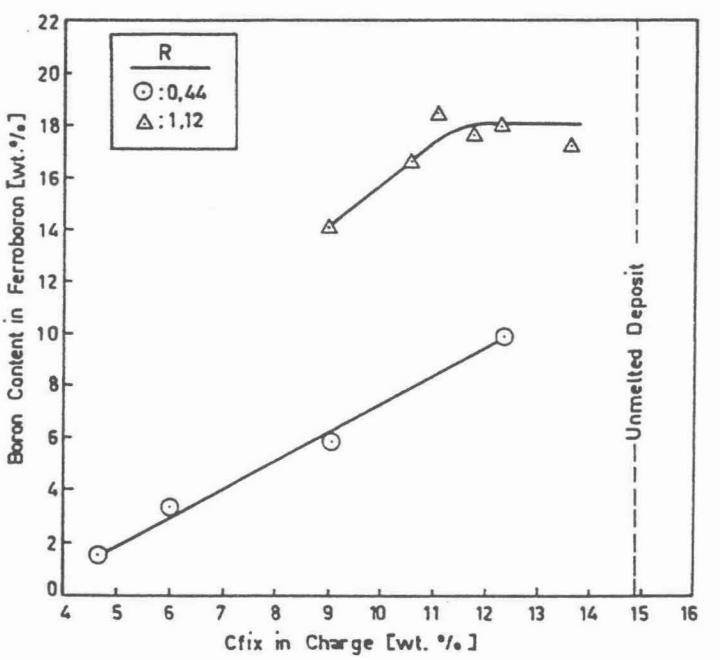
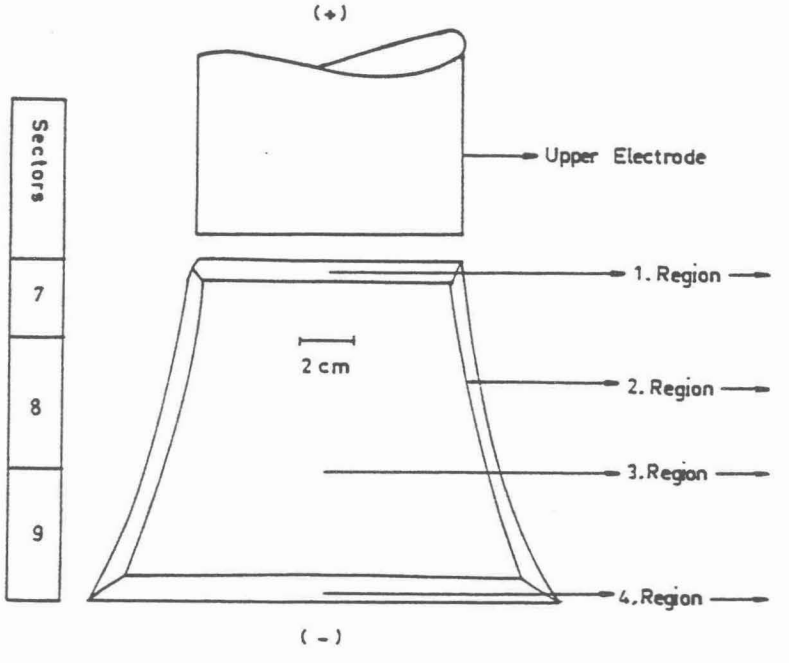


FIG 2. Changes of boron concentration at ferroboron as a function of C_{fix} in charge. ($R=H_3BO_3/Fe_2O_3$)

When production of ferroboron was made with a higher ratio of the reactants (H_3BO_3/Fe_2O_3 ratio was 1.12), the boron concentration in ferroboron was increased up to 18 %. However, conditions that prevent metal formation are initiated in a charge that contains around 15 % fixed carbon. Under these conditions (20-25 V, 1600-1800 A), an unmelted deposit forms. This deposit was closely examined and the results are shown in Table 4.

X-ray analsis revealed that each region of unmelted deposit contains FeB. The third region of the unmelted deposit having very large amount of carbon (caused by excess carbon) prevents FeB droplets to form metal bath. At the fourth region of the unmelted deposit, there exist a very thin ferroboron layer with a low C and a high B concentration. This layer migth be formed at the beginning of the reduction. Furthermore, the X-ray analysis also showed that, the carbon in the unmelted deposit was not in the form of B_4C but in the form of (Fe,C) compound. This solid deposit was accommodated right under the upper electrode, thus reducing the arc resistance greatly and leading to the cooling of the furnace.

TABLE 4. Structure and Chemical Analysis of Unmelted Deposit.



B(wt.%)	C(wt.%)
10.33	10.90
16.62	0.27
14.98	14.00
21.16	1.90

Electrical Parameters

The optimum metal production conditions, characterized by maximum boron concentration versus minimum energy consumption, are summarized in Table 5. At these conditions, when 570 kW/m^2 power density at 40.5 kW power input (average 27 V, 1500 A) was applied to furnace, the ferroboron production rate was 88 kg/m^2.hour, and the graphite electrode consumption rate was 120.5 g/kg metal. Additionally, it was experimentally observed that only a fraction (1.7 %) of charged boron was lost in the gaseous phase.

Schematic Representation of Ferroboron Formation

In order to understand possible mechanism of ferroboron formation, samples from different sectors of the charge have been taken out. These samples have been carefully examined by X-ray and chemical analysis. The results are given in Table 6.

TABLE 5. Optimum Ferroboron Production Conditions and Results.

INPUT				OUTPUT (wt %)					
H_3BO_3/Fe_2O_3	C_{fix} in charge,%	Woodchips in charge,%	Electric Energy kWh/kg B	B	Si	Mn	Al	C	S
1.12	12.35	13.33	35.13	18.0	0.5	0.5	0.05	0.1	<0.01

TABLE 6. Results of X-ray diffraction of the compounds formed at different sectors in furnace under optimum production conditions of ferroboron.

COMPOUNDS		SECTORS								
		1	2	3	4	5	6	7	8	9
H_3BO_3		◆	◆	◆						
B_2O_3			◆	◆	◆	◆	◆			
Fe_2O_3		◆	◆	◆	◆	◆	◆			
Fe_3O_4			◆	◆	◆	◆	◆			
C		◆	◆	◆	◆	◆	◆	◆		
FeB_2O_4			◆	◆	◆	◆	◆	◆		
FeB_4O_7			◆	◆	◆	◆	◆	◆		
Glassy Phase									◆	
FeB									◆	◆
ANALYSIS (wt %)	B	9.6	8.9	9.0	8.5	9.7	9.8	9.81	20.9	17.9
	C	12.8	22.0	24.8	23.7	23.7	14.9	14.9	4.9	0.1

◆: Detected by XRD

In the first and second sectors, boric acid dehydrates and converts to B_2O_3 and, while hematite is reduced to magnetite and ferrous oxide, and compounds like $FeO.B_2O_3$ and $FeO.2B_2O_3$ are formed. The ironborates formed, together with existing charcoal particles, flow towards hotter regions of the furnace.

When the ironborates approach the upper electrode tip a borate slag with a layer of 1-4 cm in thickness forms. From this slag iron and boron are reduced simultaneously. The stoichiometry of the reactions and the corroding of the upper electrode tip have proven that reduction reactions take place at the upper electrode tip as well as on the surface of coke particles which are floating on the slag phase as shown in figure 3.

Chemical analysis of slag and alloy obtained from six different experiments are given in Table 7. These values indicate that 18 % boron containing ferroboron can be

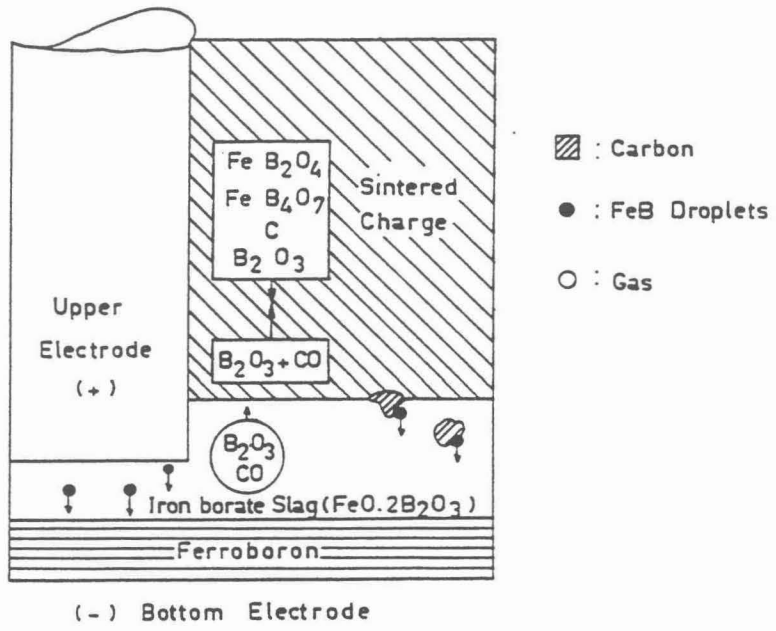


FIG 3. Schematic Showing Ferroboron Formation Mechanism.

produced from an ironborate slag which has a boron concentration of around 20 %. The molar ratio of B_2O_3/Fe_2O_3 in ironborate slag was found to be 2. These calculations show that ferroboron formation takes place through a slag reduction mechanism by the following reaction

$$FeO.2B_2O_3 + 5/2\ C_{(0.85\ coke,\ 0.15\ electrode)} \longrightarrow FeB + 3/2\ B_2O_{3(g)} + 5/2\ CO_{(g)} \quad (1)$$

Due to the stoichiometry of this reaction 3/2 moles B_2O_3 and 5/2 moles CO evolve and move towards the upper section of the furnace. The B_2O_3 condensed on the charge and makes again FeB_2O_4, FeB_4O_7 compounds refluxed to the bottom of the furnace.

TABLE 7. Boron analysis of different experiments.

H_3BO_3/Fe_2O_3	% C_{fix} in charge	% B in slag	% B in FeB
0.44	4.64	12.41	1.55
	6.01	13.83	3.31
	9.05	13.50	5.84
1.12	9.01	19.54	14.14
	12.25	19.25	18.01
	12.25	20.91	17.91

CONCLUSIONS

In the production of ferroboron in an electric arc furnace, as the charge containing boric acid, iron oxide, charcoal and woodchips dehydrates during the feeding into the furnace, and while boron oxide melts, the charge is sintered but forms the porosity needed, by using carbonized woodchips. This permits the maintenance of the reduction reaction. Ironborates formed at the upper sectors move downwards to electrode tip with the coal. With the help of high temperature, boron and iron are reduced together from a glassy slag to produce 18 % B containing ferroboron. Due to the nature of the stoichiometry of the slag reduction reaction, 1.5 mole of B_2O_3 and 2.5 mole gas per mole ferroboron evolved and move towards the cooler sectors of the furnace. While CO leaves the furnace, B_2O_3 forms ironborates again combining with FeO, which is a reduction product of Fe_2O_3, and stays in the furnace. However,excess addition of carbon around 15 % in charge reduce the resistance of the charge and results in cooling of the furnace and formation of an unmelted deposit which stops the ferroboron formation.

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