PRODUCTION OF FERRO-BORON BY ELECTRIC FURNACE

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ABSTRACT

Ferro-boron has been mainly used as an additive agent for steel and cast iron. The consumption of ferro-boron has been increasing year by year, but it is pretty small as compared with that of such as ferro-silicon or ferro-manganese. Then it has been mostly produced by alumino-thermic process.
Recently ferro-boron is drawing much attention as an additive agent for amorphous alloys and magnetic materials. The carbo-reduction process by electric furnance is now revalued for the advantages of mass production and better quality.
Ferro-boron produced by electric furnace for amorphous alloys and magnetic materials has had such disadvantages as low boron content and much impurities which were pointed out through our experience in the past. Furthermore, the difficulties on furnace operation such as melting of raw materials and formation and growth of unmelted deposits on the bottom of the furnace have been well known.

According to the author's studies, the reactions of ferro-boron have the following characteristics that differ from other alloys.

1) Reductive reaction and oxidized reaction can coexist in one furnace.

2) Degrees of carbon solubility in ferro-boron vary very much by temperature.

We have scuceeded to produce ferro-boron stably with high boron content and low impurities by selecting best raw materials and operational conditions of furnace, as well as by utilizing the reaction characters in order to prevent the aforementioned disadvantages.
At present, our ferro-boron has been produced in a large quantity and supplied not only for iron and steel-making but also for amorphous alloys and magnetic materials.

1. INTRODUCTION

Ferro-boron has been mainly used as an additive agent for steel and cast iron. The consumption of ferro-boron has been increasing year by year, but it is pretty small as compared with that of such as ferro-silicon or ferro-manganese, then it has been mostly produced by alumino-thermic process. We Nippon Denko, have had experiences of its production by electric furnace process since 1960's.

Recently ferro-boron is drawing much attention as an additive agent for amorphous alloys and magnetic materials. The carbo-reduction process by electric furnace has had various improvements and is now revalued for the advantages of mass production and better quality. In this paper, we will present the problems of conventional production process of ferro-boron and its improvements we had.

2. PROBLEMS OF CONVENTIONAL PRODUCTION PROCESS

2.1 Alumino-Thermic Process

This process is not suitable for mass production because of batch process. As far as quality, aluminium, magnesium and these alloys are used as reducing agents and also iron oxide is used for the source of oxygen, therefore the product contains considerable amount of impurities from these agents. As far as cost, prices of aluminium and magnesium are high and productivity is low because of batch process, thus the production cost cannot but be higher.

2.2 Electric Furnace Process

In case of electric furnace process, as the melting points of raw materials such as boride and ferrous materials are extremely different, there occurs segregation among raw materials when they are charged in merely mixed condition and then this makes refining impossible. Also, the formation and growth of unmelted deposit is often found under the electrodes and it makes it impossible to submerge the electrodes and makes it difficult to operate continuously for a long period.

Producing ferro-boron with higher boron content has a tendency to accelerate the formation and growth of unmelted deposit under the electrodes.

For that reason, the boron content of ferro-boron produced by electric furnace process in the market is mostly about 10 wt % and this is much lower than that of 20% of ferro-boron produced by alumino-thermic process.

Moreover, since ferro-boron produced by electric furnace process has high content of impurities such as C, Al, Ti, Mn etc., it is not adequate to be used for amorphous alloys or magnetic materials. Chemical analaysis of ferro-boron produced by conventional process is provided in Table 1.

In case of adding a small quantity of boron for steel, it has no problem to use ferro-boron produced by either alumino-thermic or electric furnace process.

In case of adding a considerable quantity of boron for amorphous alloys and magnetic materials, it has a problem to use ferro-boron produced by the conventional process because it will cause a high content of impurities.

Table 1 : Chemical Analysis of Ferro-boron

(wt%)

Method	B	C	Si	Al	Mn	Cu	P	S
Aluminothermics	19.6	0.02	0.7	4.4	0.91	0.37	0.02	0.01
Carbothermics	10.3	0.98	2.0	0.15	0.55	0.17	0.12	0.03
	16.4	0.57	2.1	0.20	0.22	0.04	0.07	0.02

3. CONCEPT AND TARGET FOR THE IMPROVEMENTS OF ELECTRIC FURNACE PROCESS

In order to produce metals with low content of impurities, selection of raw materials and multi stage refining process have been done. The refining process to extract impurities by oxygen and halogen has been applied to produce ferro-boron.[3) 4),5)] As the production cost of multi stage refining process is naturally higher than that of one stage process, we have studied to find a process to produce high boron content and low impurity ferro-boron in a same furnace. Our targets are as follows.

1) To increase boron content up to around 20% and also to maintain stable operation for a long period.

2) To reduce impurities to a level as low as possible, and especially to get good quality that should meet the purpose of final use.

4. PROBLEMS AND ITS COUNTERMEASURES IN OPERATION

4.1 Prevention of Segregation

The characteristics of boride are low melting point and low specific gravity. Therefore, the boride tends to melt in a lower temperature and separate from the other charged materials in the furnace. We call it "segregation".
As a consequence of segregation, reduction of boride would not be conducted. Therefore, as a countermeasure, briquetting or pre-melting of raw material mixture was taken in order to prevent segregation of raw materials.[1),2)] We have succeeded to prevent it by selecting raw materials of proper quality and also increasing viscosities of all raw materials in a melted condition. Consequently, the raw materials to be charged in a furnace need blending only, and the selecting range of raw materials was widened.

4.2 Unmelted Deposit under the Electrodes

4.2.1 Properties

During the operation, the growth of unmelted deposit is often found right under the electrodes. Chemical analysis of the deposit is shown in Table 2. This deposit contains extremely high carbon content and it can be separated into acid-soluble ingredients and acid-insoluble ingredients by the reagent of HCl and HNO_3 at the rate of 30% and 70% respectively. Acid-soluble ingredients are Fe, Fe_2B, FeB and so forth.

Table 3 shows the result of X-Ray diffraction on the acid-insoluble deposit. The main element is graphite and the remainder is mixture of small quantity of B_4C, SiC and FeSi. According to the results of chemical analysis and X-Ray diffraction, it is found that the deposit is composed of graphite and carbide into which ferro-boron infiltrate.

Table 2. Chemical Analysis of Unmelted Deposits (wt%)

B	C	Si	Fe	Al	Ti
11.3	36.4	0.6	51.8	0.026	<0.01

Table 3. Results of X-ray diffraction on the acid insoluble deposits

C	B_4C	SiC	FeSi
+++	+	+	+

+++ Rich

\+ Detected

4.2.2 Conditions of Generating the Deposit

According to our studies, the conditions of generating the deposit are as follows.

1) Using carbonic reductants of low reactivity such as metallurgical coke, pitch coke etc.

2) Using carbon excessively.

3) Producing ferro-boron of high boron content.

4) Others

The deposit generates and grows under one condition or several combined conditions mentioned above. As the main element of the deposit is graphite, we have found the ideal conditions not generate the deposit by selecting carbonic reductants of high reactivity and charging them less quantity than stoichiometrically required. By changing the ratio of boron and iron in raw materials under the ideal conditions, we could produce ferro-boron with high content.

5. REDUCTION OF IMPURITIES

The measures of reducing impurities differ with objective elements. One of the measures is to select raw materials and the other is to adjust the operational conditions.

5.1 Reduction of Impurities by Selecting Raw Materials

The elements among impurities which can be reduced by selecting raw materials of proper quality are such as Si, Mn, Cu, P, S etc. As our process does not need pre-treatment of raw materials, we can select and use ferrous materials in wide varieties of shapes and sizes and also of characteristic properties in accordance with the purpose of production. As the result of it, it has become possible to make the levels of impurities as low as follows.

Si = 0.19%, Mn = 0.007%, Cu = 0.002%
Cr = 0.005%, P = 0.006%

Table 4 shows the example of chemical composition of raw materials. A is a scrap with high purity. B is a scrap with high content of Si. C is a scrap with high content of Si and P. D is a carbonic reductant with high content of Si, E is a carbonic reductant with low content of Si and F is a carbonic reductant with high content of Al and low content of Mn and P.

Table 4. Chemical Analysis of Raw Materials

(wt%)

		Si	Mn	Cu	Cr	Al	Ca	Ti	C	P	S
Iron	A	<0.05	0.002	<0.001	<0.001	<0.005	0.008	<0.01	0.01	<0.005	<0.005
	B	0.67	0.256	0.013	0.030	0.029	0.013	0.01	0.02	0.032	0.010
	C	0.09	0.57	0.011	0.020	0.044	0.021	0.01	0.37	0.017	-
Carbon	D	0.77	0.019	0.001	0.001	0.029	0.85	<0.01	-	0.029	0.003
	E	0.17	0.022	0.001	0.001	0.038	1.15	<0.01	-	0.014	-
	F	0.28	0.009	0.021	0.003	0.186	0.03	<0.01	-	0.003	0.021

5.2 Reduction of Impurities by Adjusting Operational Condition

C, Al, Ti and Ca can be reduced by adjusting operational condition.

5.2.1 Carbon

Figure 1,[6] presented by the group of Professor Ohtani of Tohoku University in Japan, shows the relation between the interaction coefficient obtained from solubility change of saturated carbon by adding element X and the atomic number of additive element X. The elements of which interaction coefficients are of positive number enhace the activity of carbon and accelerate the graphitization in molten iron. On the other hand, the elements of which interaction coefficients are of negative number can be identified as the graphitization inhibitives. According to Figure 1, it can be presumed that boron content and carbon content would be in reverse correlation. Figure 2 shows the relation between the contents of boron and carbon in actual operation.

The presumption of Professor Ohtani can be said to be correct by the figure, but the relation between the contents of boron and carbon is not correlative so precisely as seen in the relation of silicon and carbon in silico-manganese. Due to our studies, the solubility of carbon in ferro-boron is widely fluctuated by temperatures as shown in Table 5. As metals are tapped at various temperatures, it is presumed that carbon content in metals is widely scattered in actual operation as shown in Figure 2. Furthermore, this fact indicates a possibility to produce low carbon metal by the operation in which the metal reduced at high temperature and then precipitating carbon in the low temperature area.

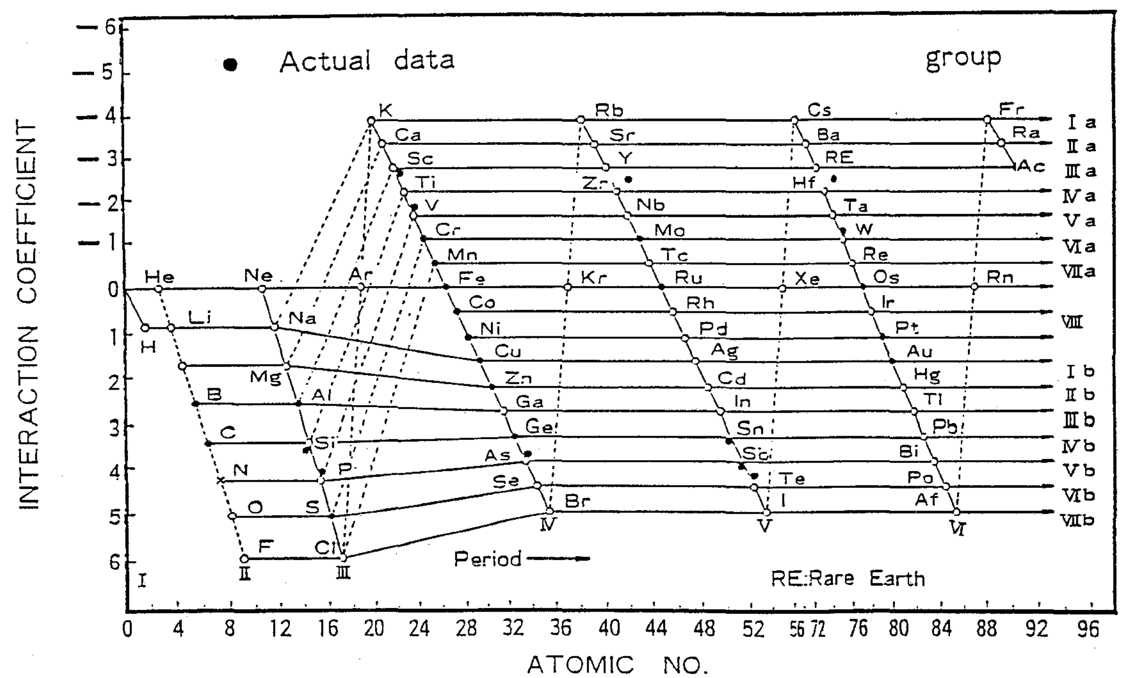

Figure 1: Relation Between Interaction Coefficient and Atomic Number (1550°C)

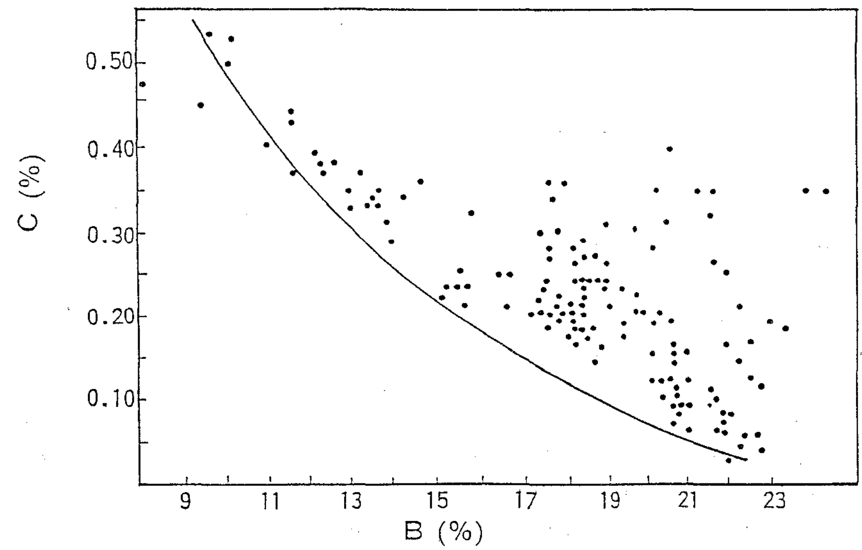

Figure 2: Influence of Boron on Carbon Content

Table 5. Solubility of Carbon in Ferro-boron

Temperature (°C)	B (Wt %)	C (Wt %)
1560	15.6	0.20
1650	15.5	0.35
1740	15.6	0.45
1850	15.2	1.50

5.2.2 Ti, Al, Ca

In production of ferro-boron, if the reducing agents are fully supplied, the metals in a furnace would be reduced in the order of the followings as shown in Figure 3.

Mn > P > B > Si > Ti > Al > Ca

On the contrary, if the reducing agents are not supplied enough, the elements of slight reducible elements such as Ti, Al, Ca etc. are not reduced sufficiently. Figure 4 show influence of reductant quantity on titanium content.
By this example, it is understood that the contents of impurities such as Ti, Al, Ca etc. are low under the condition of insufficient supply of the reducing agents. In the high temperature area above the intersecting points of the $\Delta G^0{}_T$ curves of TiO_2 and Al_2O_3 with that of CO(g) in Figure 3, TiO_2 and Al_2O_3 are reduced to form metals, but when they are lead to the lower temperature area below the abovementioned intersecting points and as an oxide such as B_2O_3 exists in this temperature area, they would be oxidized by reacting with the oxide and then the contents of Ti, Al etc. in the metal should be lowered.

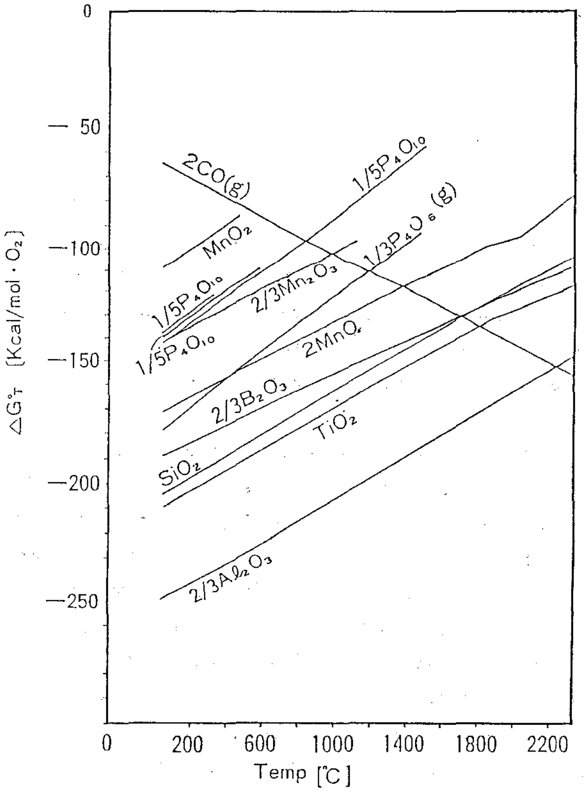

Fig. 3 Change in Free Energy of Reactions

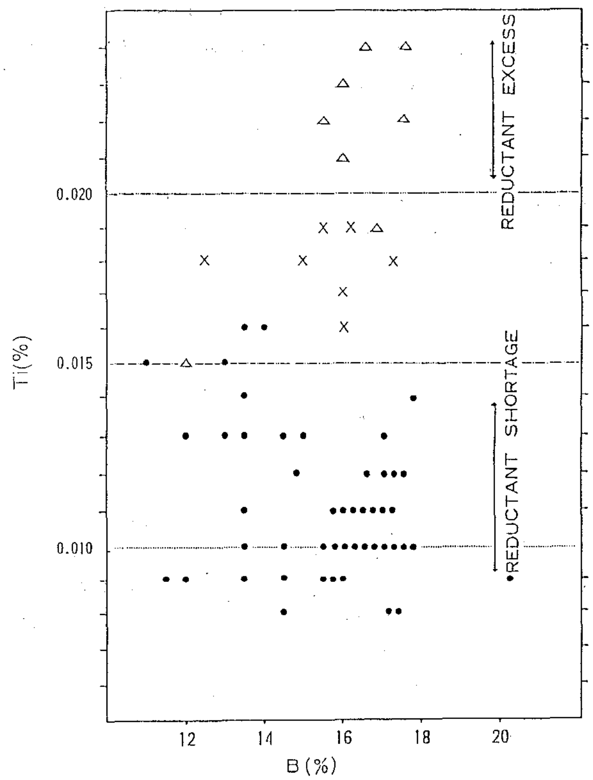

Fig. 4 Influence of Reductant Quantity on Titanium Content

5.2.3 Decreasing Impurities in a Furance

According to the therory stated in 5.2.1 and 5.2.2, it is possible to reduce the contents of C, Ti, Al and Ca in a furance by soft reduction process to generate the reduction area of high temperature and the oxidization area of low temperature in a furnace. However, the simple soft reduction process will have the following difficulties. In proportion to the quantity of carbonic reductant decreases, the electric resistance around the electrodes increases and it becomes difficult to hold the position of the electrodes. As the electrodes easily touch the generated metal, the electricity load fluctuates widely. Consequently, it becomes impossible to raise the electricity load. The way to decrease impurities in a furance is to utilize the deposit right under the electrodes as shown in Figure 5.[8] As mentioned in the above, the unmelted deposit would be generated right under the electrodes by use of carbonic reductants of low reactivity.

The growth of this deposit can be stopped by replacing carbonic reductants of low reactivity with one of higher reactivity when the deposit grows to a suitable degree. So the process is, first of all, to generate the unmelted deposit by using carbonic reductant of low reactivity and to presume the suitable degree of growth of the deposit and then at that point, to replace the carbonic reductant with one of better reactivity in raw materials. The quantity of carbonic reductant to replace should be less than 90% of stoichiometrically required and this is soft reduction process. Most of the reducing reaction is carried out in the space between the electrodes and a deposit. The generated metal reaches to a molten metal pool, dripping down through the layers of raw materials with excessive B_2O_3 around the deposit. On the way down to the pool, carbon in the metal precipitates and is oxidized and then Ti, Al and Ca are oxidized. As the metal generated in the space between the electrodes and a deposit is always put out of an arc zone, the arc discharge by carbon and the electric resistance in this space are maintained stable. By the explanation mentioned in the above, it will be understood that such a seemingly strange phenomenon as reducing area of hihg temperature and oxidizing area of low temperature exist actually at a time in one furnace.

The biggest advantage of this process is to make it possible to decrease impurities in a furance keeping the electricity load at a high level and the production cost at a low level.

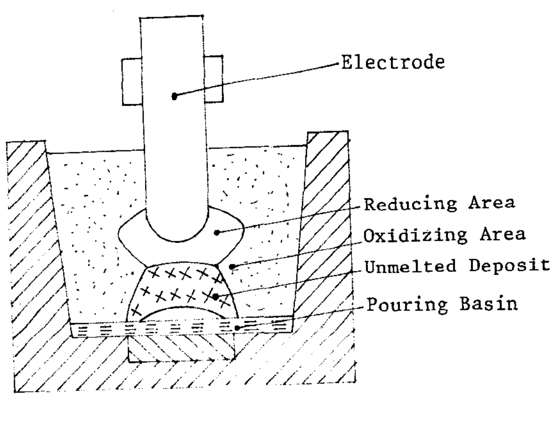

Fig. 5 Model Diagram of the Furnace

6. COMPARISON OF QUALITY

Table 6 shows a comparison of quality between ferro-boron produced by the conventional process with that by the improved one. As described here, the ratio of contents of impurities between the conventional process and the improved process are as follows.

C is 2 to 1 ; Si, P and S are 10 to 1 ; Cu is 20 to 1 ; Al and Mn are 30 to 1

Table 6. Comparison of Quality

(Wt%)

Method		B	C	Si	Al	Mn	Cu	P	S
Aluminothermics		19.6	0.02	0.7	4.4	0.91	0.37	0.02	0.01
Carbothermics	A	16.4	0.57	2.1	0.20	0.22	0.04	0.07	0.02
	B	21.4	0.18	0.50	0.011	0.27	0.016	0.025	0.001
		16.5	0.29	0.19	0.007	0.007	0.002	0.006	0.001

A : Conventional Process B : Improved Process

7. SUMMARY

Followings are the summarized features of the improved process.

1) Pre-treatment of raw materials is not necessary and raw materials can be selected in a wide range.

2) It is possible to control the growth of deposit generating under the electrodes.

3) It is possible to set the reducing area and also the oxidizing area in one furnace by the process stated in the above 2).

4) It is possible to decrease impurities by selecting raw materials and by controlling the operational conditions.

8. CONCLUSION

Our main target to produce ferro-boron with low contents of impurities at low cost has been successfully achieved. However, there are a few additional requirements for further decrease of some of impurities and we have been studying to satisfy such requirements. We have switched over most of the producing process of ferro-boron to the electric furnace process and our Hokuriku Plant is now producing ferro-boron at the rate of 1,500 MT per annum. Comparing with the conventional process, our new process has enabled us to supply ferro-boron at very competitive price for steel, amorphous alloys and magnetic materials.

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