Conference Paper

The Reduction of Boron By Silicothermal Method

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Abstract

Thermodynamic modeling (TM) of the boron reduction process from the $CaO–SiO_2–MgO–B_2O_3$ oxide system by silicon of ferrosilicon of FeSi65 and FeSi75 grades has been carried out. TM is made using the HSC 6.12 Chemistry software package developed by Outokumpu Research Oy (Finland). The equilibrium composition of oxide $CaO\text{-}SiO_2\text{-}MgO\text{-}B_2O_3$ and metallic Si-Al-Fe systems was determined using the Equilibrium Compositions module in a given temperature range of 1400–1700°C and a gas phase pressure of 1 atm. The effect of silicon of ferrosilicon grades (FeSi65 and FeSi75) on the degree of boron reduction (η_B) was studied. It has been established that an increase in the temperature of the boron reduction process from 1400 to 1700°C contributes to a decrease in its degree of reduction. Thus, the boron content decreased from 1.86 to 1.45% when using FeSi65 as a reducing agent. At a temperature of 1650°C, the boron concentration in the metal was 1.48%, which corresponds to the degree of boron reduction of 67.9%. For a similar system, using FeSi75 as a reducing agent, a decrease in the boron concentration from 1.5 to 1.13% in a given temperature range was also determined. At a temperature of 1650°C, the degree of boron reduction was 52.8%, which indicates a lower reducing ability of FeSi75 silicon as compared to FeSi65. The influence of the time of colemanite interaction with the reducing agent FeSi75, the temperature, and the type of colemanite used on the degree of boron reduction was studied experimentally. The highest values of the degree of boron reduction by ferrosilicon were achieved at 20 min exposure and a temperature of 1650°C. The results of the TM and experimental studies have shown the fundamental possibility of obtaining a high-silicon complex ferroalloy containing, %: 60–80 Si; 0,6–2,0 B and Fe-rest.

Keywords: ferroalloy, boron, colemanite

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1. Introduction

The most common introduction of boron in steel during microalloying in the form of lumpy ferroalloys or cored wire [1].

The ferroboron is widely used with a content of 6–20% B in the domestic and foreign industries. The ferroalloy is obtained by the aluminothermic method. The extraction of boron in the metal is 60-65%. Aluminum reduction is also used in the production of complex boron-containing ferroalloys with Ni, Cr, Ti. However, this method of obtaining complex ferroalloys has a high cost. The silicothermic reduction is used in production of a boron-containing silicon metal which containing Zn, Ti, Ca, and other elements.

The extraction of boron in this case is about 50% [2]. It is known that boron has a high chemical activity. Thus ferroboron microalloying requires deep deoxidation of steel, which prevents the formation of its oxides and nitrides [2–4]. In addition, the achievement of the required boron concentration in steel (0.001-0.003%) is difficult due to the small amount of injected ferroalloy. It leads to an unequal distribution of boron. Therefore, it is rational to introduce boron into the metal in the composition of complex ferroalloys together with chemically active elements (Al, Si, Ti, etc.) and with low boron content (0,8–2%). This method allows you to increase the weight of the additive boron-containing ferroalloy, improving the uniformity and degree of recovery of boron in steel [1, 5].

In the works [1, 5–7], the data of using of 65% ferrosilicon (FeSi65) as a boron reducing agent are given in order to obtain complex boron-containing ferroalloy. This method is promising since without a significant increase in the cost of technology, it is possible to obtain an alloy suitable for simultaneous deoxidation and microalloying of steel. The authors of [8] determined that with silicothermic reduction of boron introduction of calcium oxide (18% of boric anhydride) increases the extraction of boron into siliceous ligature by up to 50%; iron in the metal reduces boron extraction. The study of aluminothermic production of ferroboron alloys [9] also confirms a significant increase in the degree of boron reduction with the introduction of titanium into the alloy.

However, the silicothermal method of producing boron-containing ferroalloys is not widely used and has not been sufficiently studied.

The thermodynamic modeling (TM) and experimental studies of the process of boron reduction from slags of the CaO-SiO_2-MgO-B_2O_3 system by silicon of ferrosilicon were carried out.

2. Materials and Methods

The system CaO – SiO_2 – MgO – Al_2O_3 – B_2O_3, containing, (40,5% CaO; 7,5% SiO_2; 2% MgO; 50% B_2O_3) was source material. The silicon was used as a reducing agent. The chemical composition of the system is close to real.

Thermodynamic modeling of boron reduction by silicon of ferrosilicon was performed using the HSC Chemistry 6.12 software package. The program based on minimization of the Gibbs free energy and variational principles of thermodynamics [10]. The software was developed by Outokumpu Research Oy (Finland) and is designed to analyze chemical reactions and calculate equilibria.

The equilibrium composition of oxide CaO-SiO_2-MgO-B_2O_3 and metallic Si-Al-Fe systems was determined using the “Equilibrium Compositions» module to temperature range of 1400-1700°C in 50°C steps and a gas phase pressure of 1 atm. The system has 2.24 m3 of N_2(gas) as a neutral additive to speed up the computational procedure for finding an equilibrium composition. The amount of oxides taken is 13,8% on weight of the metal i.e., to 50 g of reducing agent (FeSi65 and FeSi75) was taken 6.9 g of boron-containing slag

The series of experiments were performed using FeSi75 grade 75% ferrosilicon to obtain additional information about the effect of the silicon content in the reducing agent on the degree of boron transfer to the alloy. The earlier experiments on the silicothermic reduction of boron with FeSi65 silicon [7] were carried out using a similar technique.

The ferrosilicon of the FeSi75 grade and boron-containing material — colemanite with a B_2O_3 content of 47–49% are used to obtain a complex ferroalloy. Colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$) is a gray mineral. The removal of moisture from colemanite occurs at 350-550°C. The loss on ignition is ∼ 23.0%. The colemanite was used in the following types: 1) powder calcined at 600°C with a particle size of <0,5 mm (49% B_2O_3); 2) briquetted of calcined powder in the form of pieces 3-5 mm in size (49% B_2O_3); 3) a material with a grain size <2,0 mm (46,9% B_2O_3) melted at 1300°C from a powder. The chemical composition of FeSi75, %: 77,5 Si; 1,5 Al; Fe - the rest. The chemical composition of colemanite is given in Table 1.

Table 1: The chemical composition of colemanite, %.

Type of colemanite	B_2O_3	CaO	MgO	SiO_2
- powder	49,0	32,9	2,5	5,0
- briquetted	49,0	32,9	2,5	5,0
- remelted	46,9	36,5	2,5	9,0

The experiments were carried out in a graphite crucible installed in an electric Tamman-type resistance furnace. The temperatures were 1550, 1600, and 1650°C and holding times of 10, 15, and 20 minutes. A crucible was charged with 50 g of ferrosilicon and colemanite in an amount stoichiometrically necessary to produce 2% boron in the alloy. The crucible was installed in the furnace and after complete melting of the ferrosilicon, colemanite was loaded onto its surface. At the same time, in order to minimize the loss of boron-containing material, it was introduced into the ferrosilicon melt through a steel tube. The melt was stirred, at the end of the exposure time the crucible with the melt was removed from the furnace, and the metal was poured into a mold. A sample of ferrosilicon for chemical analysis was taken after cooling.

3. Research Results

According to the results of thermodynamic modeling, an increase in the process temperature from 1400 to 1700°C leads to a decrease in the boron content in the metal. Thus, the boron content decreased from 1.86 to 1.45% for the $CaO\text{-}SiO_2\text{-}MgO\text{-}B_2O_3$ system using FeSi65 as a reducing agent. At a temperature of 1650°C, the boron concentration in the metal was 1,48%, which corresponds to the degree of boron reduction of 67,9%. For a similar system with using FeSi75 as a reducing agent a decrease in boron concentration from 1,5 to 1,13% in a given temperature range was also established. The degree of boron reduction was 52,8% at a temperature of 1650°C, which indicates a lower reducing ability of silicon FeSi75 compared to FeSi65.

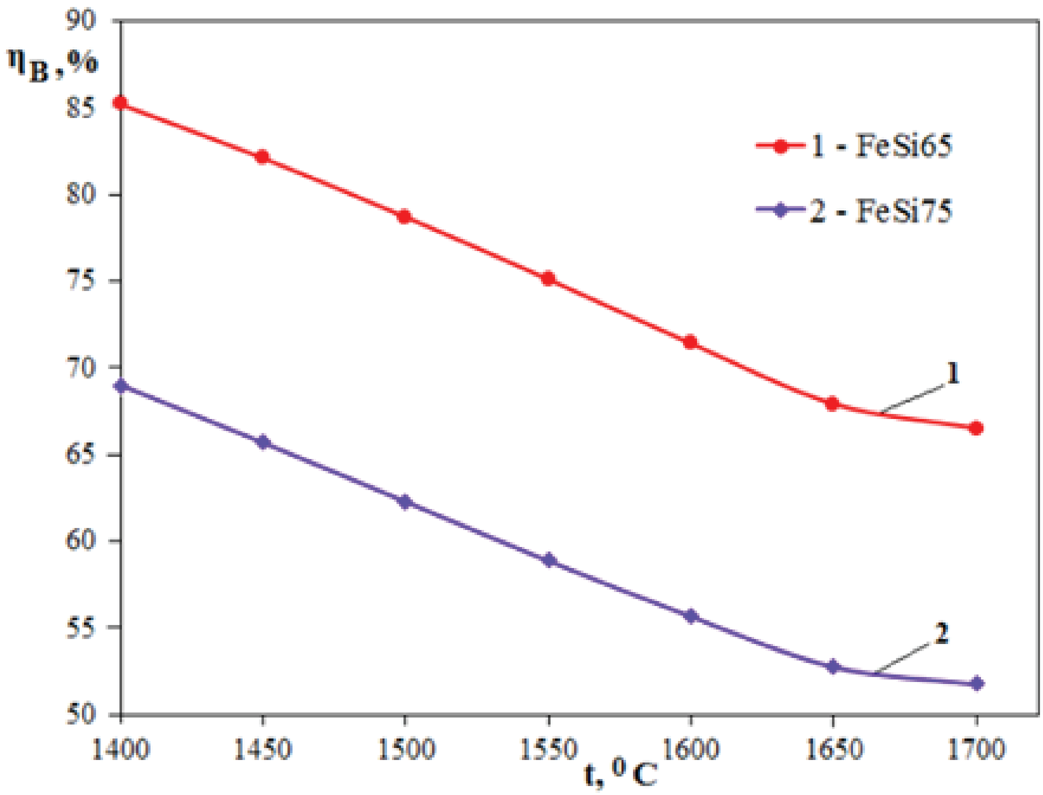

Figure 1: Results of thermodynamic modeling.

The effect of the interaction time of colemanite with a reducing agent (silicon of 75% ferrosilicon), temperature, and the type of colemanite used on the degree of boron uptake alloy has been studied experimentally. At a constant temperature (1650°C), the dependence of the degree of boron uptake on the holding time of the melt was determined. The highest values of η_B by ferrosilicium were achieved at 20 min exposure and at a temperature of 1650°C. In this case the boron transition into the alloy was 80% of the briquetted colemanite powder and 72% of the remelted colemanite, and 64,5% of the calcined powder. For example, an increase in the exposure time from 10 to 20 min increases the degree of boron assimilation for remelted colemanite from 43,5% to 72%, respectively (Figure 1). The lowest values of the degree of assimilation of boron are probably related to the dust removal of the powdery material upon its introduction into the melt, which was noted in the previous study [6], as well as their phase composition. In the remelted colemanite, stronger $CaO{\cdot}B_2O_3$ and $2CaO{\cdot}B_2O_3$ compounds are formed, which makes boron recovery difficult.

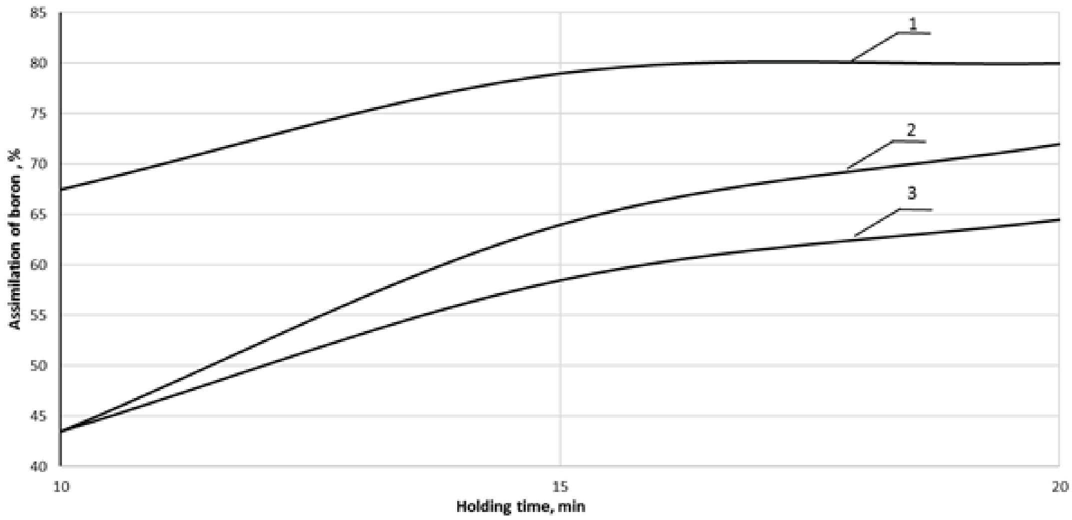

Figure 2: Dependence of the degree of assimilation of boron on the holding time for different types of colemanite at a temperature of 1650°C (1 - colemanite briquetted, 2 - remelted, 3- powder) using FeSi75.

The results of the study show that the degree of boron reduction using FeSi65 at a temperature of 1650°C and holding at 10 min [6] exceeds the data obtained with the reducing agent FeSi75 for powdered colemanite and remelted colemanite by 38,0 and 30%, respectively. An increase in the holding time of more 15 min to a lesser extent affects the increase in the degree of boron reduction (see Figure 2), while its losses are possible due to the formation of gaseous BO and B_2O_2 compounds.

X-ray phase analysis of ferrosilicon samples showed that the amount of the $FeSi_2$ phase in FeSi65 is 2 times larger, and [Si] is ~ 15% less than in FeSi75. Iron increases the degree of boron reduction due to the formation of strong chemical compounds FeB and Fe2B. The enthalpy of formation is ΔH^0_{298}= -71230 J/mol for FeB and -54470 J/mol for Fe2B [11], this fact explains the higher degree of assimilation boron ferrosilicon FeSi65.

Thus, using calculations and laboratory experiments, it was shown that it is possible in principle to obtain a high-silicon complex ferroalloy (60-80% Si) with a low boron content (0.6-2.0% B) and the main parameters of the recovery process were established.

4. Conclusions

1. The effect of temperature on the process of boron reduction from slags of CaO–SiO_2–MgO–B_2O_3 system by silicon ferrosilicon FeSi65 and FeSi75 has been studied by the method of thermodynamic modeling. It is established that with increasing temperature the boron content in the metal decreases.
2. The degree of boron reduction at a temperature of 1650 ^{0}C was determined by a calculation method using silicon from FeSi65 and FeSi75 as a reducing agent which was 67,9 and 52,8% respectively.
3. The type of injected boron-containing material has a significant impact on the degree of transition of boron into the alloy. The highest degree of assimilation is observed in bricketed colemanite - 80%. Due to the large dust removal colemanite powder showed low values of boron to alloy transition – 64,5%.
4. The results of laboratory studies have shown that an increase in the exposure time at a constant melt temperature of 1650 ^{0}C leads to an increase in the degree of boron transfer into the alloy.
5. Thermodynamic modeling and experimental studies have shown the fundamental possibility of boron reduction of the CaO-SiO_2-MgO-B_2O_3 system with silicon ferrosilicon FeSi65 and FeSi75 the best results were obtained using FeSi65.

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References

[1] Zhuchkov V.I., Sychev A.V., Babenko A.A. (2015). Study of the effect of temperature, duration of interaction and the type of ore material on the degree of boron transition to the alloy in the recovery process. Metals, no. 5, pp. 23-25.

[2] Lyakishev N.P., Pliner Yu.L., Lappo S.I. (1986). Boron-containing steels and alloys. Moscow: Metallurgy.

[3] Potapov A.I. (2013). Investigation of the processes of microalloying with boron to improve the production technology of boron steel. PhD dissertation/Master's thesis. The National University of Science and Technology "MISiS"

[4] Gasik M.I., Lyakishev N.P., Emlin B.I. (1988). Theory and technology of production of ferroalloys. Moscow: Metallurgy.

[5] Zhuchkov V.I., Noskov A.S., Zavyalov A.L. (1990). Dissolution of ferroalloys in the liquid metal. Sverdlovsk: Ural Branch of the Academy of Sciences of the USSR.

[6] Zhuchkov V.I., Sychev A.V., Akberdin A.A. et al. (2015). Research and improvement of the process of obtaining complex boron-containing ferroalloys. in Proceedings of XVI Int. conference «Modern problems of electrometallurgy of steel and ferroalloys». Chelyabinsk: SUSU Publishing Center.

[7] Zhuchkov V.I., Zayakin O.V., Leont′ev L.I. et al. (2017). Physico-chemical characteristics, preparation and use of complex boron-containing ferroalloys. Proceedings of the higher educational institutions. Ferrous metallurgy, vol. 60, no. 5, pp. 348-354.

[8] Popov V.P., Zayko V.P., Ryss M.A. et al. Silicothermal production of boron-containing ligatures. in Proceedings of CHEMP.

[9] Baev A.I., Dubrovin A.S., Chirkov N.A. (1978). Calorimetric study of boron alloys and thermodynamic analysis of the process of their aluminothermic production. Ferroalloy production. charge preparation and production technology. Thematic industry collection, no 7, pp. 33-41.

[10] Roine A. (2002) Outokumpu HSC Chemistry for Windows. Chemical reactions and Equilibrium software with extensive thermochemical database. Pori: Outokumpu research OY.

[11] Gasik M.I., Lyakishev N.P. (2005) Physicochemistry and technology of electroferroalloys. Dnepropetrovsk: System Technologies.