BORON AND CALCIUM REFINING OF FERROSILICON BY SLAG TREATMENT

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ABSTRACT

Slag refining is used to reduce the calcium content in ferrosilicon and may also reduce the concentration of boron in the metal. Data for the equilibrium of boron between silicon and several slag systems can be found in literature and these data can be used for slag refining of ferrosilicon if the interaction between boron and iron in silicon is known. The distribution of calcium and boron between ferrosilicon and calcium silicate slags was investigated experimentally and the distribution coefficient of boron was found to be in the area between 2.5 and 3 for Fe-Si alloys above 50 % Fe. The interaction coefficient between boron and iron in silicon was determined to be $\varepsilon_{Fe}^{B} = -1.8 \pm 0.4$ *at 1600°C. And the concentration dependence of calcium in ferrosilicon in equilibrium with binary calcium silicate slags was found to follow the relation*

$$[\%Ca]_{in\ FeSi} = \exp\left(-8.839 \cdot 10^{-4} \cdot [\%Si]_{in\ Fe}^{2} + 0.212 \cdot [\%Si]_{in\ Fe} + 1.841 \cdot V^{2} + 0.701 \cdot V - 16.294\right)$$

at 1600 °C where V is the CaO/SiO_2 *mass ratio.*

KEYWORDS: *Ferrosilicon, slag refining, interaction coefficient, boron and calcium distribution, calcium silicate slag.*

1. INTRODUCTION

Ferrosilicon is mainly used for deoxidation and alloying of steel. Quality requirements for many steel types are getting more and more stringent and elements present in ppm-levels in the metal are therefore getting more attention. Boron is one of the elements that is usually present in ppm-levels in ferrosilicon. However, even ppm-levels of boron can significantly change the physical properties of alloys. Also the calcium content in ferrosilicon has to be reduced to obtain a high purity metal. Ferrosilicon can be treated with a slag to reduce the calcium concentration and such a slag treatment may also remove boron from the metal. The distribution coefficient of boron between pure silicon and binary calcium silicate slags has recently been determined because of the possibility of removing boron from silicon for solar cells by slag refining [1,2]. Knowledge of the interaction between boron and iron in silicon will make it possible to use the distribution coefficient data for refining of ferrosilicon. The distribution of boron and calcium between ferrosilicon containing up to 50 % iron is in the present study investigated at 1600 °C, and the interaction coefficient between boron and iron in silicon is determined. The distribution of calcium between ferrosilicon and binary calcium silicate slags is also investigated.

2. EXPERIMENTAL

A binary calcium silicate master slag was made by melting a mixture of 150 g CaO and 150 g SiO_2 under argon atmosphere in an induction furnace. The CaO had a purity of 99.98 % while the

SiO_2 had a purity of 99.99 %. This slag was crushed to a powder and doped with approximately 100 ppm boron (as 99.98 % B_2O_3) before melting and crushing it to a powder two more times to ensure a homogeneous composition. The ferrosilicon alloys were made by filling a graphite crucible with a mixture of iron with 99.99 % purity and silicon with 8N purity. Five compositions (shown in table 1) with a total weight of 15 grams in the range from 50 % iron and 50 % silicon to 100 % silicon were used. These mixtures were melted at 1600°C under argon atmosphere for one hour in a resistance heated furnace and cooled to room temperature again. 15 grams of the boron doped calcium silicate master slag was then filled into each crucible with solidified ferrosilicon alloy. Each crucible with its contents was then placed inside the furnace and held at 1600°C for 6 hours before rapidly cooling it to room temperature. The samples were cooled to the melting point of silicon two minutes after cooling started and then cooled to 150°C below the melting point of silicon after another two minutes. One experiment where 15 grams of silicon and 15 grams of a silica-saturated binary calcium silicate slag was held under argon atmosphere at 1600°C in a quartz crucible for 18 hours was also included in this study.

Graphite, slag and metal were separated and as much slag and metal as possible were sampled from the crucible to ensure that the samples were representative of bulk composition. A tungsten carbide disk mill was used to crush the slag and silicon pieces to a homogeneous powder before chemical analysis. Boron and calcium in the metal samples and boron in the slag samples were determined by ICP-MS while the slag composition was determined by XRF. Three separate sub-samples were taken from each sample that was analyzed by ICP-MS and a 95 % confidence interval was calculated from the standard deviation between them. This confidence interval is shown as error bars in the figures.

3. RESULTS

The samples had a mass loss of 1.0 to 1.1 grams during the experiments and the slag composition after the experiments was approximately the same for all samples, as can be seen in table 1. The mass loss is expected due to formation of silicon monoxide gas that also causes the silica content to slowly decrease throughout the experiments.

The distribution coefficient of boron, L_B, is defined as the concentration of boron in slag divided by concentration of boron in the silicon alloy. The distribution coefficient of boron was not found to change much with increasing iron content as can be seen in figure 1.

The calcium content in metal did on the other hand decrease significantly with increasing iron content as shown in figure 2. The data in table 2 includes results from a previous study[1] and the data from both the previous and present study is shown in figure 3. It is seen that the calcium concentration decreases sharply with decreasing calcium content in slag.

Table 1: Results with relative standard deviation (RSD) between ICP-MS analyses of three sub-samples

	Metal composition						Slag composition			
Exp no.	**Fe, wt%**	**Si, wt%**	**Boron, ppmw**	**RSD, %**	**Calcium, mass %**	**RSD, %**	**CaO, wt%**	**SiO_2, wt%**	**Boron, ppmw**	**RSD, %**
1	50	50	23.2	7.4	0.0067	21.8	52.0	48.3	63.1	1.5
2	35	65	22.7	4.3	0.0279	13.7	51.4	48.5	70.4	2.8
3	25	75	24.3	7.9	0.0838	3.8	51.5	48.4	63.5	2.9
4	15	85	25.1	4.1	0.1787	4.1	52.0	48.3	66.3	0.9
5	0	100	25.7	4.6	0.3172	3.5	51.8	48.6	66.0	1.8

Table 2: Calcium concentration in silicon in equilibrium with binary calcium silicate slags

CaO/SiO_2, kg/kg	0.46	0.65	0.85	1.05	1.07	1.09	1.15	1.25	1.31
Holding time, h	18	6	6	6	6	3	6	3	6
Mass, % Ca	0.037	0.084	0.106	0.386	0.317	0.414	0.450	0.742	1.281
RSD, %	6.8	8.3	6.8	5.5	3.5	1.8	10.7	7.3	1.8

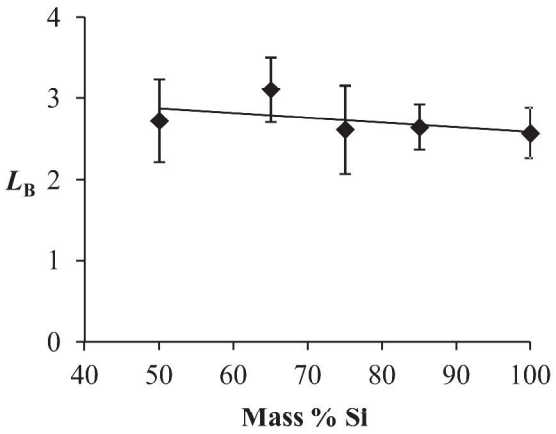

Figure 1: Distribution of boron between 51.66 % CaO – 48.34 % SiO_2 slag and ferrosilicon as a function of silicon content at 1600°C

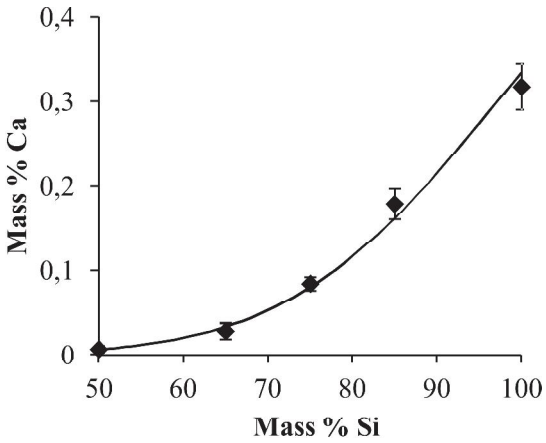

Figure 2: Calcium concentration in ferrosilicon in equilibrium with 51.66 % CaO – 48.34 % SiO_2 slag as a function of silicon content at 1600°C

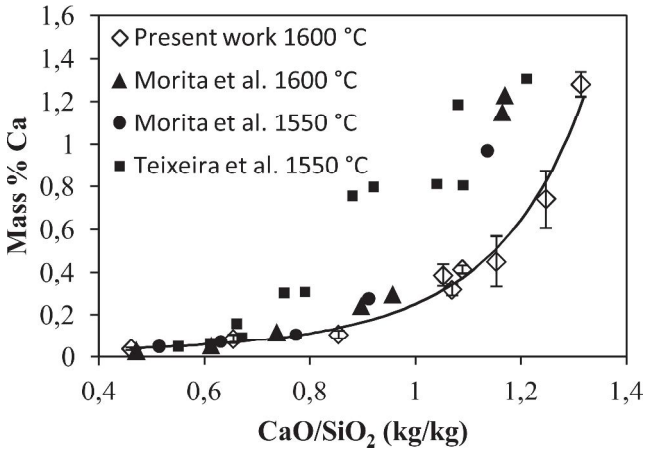

Figure 3: Calcium concentration in pure silicon in equilibrium with a calcium silicate slag as a function of CaO/SiO_2 mass ratio at 1600°C as obtained in the present study and previous studies [4, 5]

4. DISCUSSION

The distribution coefficient of boron in equilibrium with a calcium silicate slag with composition 51.66 % CaO and 48.34 % SiO_2 is almost constant with increasing iron content. This indicates that the interaction between boron and iron in silicon is weak. The distribution coefficient has previously also been shown to be almost constant with changing CaO/SiO_2 mass ratio [1,2]. The

average distribution coefficient of boron is in this study equal to 2.7 and this value can be used as a reasonably good approximate independent of composition of a binary calcium silicate slag and independent of the iron content of ferrosilicon.

The activity of silicon in ferrosilicon has previously been determined by Elliot and co-workers [3] and their values can together with the experimentally determined values for the distribution coefficient of boron be used to calculate the first order interaction coefficient between iron and boron at 1600°C. To do this we start with the chemical equilibrium of boron between slag and metal:

$$B + \tfrac{3}{4}\, SiO_2 = BO_{1.5} + \tfrac{3}{4}\, Si \tag{1}$$

where the equilibrium constant is given by:

$$K = \frac{a_{BO_{1.5}} \cdot a_{Si}^{3/4}}{a_B \cdot a_{SiO_2}^{3/4}} = \frac{x_{BO_{1.5}} \gamma_{BO_{1.5}} \cdot a_{Si}^{3/4}}{x_B \gamma_B^0 \exp\left(\varepsilon_B^{Fe} x_{Fe}\right) \cdot a_{SiO_2}^{3/4}} \tag{2}$$

Both the activity coefficient of boron oxide and the activity of SiO_2 are constant since the slag composition is constant. The activity coefficient of boron at infinite dilution in pure silicon, γ_B^0, is also constant. By collecting all constant terms on one side we get:

$$C = \frac{x_{BO_{1.5}} \cdot a_{Si}^{3/4}}{x_B \exp\left(\varepsilon_B^{Fe} x_{Fe}\right)} \tag{3}$$

where the constant C includes all the constant terms. We take the logarithm and collect the unknown terms on the right side of the equation

$$\ln\left(\frac{x_{BO_{1.5}} \cdot a_{Si}^{3/4}}{x_B}\right) = \ln(C) + \varepsilon_B^{Fe} x_{Fe} \tag{4}$$

Using the activity of silicon given by Elliot and co-workers together with the experimentally determined values of boron concentration we can plot the left side of this equation and use linear regression to find the interaction coefficient between boron and iron in silicon. The plot and the regression line is shown in figure 4.

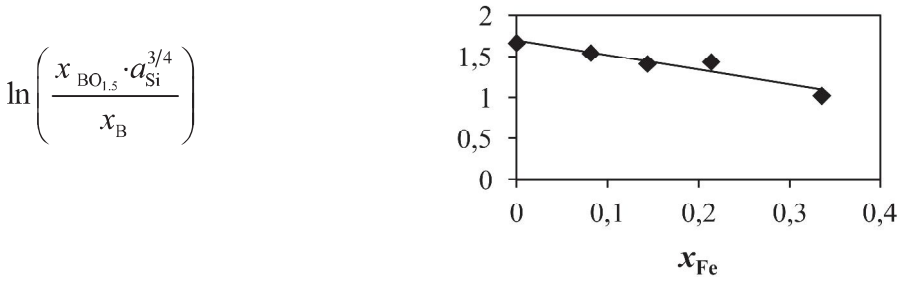

Figure 4: Experimental data and regression line for estimating the interaction coefficient between iron and boron in silicon

The interaction coefficient between boron and iron in silicon at 1600°C is found to be:

$$\varepsilon_{Fe}^{B} = -1.8 \pm 0.4$$

where the uncertainty ± 0.4 is the standard error of the slope of the regression line.

Two previous works have been done on the equilibrium distribution of calcium on the CaO-rich side of the binary calcium silicate system and the results from those are shown in figure 3 together with results from the present and previous study [4,5]. The calcium concentration as obtained in the previous and present study is lower than the values obtained by others. No obvious reason for this difference was found. The calcium concentration in equilibrium with calcium silicate slag with composition 51.66 % CaO and 48.34 % SiO_2 was found by regression to follow the relation:

$$[\%Ca]_{in\ FcSi} = \exp\left(-8.839 \cdot 10^{-4} \cdot [\%Si]_{in\ Fc}^{2} + 0.212 \cdot [\%Si]_{in\ Fc} - 13.459\right) \quad (6)$$

where the concentrations are given in mass %. This curve is also indicated as a solid line in figure 2. The calcium concentration in pure silicon as a function of CaO/SiO_2 mass ratio was found to follow the relation:

$$[\%Ca]_{in\ Si} = \exp\left(1.841 \cdot V^2 + 0.701 \cdot V - 3.933\right) \quad (7)$$

where V is the CaO/SiO_2 mass ratio. The two functions above give a very similar calcium concentration for pure silicon in equilibrium with slag containing 51.66 % CaO and 48.34 % SiO_2. The calcium concentrations found using the two expressions for pure silicon in equilibrium with slag containing 51.66 % CaO and 48.34 % SiO_2 are 0.334 and 0.339 % Ca respectively. The concentration found using equation [7] was chosen as basis for merging the two expressions [6] and [7] into one formula for the calcium content in ferrosilicon as a function of CaO/SiO_2 mass ratio and amount of silicon in ferrosilicon:

$$[\%Ca]_{in\ FcSi} = \exp\left(-8.839 \cdot 10^{-4} \cdot [\%Si]_{in\ Fc}^{2} + 0.212 \cdot [\%Si]_{in\ Fc} + 1.841 \cdot V^2 + 0.701 \cdot V - 16.294\right) \quad (8)$$

This equation is valid for the entire liquidus region of a binary calcium silicate slag at 1600 °C from ferrosilicon containing 50 % iron to pure silicon.

5. CONCLUSION

The distribution coefficient of boron between ferrosilicon alloys and a binary calcium silicate slag is in the range from 2.5 to 3 for ferrosilicon alloys above 50% Fe. Boron has a weak interaction with iron in silicon where the interaction coefficient between boron and iron in silicon at 1600°C is given by:

$$\varepsilon_{Fe}^{B} = -1.8 \pm 0.4$$

The calcium concentration decreases sharply with increasing iron content in the alloy and decreasing calcium oxide content in the slag.

The calcium concentration in ferrosilicon in equilibrium with binary calcium silicate slags at 1600°C is given by the equation:

$$[\%Ca]_{in\ FeSi} = \exp\left(-8.839 \cdot 10^{-4} \cdot [\%Si]_{in\ Fe}^{2} + 0.212 \cdot [\%Si]_{in\ Fe} + 1.841 \cdot V^2 + 0.701 \cdot V - 16.294\right)$$

where V is the CaO/SiO_2 mass ratio of the slag.

6. REFERENCES

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