Removal of Boron from Molten Silicon Using CaO–SiO₂ Based Slags

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The global shortage of solar grade silicon for the production of photovoltaic cells has motivated many researches on the refining of silicon, especially the refining of metallurgical-grade silicon. In order to obtain better control of the removal process of boron from molten silicon using silicate slags, precise thermodynamic data are required. In the present study the partition ratio of boron (L_B) between the slag and silicon phases and the activity coefficient of boron oxide in CaO–SiO₂, CaO–SiO₂–25%CaF₂, and CaO–SiO₂–40%CaF₂ slags were evaluated at 1 823 K. The activity coefficient of BO_{1.5} was investigated for slags of CaO/SiO₂ ratio varying from 0.3–7.0; further, the borate capacity of the slag is defined in this study as:

$$C_{\text{BO}_3^-} = \frac{(\text{mass}\% \text{BO}_3^{3-})}{a_B P_{\text{O}_2}^{3/4}} = \frac{K_1 a_{\text{O}_2}^{3/2}}{f_{\text{BO}_3^-}}$$

The addition of Na₂O to CaO–SiO₂ slags was found to increase the partition ratio of boron between the slag and the silicon phase.

KEY WORDS: silicon refining; solar grade silicon; solar cell; slag refining; boron removal; partition ratio; activity coefficient; slag capacity; borate capacity; CaO–SiO₂; CaO–SiO₂–CaF₂; Na₂O–CaO–SiO₂.

1. Introduction

The rapid growth of the solar cell market is causing a shortage of solar grade silicon feedstock, and therefore, alternative production processes are needed to increase the feedstock. The refining of metallurgical grade silicon is always desirable; however, the removal of boron is still a challenge. Slag refining is an option for the removal of boron from molten silicon, and an effective removal may be obtained for a certain slag composition. As presented in the previous study,¹⁾ the partition ratio of boron is strongly affected by the basicity of the slag and the addition of fluxes such as CaF₂ can increase the attainable basicity range. Another option is the addition of compounds with high basicity, such as Na₂O. Once the partition ratio of boron between the slag and the silicon phase is determined, important thermodynamic data, such as the activity coefficient of boron oxide and the borate capacity of the slag, can be calculated and compared with those of other researches.²⁾

In the present study, the partition ratio of boron and the activity coefficient of boron oxide in the slag phase were evaluated. The borate capacity of the slag was defined, and its relation with the basicity was clarified. Finally, in a short experiment, the effect of the addition of Na₂O in a binary CaO–SiO₂ system was investigated.

2. Experimental Procedures

Experiments were carried out as described in the previous paper.¹⁾ Samples of CaO–SiO₂–CaF₂ systems were prepared with the CaF₂ contents fixed at either 25% or 40% CaF₂, and the CaO/SiO₂ ratio was varied from 0.3 to 4.0 or 0.3 to 7.0, respectively. To minimize the loss of CaF₂, a screw type led was used. The samples were quenched in flushing argon. Activity calculations for silica were performed as described in the previous study¹⁾ by using the data of Zaitsev *et al.*³⁾ Since the data were generated for systems at 1 723 K, a regular solution approach was used to correct the data to correspond to a temperature of 1 823 K.

The initial and the final composition of the samples are listed in **Table 1**. The CaF₂ content in the samples after the experiment was determined by the fluoride ion selective electrode method.

The duration of the experiment for samples of the Na₂O–CaO–SiO₂ system was reduced to 1 h due to the high volatile characteristics of sodium compounds.

3. Experimental Results and Discussion

The boron content in the slag and silicon and the partition ratio of boron are shown in **Table 2**. Samples containing CaO/SiO₂ lower than 0.8 could not maintain constant composition after 18 h of equilibration due to the reaction between CaF₂ and SiO₂ as reported by Sommerville *et al.*⁴⁾

Table 1. Initial and final compositions of CaO–SiO₂–25%CaF₂ and CaO–SiO₂–40%CaF₂ slags equilibrated with silicon for 18 h at 1 823 K.

Initial composition				Final composition			
CaO (%)	SiO ₂ (%)	CaF ₂ (%)	CaO/SiO ₂	CaO (%)	SiO ₂ (%)	CaF ₂ (%)	CaO/SiO ₂
CaO–SiO ₂ –25%CaF ₂							
55.0	20.0	25.0	2.75	56.5	20.4	23.1	2.76
50.0	25.0	25.0	2.00	51.8	24.8	23.4	2.09
45.0	30.0	25.0	1.50	53.8	21.0	25.2	2.57
40.0	35.0	25.0	1.14	54.9	25.2	19.9	2.18
35.0	40.0	25.0	0.9	44.0	34.3	21.7	1.28
30.0	45.0	25.0	0.67	39.6	38.2	22.2	1.04
20.0	55.0	25.0	0.36	41.8	47.1	11.1	0.89
CaO–SiO ₂ –40%CaF ₂							
50.0	10.0	40.0	5.00	43.5	16.5	40.0	2.64
45.0	15.0	40.0	3.00	41.6	18.4	40.0	2.26
40.0	20.0	40.0	2.00	37.3	22.7	40.0	1.64
35.0	25.0	40.0	1.40	45.9	21.7	32.4	2.12
30.0	30.0	40.0	1.00	47.3	20.1	32.6	2.35

Table 2. Results for CaO–SiO₂–25%CaF₂ and CaO–SiO₂–40%CaF₂ slags after 18 h of equilibration at 1 823 K.

Initial CaO/SiO ₂	Final CaO/SiO ₂	[B] (mass ppm)	[Ca] (%)	(B) (mass ppm)	Partition
CaO–SiO ₂ –25%CaF ₂					
2.75	2.76	24.5	0.19	59.6	2.4
2.00	2.09	16.6	0.15	39.7	2.4
1.50	2.57	26.4	0.18	61.0	2.3
1.14	2.18	16.4	0.29	32.4	2.0
0.9	1.28	30.5	0.96	54.5	1.8
0.67	1.04	51.6	0.79	62.6	1.2
0.36	0.89	52.0	0.52	54.3	1.0
CaO–SiO ₂ –40%CaF ₂					
5.00	2.64	22.6	2.63	45.7	2.0
3.00	2.26	31.3	1.73	45.9	1.5
2.00	1.64	20.1	2.95	28.3	1.4
1.40	2.12	36.0	1.22	57.1	1.6
1.00	2.35	27.9	0.84	52.2	1.9

and described in Eq. (1). Samples were prepared aiming a CaO/SiO₂ ratio between 0.36–4.00 and 0.33–7.00 for the 25% CaF₂ and 40% CaF₂ system respectively. In samples where the change in the composition of the slag was too large, a constant partition ratio could not be obtained and those data were excluded from this study.

Following this reaction, for samples with a low CaO/SiO₂ ratio, CaF₂ reacts with silica forming CaO, thereby increasing the basicity of the slag.

The partition ratio of boron between the slag and the silicon phase is defined in Eq. (2), where (mass% B) represents the concentration of boron in slag phase and [mass% B] represents the concentration of boron in silicon phase. The values of L_B are shown in Fig. 1 together with the data obtained for the binary CaO–SiO₂.¹⁾ The addition of CaF₂ provided a broader basicity range when compared to the binary system, but it did not improve the partition ratio of boron. Since in this series of experiments the ratio slag/silicon was maintained constant for all samples (2.3 for binary and ternary systems) the effective amount of lime and silica added to the system were reduced. CaF₂ is neither as acidic as silica nor as basic as lime, and hence it dilutes both compounds in the slag phase.

$$L_B = \frac{(\text{mass\% B})}{[\text{mass\% B}]} \dots\dots\dots(2)$$

Fig. 1. Boron partition ratio between the slag and the silicon phase for silicate slags as a function of the final basicity of the slag equilibrated at 1 823 K.

The thermodynamic data at 1 823 K was calculated for the samples of the CaO–SiO₂–CaF₂ system containing 25% and 40% CaF₂ according to the method presented in the previous study¹⁾ and are shown in Table 3. The activity coefficient of BO_{1.5} can be calculated from equilibrium relations based on Eq. (3) as long as the Si, SiO₂ and B activity values are known. The silica activity values were taken from the work of Zaitsev *et al.*,³⁾ the values for the activity of boron were determined by Yoshikawa *et al.*⁵⁾ and the silicon activity was calculated using the Gibbs–Duhem equation. The activity coefficient of BO_{1.5} was evaluated for both 25% and 40% CaF₂ containing slags and is shown in Fig. 2 together with the data for the binary system presented in the previous study and those reported by Noguchi *et al.*²⁾

One possible reason for the difference between the results of the present study and those reported by Noguchi may be due to the difference in the activity of boron adopted in both studies. The equilibration of Si–B in boron nitride crucible requires a well controlled atmosphere in order to avoid the formation of Si₃N₄, which would yield an incorrect result. The expression used by Noguchi is shown in Eq. (4) and can be compared with that adopted in the present study, shown in Eq. (5).⁵⁾ It is easy to notice that the sign of entropy is opposite.

$$\ln \gamma_{\text{B}(\text{l})}^0 = 1.19(\pm 0.25) + \frac{289(\pm 450)}{T} \dots\dots\dots(4)$$

$$\log \gamma_{\text{B}(\text{l})}^0 = -\frac{1.1 \times 10^4}{T} + 5.82 \dots\dots\dots(5)$$

The activity coefficient of BO_{1.5} decreases with an increase in the basicity, except for basicities lower than 0.8, where boron is incorporated in the silicate network having its activity coefficient decreased as reported in the previous study.¹⁾ If the samples with basicity lower than 0.8 are excluded from plotting, the relation between $\ln \gamma_{\text{BO}_{1.5}}$ and the

Table 3. Thermodynamic data of the systems CaO–SiO₂–25%CaF₂ and CaO–SiO₂–40%CaF₂ at 1 823 K. The data regarding the binary system CaO–SiO₂ was listed in the previous study.

CaO/SiO ₂	X _{BO_{1.5}}	a _B	a _{Si}	a _{SiO₂}	γ _{BO_{1.5}}	P _{O₂}	C _{BO₃³⁻}
CaO–SiO ₂							
1.21	5.26x10 ⁻⁴	3.60x10 ⁻⁴	0.929	2.69x10 ⁻¹	2.44x10 ⁻¹	4.45x10 ⁻¹⁸	7.83x10 ¹⁵
1.08	4.66x10 ⁻⁴	4.80x10 ⁻⁴	0.935	3.96x10 ⁻¹	4.88x10 ⁻¹	6.50x10 ⁻¹⁸	3.91x10 ¹⁵
1.04	4.40x10 ⁻⁴	5.09x10 ⁻⁴	0.955	4.36x10 ⁻¹	5.80x10 ⁻¹	7.02x10 ⁻¹⁸	3.29x10 ¹⁵
1.09	4.08x10 ⁻⁴	4.47x10 ⁻⁴	0.955	3.87x10 ⁻¹	5.02x10 ⁻¹	6.22x10 ⁻¹⁸	3.80x10 ¹⁵
0.92	5.87x10 ⁻⁴	1.08x10 ⁻³	0.956	5.71x10 ⁻¹	1.12	9.18x10 ⁻¹⁸	1.70x10 ¹⁵
0.88	4.21x10 ⁻⁴	8.09x10 ⁻⁴	0.958	6.29x10 ⁻¹	1.27	1.01x10 ⁻¹⁷	1.51x10 ¹⁵
CaO–SiO ₂ –25%CaF ₂							
2.76	5.51x10 ⁻⁴	8.70x10 ⁻⁴	0.989	1.96x10 ⁻⁵	4.22x10 ⁻⁴	3.04x10 ⁻²²	4.52x10 ¹⁸
2.09	3.67x10 ⁻⁴	5.90x10 ⁻⁴	0.991	1.45x10 ⁻³	1.09x10 ⁻²	2.25x10 ⁻²⁰	1.76x10 ¹⁷
2.57	5.64x10 ⁻⁴	9.38x10 ⁻⁴	0.990	8.79x10 ⁻⁵	1.37x10 ⁻³	1.36x10 ⁻²¹	1.39x10 ¹⁸
2.18	3.00x10 ⁻⁴	5.80x10 ⁻⁴	0.984	1.70x10 ⁻⁴	2.63x10 ⁻³	2.65x10 ⁻²¹	7.25x10 ¹⁷
1.28	5.04x10 ⁻⁴	1.06x10 ⁻³	0.947	6.76x10 ⁻²	2.63x10 ⁻¹	1.10x10 ⁻¹⁸	7.26x10 ¹⁵
1.04	5.79x10 ⁻⁴	1.81x10 ⁻³	0.957	3.05x10 ⁻¹	1.20	4.91x10 ⁻¹⁸	1.59x10 ¹⁵
0.89	5.02x10 ⁻⁴	1.83x10 ⁻³	0.971	4.04x10 ⁻¹	1.71	6.40x10 ⁻¹⁸	1.12x10 ¹⁵
CaO–SiO ₂ –40%CaF ₂							
2.64	4.23x10 ⁻⁴	7.59x10 ⁻⁴	0.861	7.86x10 ⁻⁵	1.51x10 ⁻³	1.40x10 ⁻²¹	1.26x10 ¹⁸
2.26	4.25x10 ⁻⁴	1.07x10 ⁻³	0.907	3.18x10 ⁻⁴	5.85x10 ⁻³	5.40x10 ⁻²¹	3.26x10 ¹⁷
1.64	2.62x10 ⁻⁴	6.71x10 ⁻⁴	0.845	6.50x10 ⁻³	6.01x10 ⁻²	1.18x10 ⁻¹⁹	3.17x10 ¹⁶
2.12	5.28x10 ⁻⁴	1.25x10 ⁻³	0.933	7.55x10 ⁻⁴	1.03x10 ⁻²	1.24x10 ⁻²⁰	1.86x10 ¹⁷
2.35	4.82x10 ⁻⁴	9.78x10 ⁻⁴	0.953	1.36x10 ⁻⁴	2.39x10 ⁻³	2.19x10 ⁻²¹	7.99x10 ¹⁷

Fig. 2. Activity coefficient of boron oxide for silicate slags equilibrated with molten silicon at 1 823 K.

Fig. 3. Logarithmic relation between the basicity and the activity coefficient of boron oxide for silicate slags at 1 823 K.

basicity can be fitted into a linear relation, as shown in **Fig. 3** and described in Eq. (6).

$$\ln \gamma_{\text{BO}_{1.5}} = -4.00(\text{CaO/SiO}_2) + 3.67 \dots\dots\dots(6)$$

The oxidation of boron by slag treatment can be represented by Eq. (7). On the basis of the equation, the borate capacity of the slag is defined in Eq. (8) where the oxygen partial pressure is defined by the equilibrium between SiO₂ and Si, and K₁ is the reaction constant. The required data to calculate the borate capacity are listed in Table 3. The capacity of a slag of an acidic oxide such as BO₃ is expected to increase with the basicity of the slag, as shown in **Fig. 4**.

$$C_{\text{BO}_3^{3-}} = \frac{(\text{mass}\% \text{BO}_3^{3-})}{a_{\text{B}} P_{\text{O}_2}^{3/4}} = \frac{K_1 a_{\text{O}_2}^{3/2}}{f_{\text{BO}_3^{3-}}} \dots\dots\dots(8)$$

Fig. 4. Relation between the borate capacity of silicate slags and the basicity at 1 823 K.

adopted for the activity coefficient, it can be fitted by a linear relation (Eq. (9)), as shown in **Fig. 5**.

If the borate capacity data is treated in the same way as

Fig. 5. Logarithmic relation between the basicity and the borate capacity of silicate slags at 1823 K.

$$\ln C_{\text{BO}_3^{3-}} = 4.00(\text{CaO/SiO}_2) + 31.51 \quad \text{.....(9)}$$

Since there are no other data available on the borate capacity of the slags, it will be compared with the sulfide capacity according to the definition of Fincham *et al.*⁶⁾ in Eqs. (10) and (11), where K_2 is the reaction constant for Eq. (10). The relation between the borate capacity and the sulfide capacity is given by Eqs. (12)–(14). The relation between the borate capacity defined in the present study, and the data reported by Fincham and Kalyanram *et al.*⁷⁾ is shown in Fig. 6; further, as described in Eq. (14), the expected slope of the curve is 3/2.

$$C_{\text{S}^{2-}} = \frac{(\text{mass}\% \text{S}^{2-}) P_{\text{O}_2}^{1/2}}{P_{\text{S}_2}^{1/2}} = \frac{K_2 a_{\text{O}^{2-}}}{f_{\text{S}^{2-}}} \quad \text{.....(11)}$$

$$a_{\text{O}^{2-}} = \frac{C_{\text{S}^{2-}} f_{\text{S}^{2-}}}{K_2} \quad \text{.....(12)}$$

$$C_{\text{BO}_3^{3-}} = \frac{K_1}{f_{\text{BO}_3^{3-}}} \left(\frac{C_{\text{S}^{2-}} f_{\text{S}^{2-}}}{K_2} \right)^{3/2} \quad \text{.....(13)}$$

$$\log C_{\text{BO}_3^{3-}} = \frac{3}{2} \log C_{\text{S}^{2-}} + \log \frac{K_1}{K_2^{3/2}} + \log \frac{f_{\text{S}^{2-}}^{3/2}}{f_{\text{BO}_3^{3-}}} \quad \text{...(14)}$$

The slopes of the line in Fig. 6 are 1.88 and 1.43. The slope value 1.5 lies between these two values, which suggests reasonable agreement between the sulfide capacity and borate capacity.

On the basis of the results for the binary and ternary slag systems, it is apparent that if compounds with a higher basicity than that of CaO (or CaF₂) are used, a better partition ratio and a higher value for capacity may be obtained.⁸⁾ The use of Na₂O (in the form of Na₂O or Na₂CO₃) may increase the basicity and can also decrease the melting point of the slag. However, sodium oxide can be easily reduced to the silicon phase and becomes volatile at high temperatures,

Fig. 6. Relation between the borate and the sulfide capacity of silicate slags.

Fig. 7. Effect of addition of Na₂O on the partition ratio of boron for CaO–SiO₂ slags at 1823 K.

thereby making it difficult to work for a prolonged period. Sodium oxide was added to a slag with composition similar to that employed when the best partition ratio was obtained for the CaO–SiO₂ slag (CaO/SiO₂=1.21). The duration of the experiment was reduced to 1 h, and three samples were prepared: 0% Na₂O, 7% Na₂O and 10% Na₂O. As shown in Fig. 7, the addition of Na₂O promoted an increase in the partition ratio of boron.

4. Conclusions

In the present study, the use of CaO–SiO₂ based slags for the removal of boron from molten silicon was clarified and the following results were obtained.

(1) The partition ratio of boron was investigated for CaO–SiO₂–(25% and 40%)CaF₂ slag systems at 1823 K, for the basicity ranges 0.4–4.0 and 0.3–7.0 respectively.

(2) The activity coefficient of boron oxide was calculated for CaO–SiO₂ based slags at 1823 K and could be represented as:

$$\ln \gamma_{\text{BO}_{1.5}} = -4.00(\text{CaO/SiO}_2) + 3.67$$

(3) In the present study, the borate capacity of the slag was defined as

$$C_{\text{BO}_3^{3-}} = \frac{(\text{mass}\% \text{BO}_3^{3-})}{a_{\text{B}} P_{\text{O}_2}^{3/4}} = \frac{K_1 a_{\text{O}^{2-}}^{3/2}}{f_{\text{BO}_3^{3-}}}$$

and can be represented as $\ln C_{\text{BO}_3^{3-}} = 4.00(\text{CaO}/\text{SiO}_2) + 31.51$ for the CaO–SiO₂ based slags at 1 823 K.

(4) The partition ratio of boron between the slag and silicon phases is not increased by the addition of CaF₂; in context, it is improved by the addition of Na₂O.

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