Removal of Boron from Silicon-Tin Solvent by Slag Treatment

XIAODONG MA, TAKESHI YOSHIKAWA, and KAZUKI MORITA

To eliminate B effectively from Si for its use in a solar cell, a novel process involving the slag refining of molten Si with Sn addition was investigated. The partition ratio of B between CaO-SiO_2-24 mol pct CaF_2 slag and Si-Sn alloy at 1673 K (1400 °C) was determined by the chemical equilibrium technique. It was found that the partition ratio of B was remarkably increased with the increase in Sn content of alloy, which attributes to the increase in activity coefficient of B as well as the oxygen partial pressure. The partition function was accounted as much as 200 when the alloy composition was Si-82.4 mol pct Sn, which was much higher than the reported values in the range of 1 to 3. The required amounts of slag used for B removal from Si-30, 50, and 70 mol pct Sn melts were only 15.6 pct, 6.5 pct, and 1.2 pct of that used for the removal of B directly from MG-Si without Sn addition in a single slag treatment.

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I. INTRODUCTION

THE availability of abundant and low-cost solar grade silicon (SOG-Si) feedstock is essential for the widespread use of solar cells. Currently, the modified Siemens process and a fluidized bed reactor process have been developed to overcome the cost and energy problems associated with the conventional Siemens process. However, the cost-reduction potential of these processes is limited because of low Si productivity due to converting Si into gaseous compounds followed by distillation and reduction into solid Si. To explore a sustainable process for producing SOG-Si, a metallurgical refining process that uses MG-Si as a starting material was considered as a promising method for reducing the production cost further and being specialized in terms of producing SOG-Si on a large scale.

Among the typical harmful impurities for the Si solar cell such as Fe, Ti, Al, P, and B, metallic impurities can be removed by directional solidification due to extremely low segregation coefficients.[1] Phosphorus has a high vapor pressure, which can be removed under high vacuum melting.[2] However, it is difficult to remove B during solidification refining and the vacuum treatment due to its large segregation coefficient in Si (0.8)[3] and its comparatively low vapor pressure. Considering a strong affinity of B for oxygen, it can be oxidized as shown in Eq. [1].

$$B_{(l)} + \frac{3}{4}O_{2(g)} = BO_{1.5(l)} \qquad [1]$$

Slag refining is a promising way for the oxidation removal of B from molten Si. The following reaction of Si oxidation takes place simultaneously:

$$Si_{(l)} + O_{2(g)} = SiO_{2(l)} \qquad [2]$$

The total reaction relating to B removal from molten Si by slag treatment can be represented in Eq. [3], and the partition ratio of B in molar basis L'_B is obtained as Eq. [6].

$$B_{(l)} + \frac{3}{4}SiO_{2(l)} = BO_{1.5(l)} + \frac{3}{4}Si_{(l)} \qquad [3]$$

$$\Delta G^\circ = 45,490 - 24.1T \ \ \mathrm{J/mol}^{[4]} \qquad [4]$$

$$K_3 = \frac{(a_{BO_{1.5}})(a_{Si})^{3/4}}{a_B(a_{SiO_2})^{3/4}} = \frac{(\gamma_{BO_{1.5}}X_{BO_{1.5}})}{(\gamma_B X_B)} \cdot \left(\frac{a_{Si}}{a_{SiO_2}}\right)^{3/4} \qquad [5]$$

$$L'_B = \frac{X_{BO_{1.5}}}{X_B} = \frac{K_3 \cdot (\gamma_B)}{(\gamma_{BO_{1.5}})} \cdot \left(\frac{a_{SiO_2}}{a_{Si}}\right)^{3/4} \qquad [6]$$

where the subscripts l and g in parenthesis donate the liquid and gas standard state, K_3 is the equilibrium constant, a_i represents the activity of component i in the slag or metal phase, and γ_B and $\gamma_{BO_{1.5}}$are activity coefficient of B and $BO_{1.5}$, respectively.

The partition ratio of B between the slag and metal phase is a significant indicator to evaluate the removal of B by slag treatment. According to Eq. [6], it is affected by three terms: (1) the activity coefficient of B in the metal phase, (2) activity coefficient of $BO_{1.5}$ in the slag phase, and (3) oxygen partial pressure, which is controlled by Eq. [2]. Researchers[5–10] investigated a variety of slag systems such as CaO-SiO_2 and SiO_2-CaO-CaF_2 (-Na_2O, -MgO, -BaO, -Al_2O_3-MgO) with the aim for a high partition ratio of B between slag and molten

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Si. Those results are summarized in Figure 1. However, the values were mostly around 2, and the highest reported value was 5.5 when using SiO_2-48.3 mol pct CaO slag at 1823 K (1550 °C). Those values were not high enough to remove B in molten Si from a typical value of 40 ppmw to the allowable content of 0.3 ppmw for solar cell.[11] Therefore, a large amount of slag was needed once, and slag treatment should be repeated several times. The published literature focused only on the optimization of slag compositions to increase the partition ratio of B. Although the increase in the slag basicity decreases the activity coefficient of $BO_{1.5}$, it also decreases the activity of SiO_2, resulting in the limitation of increase in oxygen partial pressure. Therefore, such a contradictory effect results in the low partition ratio of B between slag and molten Si.

On the other hand, the authors have investigated the solvent refining of Si using a Si-Sn alloy.[12] We found a remarkable increase in the activity coefficient of B by the addition of Sn to Si from the equilibrium relation between the Si-Sn melt and SiB_6 or B solid solution.[13] Thus, by applying the slag treatment to Si-Sn melt, higher partition ratio of B can be expected according to Eq. [6].

The separation of refined Si from the solvent is another important issue for a more effective removal of B. We consider the total process for Si refining by using Si-Sn solvent, that is (1) alloying MG-Si with Sn to form the Si-Sn melt, (2) slag treatment, (3) solidification of Si from Si-Sn melt, and (4) collection of the refined Si crystals by acid leaching. On the other hand, Sn is electrically inactive element for solar cell, and as much as 10 ppmw level Sn can be tolerated for the use of solar cell. Although the incorporation of Sn in refined Si is inevitable because of its solid solubility, it can be easily removed by vacuum melting because of its high vapor pressure. Thus, this article was focused on the removal of B by Si-Sn solvent refining with slag.

In the current work, the partition ratios of B between SiO_2-CaO-24 mol pct CaF_2 slags and Si-Sn alloys were measured at 1673 K (1400 °C) by the chemical equilibration technique, varying the compositions of slags and alloys. The required amount of slag for B removal from Si-Sn melt was then discussed for designing the removal of B from Si-Sn melt.

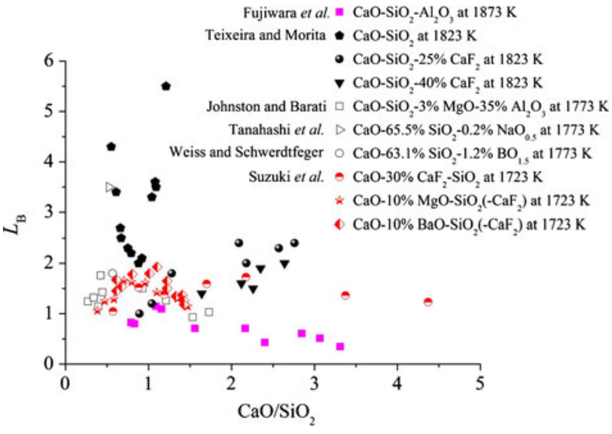

Fig. 1—Relationship between partition ratio of B and CaO/SiO_2 ratio in slag/Si equilibrium.

II. EXPERIMENTAL

The CaO-SiO_2-CaF_2 slag was selected to carry out the experiment below the melting point of Si. The CaF_2 content was fixed as 24 mol pct CaF_2 in the slag to obtain a wide liquid region at 1673 K (1400 °C). For the equilibration of Si-Sn alloy with SiO_2-CaO-24 mol pct CaF_2 slag, a $MoSi_2$ electric furnace connected to a proportional-integral-derivative (PID) controller with a Pt/6 pct Rh–Pt/30 pct Rh thermocouple was used. Three grams of premelted Si-Sn alloys added with 90 to 900 ppmw B were charged in a graphite crucible with mixture of 9 g SiO_2-CaO-24 mol pct CaF_2 slags (CaO/SiO_2 = 0.32 to 4.35). The crucible was then kept at 1673 K (1400 °C) under the Ar gas flow of 200 mL/min for 18 hours, which was predetermined by preliminary experiments. Fluctuation of the temperature in the furnace was maintained within ±1 K. Because the vapor pressure of pure Sn is as high as 12 Pa[14] at 1673 K (1400 °C), the crucible was sealed with a graphite lid. Moisture, CO_2, and oxygen in the Ar gas were removed by passing it through magnesium perchlorate, soda-lime, and magnesium turnings heated at 823 K (550 °C). After equilibrium, the graphite crucible was quickly withdrawn from the furnace and quenched in a water bath. The B, Ca, and Sn contents of the slag and the alloy were analyzed by inductively coupled plasma-atomic emission spectrometry. The Si contents of the slag and alloy were measured by SiO_2 gravimetric method. The CaF_2 content of the slag was determined by the fluoride ion selective electrode method.

III. RESULTS AND DISCUSSION

A. *The Effect of Slag Composition*

The SiO_2-CaO-24 mol pct CaF_2 slags with the CaO/SiO_2 ratio of 0.32 to 4.35 were equilibrated with Si-30.5 mol pct Sn alloys. The final compositions of the slags and alloys are listed in Table I. For samples S-1 to S-5, the alloys showed a good separation from slags.

The slag reacted with Si-Sn alloy in the samples of S-6 and S-7.

The alloy of sample S-6, however, was partially identified and the separation was not observed in sample S-7 due to the remarkable reaction with slag. Thus, the samples S-6 and S-7 were excluded in the following thermodynamic evaluation.

The partition ratio of B between the slag and alloy is defined as (mass pct B in slag)/(mass pct B in alloy). It is plotted against CaO/SiO_2 ratio in Figure 2, together with the reported data where molten Si was equilibrated with CaO-SiO_2-(20 or 33 mol pct) CaF_2 slag at 1823 K (1550 °C)[10] for comparison. The partition ratio of B between slag and Si-Sn melt was increased with the increase in CaO/SiO_2 ratio, and was more than five times higher than that for slag/Si equilibration.

Table I. Final Compositions for the CaO-SiO_2-24 Molecular Percentage CaF_2 Slag System Equilibrated with Si-30.5 Molecular Percentage Sn Alloys at 1673 K (1400 °C) for 18 h

	Final Compositions					
Slag	CaO (mol pct)	SiO_2 (mol pct)	CaF_2 (mol pct)	Sn (ppmw)	B (ppmw)	CaO/SiO_2
S-1	20.5	56.6	22.9	178	105	0.36
S-2	27.4	49.7	23.0	150	121	0.55
S-3	36.2	42.9	20.9	19	122	0.84
S-4	40.1	38.1	21.8	22	118	1.05
S-5	45.6	33.1	21.3	28	123	1.38
S-6	51.0*	25.0*	24.0*	—	129	2.05*
S-7	61.8*	14.2*	24.0*	—	—	4.35*

	Final Compositions				
Alloy	Si (mol pct)	Sn (mol pct)	Ca (ppmw)	B (ppmw)	L_B
S-1	70.1	29.9	405	14.0	7.5
S-2	70.9	29.1	498	13.3	9.1
S-3	71.1	28.9	524	11.0	11.1
S-4	71.5	28.4	672	9.7	12.2
S-5	72.4	27.6	1300	9.6	12.8
S-6	69.5*	30.5*	—	9.2	14.0
S-7	69.5*	30.5*	—	—	

* The initial composition.

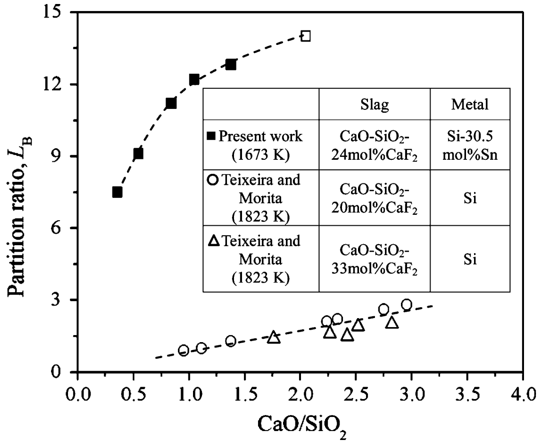

Fig. 2—Relationship between partition ratio of B and CaO/SiO_2 ratio. (□): initial ratio of CaO/SiO_2, where the slag reacted with alloy.

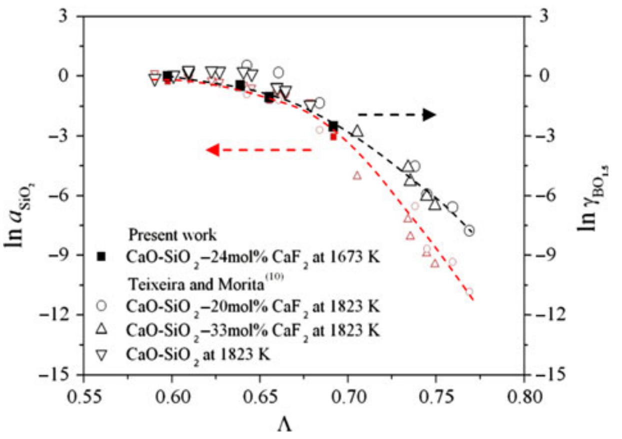

Fig. 3—Relationship between the activity coefficient of $BO_{1.5}$, activity of SiO_2 and the optical basicity of slags.

The activity coefficient of $BO_{1.5}$ can be calculated from equilibrium relations based on Eq. [6] so long as the activities of B, Si, and SiO_2 are known. The activity coefficient of B in the Si-Sn melt was used of the values determined in the current work.[13] The activity of Si in the melt was estimated from the reported excess Gibbs energy of the liquid Si-Sn alloy,[15] where the composition of the Si-Sn-B-Ca melt was converted into that of the Si-Sn binary system, assuming the constant ratio, X_{Si}/X_{Sn}, and the negligible effect of B and Ca on the activity of Si. Zaitsev *et al.*[16] determined the thermodynamic properties of the CaO-SiO_2-CaF_2 system by using the Knudsen mass spectrometry technique and assessed isoactivity contours of SiO_2 at 1700 K (1427 °C) with an associated solution model. The SiO_2 activities of samples S-2 to S-5 were estimated from the reported data of Zaitsev *et al.*[16] by using a regular solution correction from 1700 K to 1673 K (1427 °C to 1400 °C). As the composition of S-1 sample exists in the SiO_2-liquid coexisting region in the assessed phase diagram by Zaitsev *et al.*,[16] it was not employed in thermodynamic evaluation. Thereafter, the activity coefficient of $BO_{1.5}$ is derived from Eq. [6].

The concept of optical basicity was often used to relate the different slag composition and activity coefficient of $BO_{1.5}$ of slag. The optical basicity of pure CaO, SiO_2, and CaF_2 are taken as 1.00, 0.47, and 0.67, respectively.[17] The relationship between the activity coefficient of $BO_{1.5}$ and optical basicity is shown in Figure 3, together with the reported data in CaO-SiO_2 (-CaF_2) system by Teixeira and Morita[10] for comparison. The activity of SiO_2 taken from reported data by

Table II. Final Compositions for the CaO-SiO_2-24 Molecular Percentage CaF_2 Slag System Equilibrated with Si-Sn Alloys for 18 h

	Final Compositions					
Slag	CaO (mol pct)	SiO_2 (mol pct)	CaF_2 (mol pct)	Sn (ppmw)	B (ppmw)	CaO/SiO_2
A-1	44.3	33.9	21.8	28.6	146	1.31
A-2	44.0	34.1	21.9	54.8	181	1.29
A-3	44.9	33.5	21.6	44.5	152	1.34
A-4	45.6	33.1	21.3	28.5	122	1.38
A-5	45.3	33.3	21.4	34.0	245	1.36
A-6	45.5	33.2	21.3	42.3	124	1.37
A-7	45.4	33.2	21.4	27.7	111	1.37
A-8	46.0	32.8	21.1	28.0	32	1.40

	Final Compositions				
Alloy	Si (mol pct)	Sn (mol pct)	Ca (ppmw)	B (ppmw)	L_B
A-1	96.5	3.5	1100	63.5	2.3
A-2	95.0	5.0	1260	70.6	2.6
A-3	80.5	19.5	1140	24.2	6.3
A-4	72.4	27.6	1300	9.6	12.8
A-5	62.9	37.1	888	11	22.3
A-6	52.9	47.1	587	4.2	29.5
A-7	39.4	60.6	549	1.3	85.4
A-8	17.6	82.4	235	0.16	200

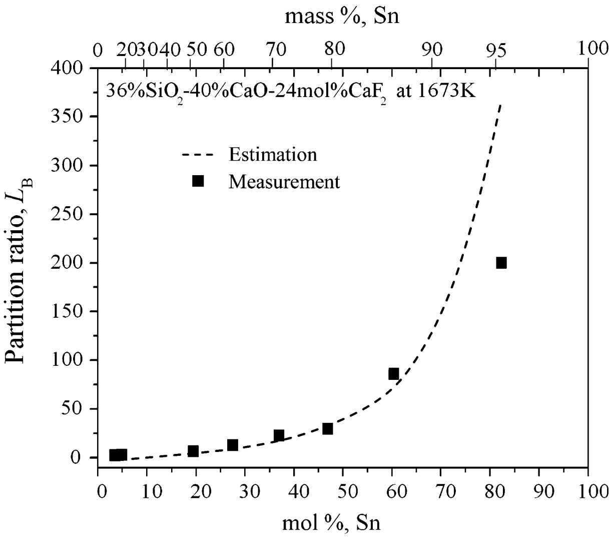

Fig. 4—Relationship between partition ratio of B and Sn content of Si-Sn melt at 1673 K (1400 °C).

Zaitsev *et al.*[16] is also included in Figure 3. The activity coefficient of $BO_{1.5}$ in this study showed a good agreement with the reported data. The activity coefficient of $BO_{1.5}$ and activity of SiO_2 were decreased with an increase in optical basicity.

B. *Dependence of B Partition Ratio on Alloy Composition*

The slag with composition of 40.5 pct CaO-35.5 pct SiO_2-24 mol pct CaF_2 was selected to be equilibrated with the Si-Sn alloys varying the Sn content from 5 pct to 82 mol pct. The final compositions of the samples are listed in Table II.

The partition ratio of B is plotted as a function of Sn content in Figure 4. It was found that the partition ratio of B was remarkably increased with increasing Sn content. The partition function was accounted as much as 200 when the alloy composition was Si-82.4 mol pct Sn. On the other hand, the partition ratio of B is also estimated according to Eq. [6], by using the determined activity coefficient of B,[13] activity coefficient of $BO_{1.5}$ estimated in the previous section and the referred data of SiO_2 and Si activities.[15, 16] The estimated values are also shown in Figure 4 with a dashed line, which shows a good agreement with experimental values.

There are twofold effects by increasing the Sn content in the alloys on the partition ratio of B: an increase in activity coefficient of B and a decrease in activity of Si in the alloy, according to Eq. [6] when the identical slag was used. The activity coefficient of B in the Si-Sn melt was found to be three orders of magnitude larger in the Sn-rich side than that in the Si-rich side.[13] Meanwhile, the oxygen partial pressure was controlled by the equilibrium between SiO_2 and Si, where the activity of Si is decreased with the increase in Sn content, resulting in the increase in the oxygen partial pressure. Thus, an increase of both the activity coefficient of B and the oxygen partial pressure bring a significant increase in partition ratio of B.

As mentioned above, a variety of slags was examined for the removal of B in the slag/Si equilibrium. However, the effect on the partition ratio of B was limited in changing slag chemistry because both high oxygen partial pressure and low activity coefficient of $BO_{1.5}$ were incompatible. In this study, particular interest was focused on the effect of Sn addition, which became the primary factor for increasing the partition ratio of B. The maximum partition ratio of 200 is much higher than the reported ones.

C. *The Required Slag Amount for Removal of B from Si-Sn Melt*

Based on the obtained partition ratio of B as a function of Sn content, a quantitative consideration was performed on the slag amount required for removal of B from Si-Sn melt. According to the mass balance of B, the target content of B in the alloy and removal fraction of B can be calculated by Eqs. [7] and [8]. The repeated slag refining was considered to save the use of slag amount for practical application.

$$[\text{ppmw B}]_{\text{final}} = \frac{[\text{ppmw B}]_{\text{inMG-Si}} \cdot \omega_{\text{Si in alloy}}}{(1 + mL_{\text{B}})^{\text{n}}} \quad [7]$$

$$\text{Removal fraction of B} = \left(1 - \frac{1}{(1 + mL_{\text{B}})^{\text{n}}}\right) \times 100\text{pct} \quad [8]$$

where $[\text{ppmw B}]_{\text{inMG-Si}}$ is the content of B in the initial MG-Si (ppmw) and was set to 40 ppmw, $\omega_{\text{Si in alloy}}$ is the mass fraction of Si in the Si-Sn alloy, and m and n are the mass ratio of slag to alloy and numbers of slag refining, respectively.

For instance, when the alloy and slag compositions are fixed to Si-30.5 mol pct Sn and 40.5 pct CaO-35.5 pct SiO_2-24 mol pct CaF_2, respectively, the removal fraction of B from the melt against mass ratio of slag to alloy (m) with variation of slag refining times (n = 1 to 3) estimated by Eq. [8] is shown in Figure 5 with solid lines. To obtain a 90 pct removal of B by a single slag treatment, the mass ratio of slag to alloy of 0.4 is required. However, by repeating the slag refining two and three times, it decreased to 0.1 and 0.05, respectively. To verify the above estimation, a consecutive slag refining experiment at 1673 K (1400 °C) was

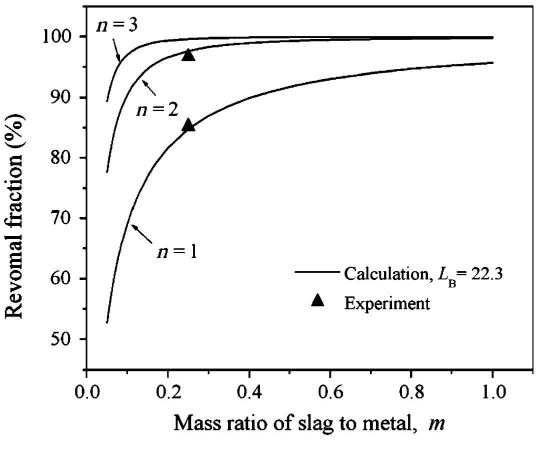

Fig. 5—Relationship between removal fraction of B and mass ratio of slag (40.5 pct CaO-35.5 pct SiO_2-24 mol pct CaF_2) to alloy (Si-40.5 mol pct Sn) with varying numbers of slag refining from 1 to 3.

Table III. Experimental Conditions and Results in a Consecutive Slag Treatment at 1673 K (1400 °C)*

Refining Times	Initial Slag	Initial Alloy	B Content in Slag After Run	B Content in Alloy After Run	Removal Fraction of B
First run	40.5 pct CaO-35.5 pct SiO_2 -24mol pct CaF_2 (6 g)	Si-59.5 mol pct Sn (478 ppmw B) (24 g)	1470 ppmw	70.9 ppmw	85.2 pct
Second run	40.5 pct CaO-35.5 pct SiO_2 -24mol pct CaF_2 (5.75 g)	The alloy after first fun (23 g)*	291 ppmw	15.6 ppmw	96.7 pct

* An approximately 1 g sample fragment was employed for chemical analysis.

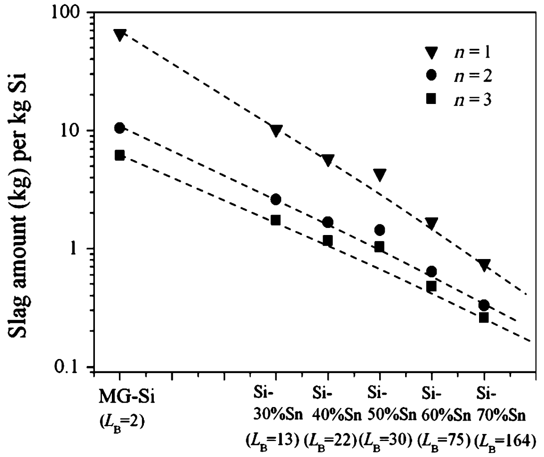

Fig. 6—The required slag amount as a function of alloy composition with varying numbers of slag refining from 1 to 3.

conducted by using an inductive furnace. The experimental conditions and results are listed in Table III.

The removal fraction of B in each run is plotted in Figure 5 and shows a good agreement with the calculated lines. It was thus confirmed that the parameters for slag refining such as mass ratio of slag to metal and refining times should be designed well in Eq. [7] to achieve to the removal of B.

The required amount of 40.5 pct CaO-35.5 pct SiO_2-24 mol pct CaF_2 slag per unit mass of Si for removal of B to 0.3 ppmw with varying numbers of slag refining is estimated and shown in Figure 6. Here, it is provided that MG-Si containing 40 ppmw B was alloyed with pure Sn to prepare the Si-30 mol pct Sn to –70 mol pct melts. The required amount of slag was decreased with the increase in partition ratio of B by adding Sn. When the slag treatment was conducted once, the required amount was decreased from 66.2 to 10.3, 4.3, and 0.75 by adding 30 mol pct, 50 mol pct, and 70 mol pct Sn, respectively, and it was decreased from 6.2 to 1.7, 1.0, and 0.26 when conducting three times. Therefore, a significant amount of slag can be saved for removal of B by the addition of Sn to Si in slag refining process.

IV. CONCLUSIONS

In the current study, higher partition ratio of B was clarified when the Si-Sn melt was equilibrated with the CaO-SiO_2-24mol%CaF_2 slag, and the following results were obtained.

1. The partition ratio of B between slag and alloy phase was increased with the increase in the ratio of CaO/SiO_2 at initial composition of Si-30.5 mol pct Sn alloy. The activity coefficient of $BO_{1.5}$ and activity of SiO_2 were decreased with the increase in optical basicity.
2. It was found that the partition ratio of B was remarkably increased from 2 to 200 with the increase in the Sn content from 5 pct to 82 mol pct at the fixed slag composition of 40.5 pct CaO-35.5 pct SiO_2-24 mol pct CaF_2. This is owing to twofold effects by increasing Sn content on the partition ratio of B, both activity coefficient of B and oxygen partial pressure are increased.
3. As the higher partition ratio of B was obtained, the required amounts of slag used for B removal from Si-30, 50, and 70 mol pct Sn melts were only 15.6 pct, 6.5 pct, and 1.2 pct of that used for the removal of B directly from MG-Si without Sn addition in a single slag treatment.

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