

Removal of boron and phosphorus from silicon using CaO-SiO₂-Na₂O-Al₂O₃ flux

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Abstract: In the present study a combination of solvent refining and flux treatment of silicon was carried out, aiming to remove boron and phosphorus to acceptable levels for solar applications. Metallurgical grade silicon (MG-Si) was alloyed with pure copper, and the alloy was subjected to a refining by liquid CaO-SiO₂-Na₂O-Al₂O₃ slags at 1500 °C. The distributions of B and P between the slags and the alloy was examined under a range of slag compositions, varying in CaO:SiO₂ and SiO₂:Al₂O₃ ratios and the amount of Na₂O. The results showed that both basicity and oxygen potential have a strong influence on the distributions of B and P, and the basicity and the oxygen potential competed with each other to control the distributions. When the oxygen partial pressure (P_{O_2}) was higher than a critical oxygen partial pressure, distributions increased with basicity, and in the low P_{O_2} range the distributions increased with oxygen potential. The addition of Na₂O to the slag system was found to increase the distributions of boron and phosphorus. A thermodynamic evaluation of the system showed that alloying copper with MG-Si leads to substantial increase of boron distribution coefficient. The highest boron and phosphorus distribution coefficients are 47 and 0.7, respectively. Using these optimum slags to reduce boron and phosphorus in MG-Si to solar grade level, a slag mass about 0.28 times and 27 times mass of alloy would be required, respectively.

Key words: Metallurgical silicon, Solar silicon, Slag treatment, Boron, Phosphorus.

1. Introduction

The use of fossil fuels has been associated to the release of greenhouse gases, leading to global warming. As a consequence the need for renewable and clean energy has increased. Among various renewable energy sources, such as biomass, wind and hydro power, solar energy is most abundant, noting that Sun's energy received by earth in one minute, if fully harvested, can supply world's energy demand of an entire year¹. However, the high manufacturing costs of photovoltaic cells have hampered the use of solar energy even with increasing government subsidies. Today's US residential solar electricity price ranges from 30 to 66 cents/kWh, which is about 3 to 6 times larger than the fossil fuel or nuclear energy based electricity^{2, 3}. The largest single cost item of the photovoltaic cells is the cost of high purity silicon, accounting for one third of the finished module cost.

In recent years a lot of research has been conducted on refining of metallurgical grade silicon (MG-Si, purity>96%) to solar grade silicon (SoG-Si), with the ultimate goal of reducing the production cost. Metallurgical refining route has drawn the most attention due to the low operational cost. The reduction of the impurities in silicon to a certain level has to be achieved for a high efficiency solar cell, since the impurities dictate the device performance. With increasing amount of impurities in a solar cell, the diffusion length of carriers (hole-electron pairs) decreases, which results in the recombination of the carriers before reaching the junction. As a result, the carriers do not contribute to current generation,

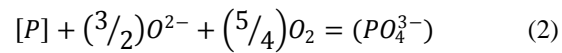
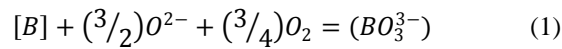
and the cell efficiency is dropped⁴. Among various elements, Al, As, B, and P are considered most detrimental due to the doping effect they have on Si.

Directional solidification as a well-established process, can remove those impurities with low segregation coefficients, but has little effect on boron and phosphorous that possess segregation coefficients substantially above any other impurity^{5,6}.

Vacuum refining, an alternative metallurgical purification method may be used for removing elements with high vapor pressure, such as P and Ca⁷. However, long processing time and the need for extra low vacuum levels make this method unattractive.

Recrystallization of silicon from alloys is another possible method of removing boron and phosphorous. By alloying silicon with other metals, such as aluminum which have higher affinity for impurities in liquid phase, the segregation coefficients of boron and phosphorous would be decreased⁸. During solidification, pure primary silicon phase in dendrite form precipitates out first, and impurities are remained in the eutectic structure. However, silicon recrystallization may not be a cost effective method, since the concentrations of boron and phosphorous in the left over alloy will quickly rise above the acceptable levels for silicon recrystallization. The alloy must either be cleaned or sold after several refining cycles.

Oxidizing/slugging refining is another metallurgical refining technique. In the presence of a basic flux and under oxidizing conditions, boron and phosphorous form stable acidic oxides that report to the slag phase, according to Reactions 1 and 2.



Suzuki *et al.*⁹, have determined the equilibrium distribution of boron for a number of slag systems, such as CaO-SiO₂, CaO-CaF₂-SiO₂, CaO-MgO-SiO₂(-CaF₂) and CaO-BaO-SiO₂(-CaF₂), as a function of slag compositions at 1723 to 1873 K under Ar atmosphere. The use of SiO₂ in slag reduces the basicity, but prevents unacceptably high losses of silicon to the slag. Teixeira *et al.*¹⁰, have shown that increasing Na₂O in the flux increased the boron distribution ratio, L_B and decreased the flux melting temperature. However, it has been discussed that under optimized conditions and highest distribution ratios of 6 and 3 for boron and phosphorous respectively, still a prohibitive amount of slag is required for sufficient refining^{10, 11}.

A fluxing approach to refine MG-Si, along with alloying with pure copper in the molten state is proposed in the present investigation. This treatment combines solvent refining and slag treatment techniques in one step to achieve SoG-Si specification. Silicon is alloyed with copper to (a) increase the alloy density for easy phase separation between the molten slag and the alloy, (b) decrease the alloy melting temperature, enabling the use of more reactive flux at low temperature that is otherwise very corrosive (at high temperature), and (c) allow precipitation of silicon from melt and improve its purity through gettering mechanism. The solvent refining aspect of the study will be discussed in future publications.

2. Experimental

2.1 Experimental preparation and procedure

The concentrations of boron and phosphorus in MG-Si were lower than 20 ppmw, which makes the analysis of the purified silicon difficult. Therefore, the boron and phosphorus doped 30wt%Si-Cu alloys were used to carry out all experiments. Boron and phosphorus in the doped alloy were maintained around 3000ppm each. The CaO-Na₂O-Al₂O₃-SiO₂ fluxes with the desired composition were weighted and mixed thoroughly before each experiment. 10 gram of fluxes was charged into an alumina crucible, and the crucible was heated to 1500 °C in a resistance furnace under Ar atmosphere. When the fluxes were fully molten, 1 gram of solid doped alloy was released into the molten flux. At the end of the experiment, the crucible containing the molten alloy and slag was quenched in a water bath. After drying, the slag and metal phases were separated from crucible and ground to powder for acid digestion and ICP analysis. On the basis of boron and phosphorus contents in the alloys after a number of refining experiments with same slag at different reaction times (Figure 1), a reaction time of 10 min was used in subsequent experiments as the equilibrium.

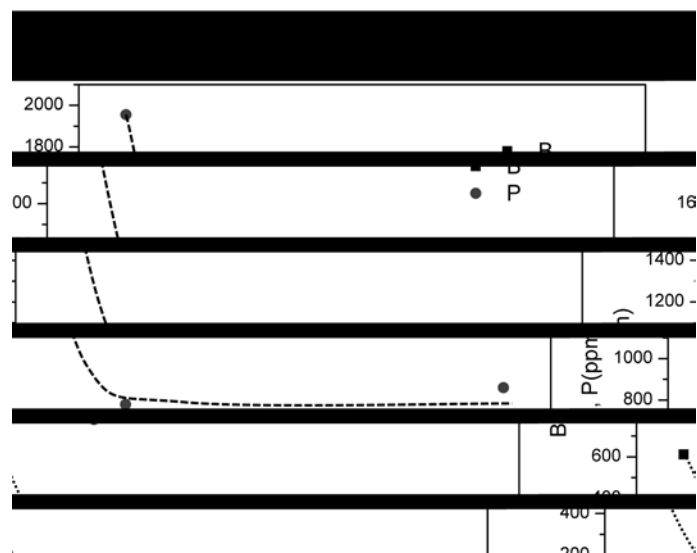


Fig 1. Variation in B and P contents in doped Si-Cu alloys over time for starting composition of 32wt%CaO-20%Na₂O-24%Al₂O₃-24%SiO₂.

2.2 Analysis

Cu-Si alloys before and after refining were digested in a mixture of nitric and hydrofluoric acids in Teflon beaker at about 45 °C and the B and P in the solutions were analyzed by ICP-AES (Optima ICP 7100DV) in Analyte LabTM, University of Toronto. Slags were fused with potassium hydroxide in Zirconium crucible at around 450 °C and then digested in diluted hydrochloric acid prior to ICP analysis for the trace elements, such as B, P and Fe. The major constituents of the slags were measured by XRF.

3. Results

The distribution coefficients and removal efficiencies of B and P were calculated from the experimental results. The distribution coefficient is the ratio of the concentration (ppm) of impurity M in the slag phase to that in the metal phase after refining. The ratio can be expressed as

$$L_M = \frac{(M)}{[M]} \quad (3)$$

As seen in Table 1, the final slag composition determined by XRF was different from its initial composition due to the partial oxidation of silicon and dissolution of alumina crucible in the slag. The distribution data are accordingly presented as a function of the final slag composition.

Table 1. Composition of slags before and after equilibrium refining experiments.

Test ID	Initial Composition (wt%)				Final composition (wt%)			
	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO
Test 1-1	20	24	20	36	11.0	26.2	26.9	34.3
Test 1-2	20	24	20	36	11.0	25.2	27.6	34.0
Test 1-3	20	24	28	28	15.7	26.3	31.5	26.0
Test 1-4	20	24	31	25	17.0	24.2	34.8	22.6
Test 1-5	20	24	36	20	19.7	24.4	37.3	18.2
Test 1-6	20	24	41	15	21.1	23.8	41.2	13.5
Test 1-7	20	24	46	10	20.8	23.0	46.5	9.0
Test 2-1	20	8	36	36	14.1	18.0	36.9	29.8
Test 2-2	20	11	33	36	13.5	18.5	35.7	31.3
Test 2-3	20	14	30	36	12.6	19.6	34.3	32.5
Test 2-4	20	17	27	36	13.3	20.6	32.1	33.5
Test 2-5	20	20	24	36	11.8	22.4	30.4	33.9
Test 2-6	20	26	18	36	10.1	28.5	25.5	35.2
Test 3-1	0	21.3	33.8	45	0.2	20.1	36.4	42.4
Test 3-2	5	20.2	32.1	42.8	4.6	21.6	34.0	38.7
Test 3-3	10	19.1	30.4	40.5	6.8	31.6	27.6	33.5
Test 3-4	20	17	27	36	13.3	20.6	32.1	33.5
Test 3-5	30	14.9	23.6	31.5	17.7	20.8	31.7	28.9
Test 3-6	40	12.8	20.3	27	26.4	19.0	27.1	25.7

3.1 Varying CaO: SiO₂

The influence of slag basicity on removal of impurities from Si-Cu alloy was investigated by varying CaO:SiO₂ ratios of the CaO-Na₂O-Al₂O₃-SiO₂ slag. Values of L_M are illustrated in Figure 2 against the final CaO:SiO₂ ratios. All experiments were conducted in alumina crucibles with CaO-Na₂O-Al₂O₃-SiO₂ slag in which Na₂O and Al₂O₃ were initially fixed at 20 and 24wt%, respectively. For both boron and phosphorus, the strong dependence of L_M on basicity is clear. The distribution coefficients increase linearly with basicity over the entire range studied. The values of L_B are much greater than unity for all experiments, and the maximum reached is around 31, indicating that boron reports preferentially to the slag phase. Although L_P increases with basicity, the actual values of L_P are all less than unity, indicating that phosphorus favors the alloy phase.

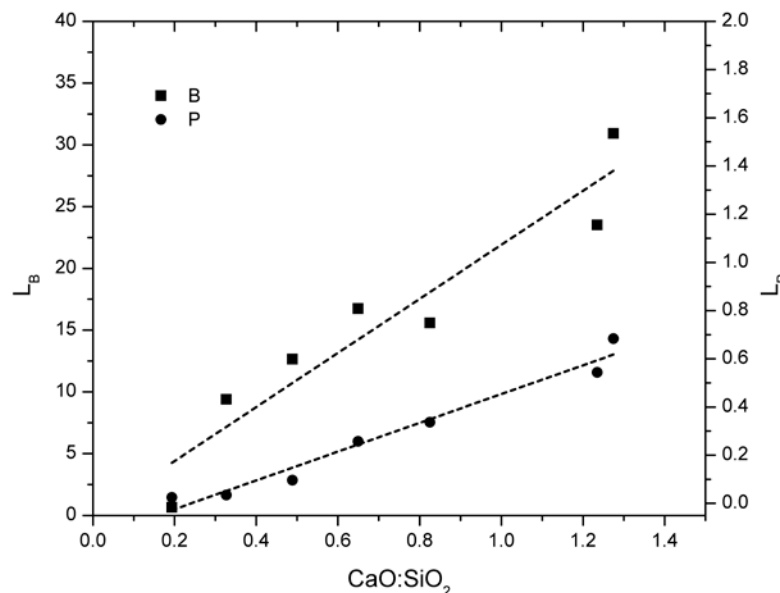


Fig 2. Distribution coefficients of impurities between slag and Si-Cu alloy as a function of the final basicity of the slag equilibrated at 1500 °C.

3.2 Varying SiO₂:Al₂O₃

The influence of oxygen potential of the slag on removal of impurities from Si-Cu alloy was investigated by varying SiO₂:Al₂O₃ ratios of the CaO-Na₂O-Al₂O₃-SiO₂ slag. Values of L_M are illustrated in Figure 3 against final SiO₂:Al₂O₃ ratios. All experiments were conducted in alumina crucibles with CaO-Na₂O-Al₂O₃-SiO₂ slag in which CaO and Na₂O were initially fixed at 36 and 20wt%, respectively. Values for boron and phosphorus follow a similar trend as they increase with increasing ratio of SiO₂:Al₂O₃ until reach a maximum observed at SiO₂:Al₂O₃ 1.7. These results suggest that the distribution coefficients of boron and phosphorus are strongly affected by both the oxygen potential and the basicity of the slag in the studied range of SiO₂:Al₂O₃ ratio. With increasing in SiO₂:Al₂O₃, on one hand the oxygen potential is increased, and on the other hand, the slag becomes less basic as SiO₂ is more acidic in nature than Al₂O₃.

This is evident by the fact that the optical basicity (Λ) of SiO_2 (0.48) is lower than that of Al_2O_3 (0.61)¹². The values of L_B are still much greater than unity for all experiments, and the maximum reached is around 46, indicating again the preference of boron for the slag phase. All L_P values are less than unity, indicating a preference to remain in the alloy phase.

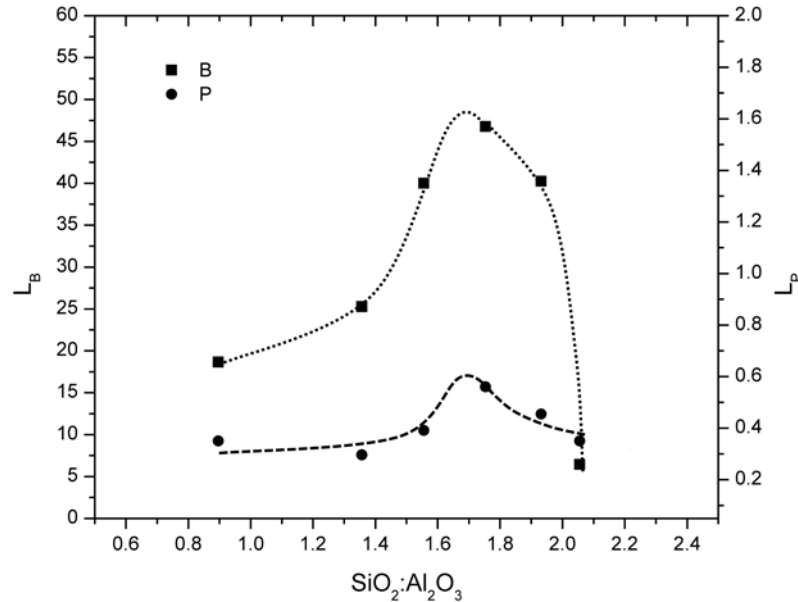


Fig 3. Distribution coefficients of impurities between slag and Si-Cu alloy as a function of varying $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios of slag equilibrated at 1500 °C.

3.3 Addition of Na_2O to $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ slag

The influence of Na_2O addition to the slag on removal of impurities from Si-Cu alloy was investigated by varying the amount of Na_2O added into the $\text{CaO}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ slag. Values of L_M are illustrated in Figure 4 against the starting weight percentage of Na_2O to the slag. All experiments were conducted in alumina crucibles with $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ slag in which the mass ratio of $\text{CaO}:\text{Al}_2\text{O}_3:\text{SiO}_2$ remained constant at 45:21.25:33.75. The duration of the experiments was 10 min, and the samples were prepared with varying Na_2O content: 0, 5, 10, 20 and 30wt%. For both boron and phosphorus, the distribution coefficients go through a maximum at 10wt% Na_2O . Further addition of Na_2O to the slag decreases the distribution coefficients. For phosphorus, the effect of Na_2O on L_P is similar at 30wt% and at 5wt%. By comparing Na_2O free slag (0wt% Na_2O in Figure 4), the distributions of boron and phosphorus can be increased up to 2 and 7 times, respectively.

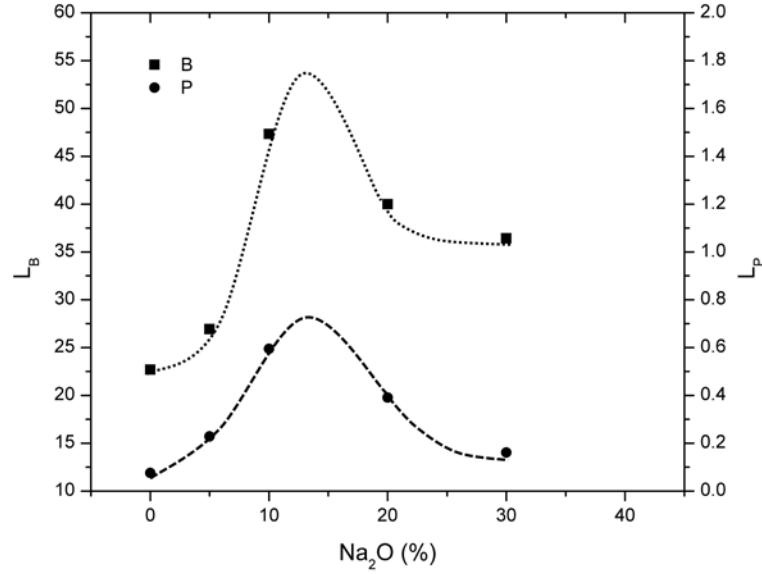
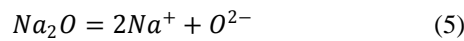
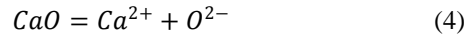


Fig 4. Effect of addition of Na₂O on the distribution coefficients of impurities for CaO- Al₂O₃-SiO₂ slag at 1500 °C.

4. Discussion

4.1 Dependence of distributions on basicity and oxygen potential

As mentioned earlier in Reactions 1 and 2, boron and phosphorus enter a basic slag phase as oxides with silica acting as the oxidizing agent. In each case, oxygen ions are provided by basic oxides such as lime and sodium oxide and the oxygen partial pressure (P_{O_2}) is from equilibrium between Si and SiO₂.



The equilibrium constants for Reaction 1 and 2 is shown in Equations (7) and (8), where f_M and $f_{MO_n^{3-}}$ are the activity coefficients of species M and MO_n^{3-} in liquid alloy and slag relative to 1 mass pct of M and MO_n^{3-} , respectively. Constants $C_{1,2}$ are conversion factors of mass% of BO_3^{3-} and PO_4^{3-} to mass% of boron and phosphorus in the slag phase, and constant $C_{3,4}$ are conversion factors of the reference state for the activity coefficients of species M in liquid alloy from 1 mass pct M to pure liquid M.

$$K_1 = \frac{a_{BO_3^{3-}}}{a_B \cdot a_{O_2}^{3/4} \cdot a_{O^{2-}}^{3/2}} = \frac{C_1 \cdot (B) \cdot f_{BO_3^{3-}}}{[B] \cdot f_B \cdot P_{O_2}^{3/4} \cdot a_{O^{2-}}^{3/2}} = \frac{C_1 \cdot (B) \cdot f_{BO_3^{3-}}}{C_3 \cdot [B] \cdot \gamma_B \cdot P_{O_2}^{3/4} \cdot a_{O^{2-}}^{3/2}} \quad (7)$$

$$K_2 = \frac{a_{PO_4^{3-}}}{a_P \cdot a_{O_2}^{5/4} \cdot a_{O^{2-}}^{3/2}} = \frac{C_2 \cdot (P) \cdot f_{PO_4^{3-}}}{[P] \cdot f_P \cdot P_{O_2}^{5/4} \cdot a_{O^{2-}}^{3/2}} = \frac{C_2 \cdot (P) \cdot f_{PO_4^{3-}}}{C_4 \cdot [P] \cdot \gamma_P \cdot P_{O_2}^{5/4} \cdot a_{O^{2-}}^{3/2}} \quad (8)$$

In terms of distribution coefficients, Equations (7) and (8) can be expressed as Equations (9) and (10), where constants C_5 and C_6 are ratios of C_1 to C_3 and C_2 to C_4 , respectively, and K_6 is the equilibrium constant for Reaction 5.

$$L_B = \frac{(B)}{[B]} = K_1 C_5 \frac{\gamma_B \cdot P_{O_2}^{3/4} \cdot a_{O_2}^{3/2}}{f_{BO}^{3/2}} = K_1 C_5 \frac{\gamma_B \cdot a_{O_2}^{3/2}}{f_{BO}^{3/2}} \cdot \left(\frac{K_6 \cdot a_{SiO_2}}{a_{Si}} \right)^{3/4} \quad (9)$$

$$L_P = \frac{(P)}{[P]} = K_2 C_6 \frac{\gamma_P \cdot P_{O_2}^{5/4} \cdot a_{O_2}^{3/2}}{f_{PO}^{3/2}} = K_2 C_6 \frac{\gamma_P \cdot a_{O_2}^{3/2}}{f_{PO}^{3/2}} \cdot \left(\frac{K_6 \cdot a_{SiO_2}}{a_{Si}} \right)^{5/4} \quad (10)$$

Due to their small concentrations in Si-Cu and slag phases, it may be assumed that the activity coefficients of boron, phosphorus (γ_B, γ_P) and their oxides ($f_{BO}^{3/2}, f_{PO}^{3/2}$) do not change considerably over the refining process for a particular system. As shown in Equations (9) and (10), the distributions of boron and phosphorus are function of oxygen potential and basicity. In the varying $SiO_2:Al_2O_3$ system, the P_{O_2} was lower for the small ratio, so the observed increase in L_B and L_P with varying $SiO_2:Al_2O_3$ ratio in this system is because of increasing P_{O_2} . However, once the P_{O_2} is beyond the $P_{O_2,critical}$, the effect of the slag basicity overcomes the effect of oxygen potential, leading to a drop in distributions. Distribution coefficients for boron and phosphorus in the varying Na_2O system follow a similar trend to those observed in the varying $SiO_2:Al_2O_3$. However, Na_2O addition increased distribution coefficients as Na_2O has a high optical basicity ($\Lambda=1.15$) than all other slag constituents¹². At the expense of having a highly basic slag, the P_{O_2} in turn is reduced due to stronger effect on lowering a_{SiO_2} . In the system with varying $CaO:SiO_2$, P_{O_2} was high. Even with the highest ratio at 1.3, the P_{O_2} was still above the $P_{O_2,critical}$. Therefore, over the entire range of $CaO:SiO_2$ studied, it is apparent that basicity always has a stronger influence than P_{O_2} on the boron and phosphorus removal, as is evident from the increase in the L_M .

Considering the effect of basicity, phosphorus should be easier to be removed to a basic slag, as it has a more acidic oxide ($\Lambda =0.4$) than boron ($\Lambda =0.42$)¹². However, the effect of oxygen potential should be stronger on boron, as its oxide is more stable than phosphorus. In addition to these two factors, the activity coefficient of boron or phosphorus influences their distributions. The results show that the combined effect of all these factors gives rise to more favorable removal of boron, under the examined experimental conditions.

4.2 The effect of alloying copper on distribution of boron

The distribution coefficient of boron in the present work is considerably higher than those reported by Teixeira and Morita¹⁰ and Johnston and Barati¹¹. Although small variations could be attributed to the different slag composition, the reason for such a significant difference is believed to be the effect of alloying. In their experiments, slag was used to treat MG-Si, while in the present study, Si-Cu alloy was subjected to slag treatment. Comparing to MG-Si system, for the 30wt%Si-Cu alloy, the activity of silicon (a_{Si}) in the liquid alloy relative to the pure silicon is decreased to 0.152 from almost 1 in the liquid silicon¹³. As a result, $P_{O_2}^{3/4}$ was increased 4 times in the current study. Also, it is expected that presence of copper affects the activity coefficient of boron. There is no data on activity coefficient of boron (γ_B) in the liquid Si-Cu. The value of γ_B , however is higher in liquid copper (0.24) than that in liquid silicon (0.14)^{14,15}. It is therefore expected that in the Cu-Si alloy, the activity coefficients of boron is higher than that in MG-Si, which

according to Equation (9) should lead to higher L_B . Assuming a similar slag chemistry in either case, the ratio of the distribution of boron in current work to that reported by Teixeira and Morita and Johnston and Barati is expressed by Equation (11). This ratio can be in the range of 4-23 depending on the actual value of γ_B in the liquid alloy.

$$R = \frac{L_{B,Si-Cu}}{L_{B,MG-Si}} = \left(\frac{\gamma_{B,Si-Cu}}{\gamma_{B,MG-Si}} \right) \cdot \left(\frac{P_{O_2,Si-Cu}}{P_{O_2,MG-Si}} \right)^{3/4} = \left(\frac{\gamma_{B,Si-Cu}}{\gamma_{B,MG-Si}} \right) \cdot \left(\frac{a_{Si,MG-Si}}{a_{Si,Si-Cu}} \right)^{3/4} \quad (11)$$

4.3 Impurity removal efficiency

Removal efficiency (R) of impurity can be expressed as a function of L_M shown as Equation (12), where m_{Si} and m_{slag} are the mass of silicon and slag, respectively.

$$R = \frac{L_M}{L_M + \frac{m_{Si}}{m_{slag}}} \quad (12)$$

In the present work, the highest distribution coefficients were 47 and 0.7, for boron and phosphorus respectively. To reduce boron and phosphorus in a typical MG-Si from 15 and 20 ppmw to the final level 1 ppmw each, the required removal efficiencies are 93% for boron and 95% for phosphorus. To achieve this reduction with the slags that yielded the highest L_M , the slag mass is roughly 0.28 times that of alloy for treatment of boron and 27 times that of alloy for treatment of phosphorus. It thus appears that boron removal may be achieved with a reasonable slag mass while meeting the desired phosphorus level may be impractical for industrial practices due to high processing cost and technical challenges associated with large slag/metal mass. These removal efficiencies are however for the slag treatment only. It is expected that the silicon dendrites recovered from the alloy will have higher purity than the molten Cu-Si. This will affect the actual slag mass required, and will be presented in our future reports.

5. Conclusions

The distributions of boron and phosphorus between CaO-SiO₂-Na₂O-Al₂O₃ slags and Si-Cu alloy was examined at 1500 °C by varying in CaO:SiO₂ and SiO₂:Al₂O₃ ratios and the amount of Na₂O. It was found that the distribution coefficient is strongly influenced by both basicity and oxygen potential. However the two factors compete with each other to control the distributions, since increasing the basicity of the slags is accompanied by a decrease in oxygen potential due to the decrease in SiO₂ content. The critical oxygen partial pressure ($P_{O_2,critical}$) was found useful to identify the dominant parameter. When the P_{O_2} was smaller than $P_{O_2,critical}$, oxygen potential had a stronger influence on distributions, and the distributions increased with increasing P_{O_2} ; when P_{O_2} was higher than $P_{O_2,critical}$, basicity dominated distributions, and the values increased with increasing basicity. It is suggested that a strongly basic slag with its P_{O_2} at the critical value would be most useful for extracting boron and phosphorus. Due to the relatively low value of distribution coefficient of phosphorus, it may not be practical to remove phosphorus with current studied slag system, but this slag treatment would reduce boron to the required level for SoG-Si with a single slagging step and small amount of slag (28wt% of treated alloy).

Acknowledgement

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