REMOVING BORON FROM METALLURGICAL GRADE SILICON BY A HIGH BASIC SLAG REFINING TECHNIQUE

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Abstract

A new purification method of removing boron from metallurgical grade silicon (MG-Si) using a high basicity slag was developed in this paper. The typical impurities Al, Ca, Ti, P etc in MG-Si can be removed by the binary calcium silicate slag and it is especially efficient for removing impurity Boron. It was found that the maximal distribution coefficient of boron between calcium silicate slag and silicon reaches to 1.57 when the mass ratio of CaO/SiO$_2$ was 1.5 and the composition was 60%CaO-40%SiO$_2$. It showed that the oxidizability of calcium silicate slag was affected and restricted by the basicity and the mass ratio of acid oxide SiO$_2$ slag according to the thermodynamic relationship. The boron concentration in MG-Si can be reduced from $18 \times 10^{-6}$ to $4.5 \times 10^{-6}$ and $1.4 \times 10^{-6}$, respectively, when using the ternary slags 40.5%CaO-49.5%SiO$_2$-10%Li$_2$O and 32CaO-38%SiO$_2$-30%Li$_2$O.

Keywords: Metallurgical grade silicon; boron; molten slag; basicity; distribution coefficient

1. Introduction

Silicon is widely used as a photoelectric conversion material due to its relatively low cost and high performance [1] and silicon-base solar cells are a conventional and low-cost semiconductor material applied in photovoltaic (PV) technology with at least 90% of photovoltaic market [2, 3]. Presently, the market demand for solar grade silicon (SoG-Si) has been growing rapidly. In order to meet the high demands on the purity of solar grade silicon (SoG-Si) for a target purity of 99.9999% (6 nines), some inexpensive metallurgical purification techniques have been developed to purify metallurgical grade silicon (MG-Si) to SoG-Si [4-6].

It is well known that boron is an especially obstinate impurity element that is difficult to be removed from MG-Si as a result of its large segregation coefficient (0.83) in silicon and its low volatility compared to silicon [7]. The molten slag refining is a traditional method using in the purification of steel making [8] and it was also proved that the molten slag refining based on calcium silicate system is an efficient agent of removing boron from molten metallurgical grade silicon (MG-Si). Impurity boron in MG-Si can be oxidized into boric oxide, which will then enter a basic slag based on calcium silicate system in the form of lime borate [9-11].

In previous studies, Diet [12] described that impurity boron in silicon can be reduced from $18 \times 10^{-6}$ to $1 \times 10^{-6}$ using a calcium silicate slag in an arc furnace. Johnston et al. [13] studied the effects of basicity and oxygen potential of Al$_2$O$_3$-CaO-MgO-SiO$_2$ and Al$_2$O$_3$-BaO-SiO$_2$ slags on removing boron and found that the removal efficiency of boron reached to 80%. Li et al. [14] reported that boron in MG-Si was successfully reduced from $15 \times 10^{-6}$ to $2 \times 10^{-6}$ using a ternary slag CaO-SiO$_2$-Al$_2$O$_3$ by an electromagnetic induction slag melting (EISM) method. In this paper, the mechanism of removing boron using molten slag based on CaO-SiO$_2$ system was studied and then the effects of slag composition and slag basicity on removing boron were primarily investigated by using an high basic slag refining technique in an induction heating method.

2. Experimental

The metallurgical grade silicon block with a boron concentration of $18 \times 10^{-6}$ was pulverized into powder
with a particle size of 50-200 μm. At the same time, the reagent grade chemicals of CaO, SiO₂, Li₂O and K₂O were prepared and the different composition of binary and ternary slag systems CaO-SiO₂, CaO-SiO₂-Li₂O and CaO-SiO₂-K₂O were obtained in advance for slag refining. The metallurgical grade silicon powder and the slags were respectively mixed with different ratio of slag to silicon. Then, the mixture was loaded to a graphite crucible, which was put into a quartz tube of the high frequency induction furnace. The quartz tube was blown argon (Ar) for protection. The crucible was heated up for removing boron at 1600 °C for 2h. The experimental installation was shown in Figure 1. Lastly, the experiment was completed and the refined slag and silicon from cooled sample was drawn out for a chemical analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Elan-5000A USA).

3. Results and discussion

3.1. Distribution ratio of boron between calcium silicate slag and silicon

The boron in silicon (expressed as [B]) can be oxidized into boric oxide by free oxygen ion and oxygen. The generated boric oxide will enter a basic slag phase based on calcium oxide in the form of negative ion BO₃²⁻ and a calcium borate phase is finally generated via the ionic Eq. (1).

\[ \text{[B]} + \frac{3}{2} \text{O}^2- + \frac{3}{4} \text{O}_2 = (\text{BO}_3)^2- \] (1)

The deboronization ability of calcium silicate slag from MG-Si is usually expressed with the distribution coefficient of boron \((L_B)\) defined as Eq. (2) [15].

\[ L_B = \frac{w_{(B)}}{w_{(B)}} \] (2)

Where \(w_{(B)}\) and \(w_{(B)}\) represent the equilibrium concentrations of boron in the refined silicon and the refined slag, respectively. In order to study the distribution ratio of boron between CaO-SiO₂ binary slag and refined silicon, the experiments of removing boron from MG-Si with different composition of CaO/SiO₂ were carried out at 1600 °C. The mass ratio of slag to MG-Si and the refining time were 1:1 and 3h, respectively. The boron concentrations in the refined silicon and the refined slag were then obtained. The distribution coefficient of boron are calculated and shown in Figure 2.

The concentration of boron in silicon reduces with the increase of the ratio of CaO in calcium silicate slag and on the contrary it increases in slag. However, the variation trend of boron concentrations in silicon and slag are reversed when the mass ratio of CaO/SiO₂ is more than 1.5. It is found that the concentration of boron in refined silicon reduces to about 4×10⁻⁶ with 1.5 of CaO/SiO₂ mass ratio and it was also found from the distribution coefficient curve that the maximal value of \(L_B\) reaches to 1.57 with 1.5 of CaO/SiO₂ mass ratio. This shows that a satisfied result of removing boron from MG-Si is difficult using a calcium silicate binary slag and the optimal composition is 60%CaO-40%SiO₂.

It is reported that the efficiency of removing boron
can be improved by increasing the basicity of slag [13]. The basicity values of some oxides are listed in Table 1 and it is calculated that the optical basicity of CaO-SiO$_2$ binary slag is 0.71 according to Eq. (3).

$$\Lambda = \varepsilon(x_{CaO} - \Lambda_{CaO} + 2x_{SiO2} - \Lambda_{SiO2}) / (x_{CaO} + 2x_{SiO2})$$

(3)

Where, $\Lambda$ represents the basicity of molten slag. $\Lambda_{CaO}$ and $\Lambda_{SiO2}$ are the optical basicities of oxides CaO and SiO$_2$. $x_{CaO}$ and $x_{SiO2}$ are mole fractions of CaO and SiO$_2$ in slag, respectively.

### 3.2. Effects of slag basicity on removing boron

In order to study the effect of slag basicity on removing boron, the basic oxides Li$_2$O and K$_2$O were added to a calcium silicate with the composition of 45%CaO-55%SiO$_2$. The compositions of ternary refining slag systems are shown in Table 2.

The refining experiments were carried out in the induction furnace at 1600 °C with the amounts of Li$_2$O and K$_2$O in ternary slag varying from 2.5 -20% and 3 - 40%, respectively. The mass ratio of ternary slag to Mg-Si and the refining time were 1:1 and 2h, respectively. The basicities of ternary slags CaO-SiO$_2$-Li$_2$O and CaO-SiO$_2$-K$_2$O can be calculated as Eqs. (4) and (5).

$$\Lambda = \sum_{B=1}^{2} x_{B} \Lambda_{B}$$

(4)

$$x_{B} = n_{B} x_{B} / \sum_{B=1}^{2} n_{B} x_{B}$$

(5)

Where $\Lambda_{B}$ represents the optical basicity of oxide B. $x_{CaO}$ and $x_{SiO2}$ are the mole fraction of oxide B and the mole fraction of oxygen ion in oxide B, respectively. $n_{B}$ represents the amount of oxygen atom in the molecule of oxide B.

Figure 3 shows the variation trend of boron concentration in the refined silicon with 2.5 -20% of Li$_2$O in the ternary refining slag CaO-SiO$_2$-Li$_2$O. It is calculated according to Eqs. (4) and (5) that the basicity of this ternary slag varies from 0.65 to 0.73. It is found that the boron concentration in the refined silicon reduces with the increase of Li$_2$O mass ratio in slag and it reaches to about $4.5 \times 10^{-6}$ with 10% of Li$_2$O mass ratio. The addition of Li$_2$O increases the basicity of slag, which improves the deboronization ability of calcium silicate slag. However, it is not helpful any more when it is higher than 10%. The boron concentration in the refined silicon increases again. It is concluded that the oxidizability of slag weakens with more basic oxides CaO and Li$_2$O and less acid oxide SiO$_2$ in slag. So the optimal composition of lithia slag for removing boron is 40.5%CaO-49.5%SiO$_2$-10%Li$_2$O, where the basicity of slag is 0.68.

The oxidizability of molten slag may be expressed as Eq. (6).

$$3/4(SiO_2) + 3/2(CaO) + [B] = 3/4Si(l) + (Ca_{3/2}BO_3)$$

(6)

The molten silicon and slag are considered as a dilute solution. The equilibrium constant of Eq. (6) might be written as Eq. (7) on condition that the standard state for the Henry’s law is chosen.

$$K_p = v(Ca_{2/3}BO_3) \cdot f(Ca_{2/3}BO_3) \cdot a_{Si}^{3/4} / (a_{Ca_{2/3}BO_3} \cdot a_{CaO}^{2/3} \cdot f[B] \cdot f_{[B]}$$

(7)

Where $v(Ca_{2/3}BO_3)$ and $v$ represent the concentration of calcium borate in slag and the concentration of boron in silicon, respectively. Parameters $a$ and $f$ are

### Table 1. Optical basicity parameters of some oxides ($\Lambda$)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>K$_2$O</th>
<th>Li$_2$O</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>B$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda$</td>
<td>-1.45</td>
<td>-1.15</td>
<td>-0.52</td>
<td>-0.48</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

### Table 2. Compositions of the ternary refining slags CaO-SiO$_2$-Li$_2$O and CaO-SiO$_2$-K$_2$O (mass%)

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Composition of refining slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>43.88 42.75 40.5 36 43.65 41.9 38.56 35.01 31.14 27</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>53.62 52.25 49.5 44 53.35 51.2 47.14 42.79 38.06 33</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>2.5 5 10 20 0 0 0 0 0 0</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0 0 0 0 3 6.9 14.3 22.2 30.8 40</td>
</tr>
</tbody>
</table>
the activity and the activity coefficient. For the Henry’s law, it is considered as $f(\text{CaO}_{\text{BO}}) = f(B) = 1$ and $a_{\text{BO}} = 1$. The distribution coefficient of boron might be written as Eq. (8).

$$\log f_B = 3/4 \log a_{\text{BO}} + 3/2 \log a_{\text{Ca}} + \log K_p - 1.04$$ (8)

Obviously, it is helpful for removing boron using slag refining with a higher basicity. The oxide K$_2$O with a basicity value of 1.4 as listed in Table 1 was added to the calcium silicate slag for removing boron. Figure 4 shows the variation of boron concentration in the refined silicon using different composition of ternary slag CaO-SiO$_2$-K$_2$O. The mass ratio of K$_2$O in slag varies from 3% to 40% and the basicity of slag increases from 0.64 to 0.72. It is found that the efficiency of removing boron improves greatly. The boron concentration in silicon reduces from $3.87 \times 10^{-6}$ to $1.4 \times 10^{-6}$. The efficiency of removing boron reaches to 92.2%. On the contrary, however, it reduces again when the ratio of K$_2$O in slag exceeds 30% although the basicity of slag increases continuously. It is concluded that the oxidizability of slag is weakened with SiO$_2$ mass ratio of 37% in slag. So it is thought that the optimal composition for a potash slag is 32%CaO-38%SiO$_2$-30%K$_2$O for removing boron from MG-Si, where the basicity of slag is 0.7.

4. Conclusions

1) The boron concentration in refined silicon is reduced with the increase of ratio for CaO in slag. The maximal distribution coefficient of boron between calcium silicate slag and silicon is 1.57 when the mass ratio of CaO/SiO$_2$ is 1.5 and the composition is 60%CaO-40%SiO$_2$ with a basicity of 0.71.

2) It shows a positive act for the oxidizability of calcium silicate slag with a higher slag basicity and it will weaken with a low mass ratio of SiO$_2$ in slag.

3) The additions of Li$_2$O and K$_2$O in calcium silicate slag are helpful for removing boron. The boron concentration in silicon is reduced to $4.5 \times 10^{-6}$ and $1.4 \times 10^{-6}$, respectively, using the slags of 40.5%CaO-49.5%SiO$_2$-10%Li$_2$O and 32CaO-38%SiO$_2$-30%K$_2$O. The basicities of slags are 0.68 and 0.7, respectively.

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References