Removal of boron from metallurgical grade silicon by electromagnetic induction slag melting

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Abstract: A new purification process was developed to remove impurities in metallurgical grade silicon (MG-Si) by electromagnetic induction slag melting (EISM). Vacuum melting furnace was used to purify boron in different slag systems. The results show that the removal effect in SiO2-CaO-Al2O3 systems is better than that in other slag systems by EISM. The boron content in MG-Si is successfully reduced from 1.5×10−5 to 0.2×10−5 during EISM at 1 823 K for 2 h. Meanwhile, Al, Ca and Mg elements in MG-Si are also well removed and their removal efficiencies reach 85.0%, 50.2% and 66.7%, respectively, which indicates that EISM is very effective to remove boron and metal impurities in silicon.

Key words: metallurgical grade silicon; slag system; partition ratio

1 Introduction

The production of solar cells increased rapidly in recent years. The market which uses the scrap of semiconductor grade silicon (SEG-Si) is difficult to afford a steady supply of this material. Therefore, alternative production processes are needed to increase the feedstock. The refinement of metallurgical grade silicon (MG-Si) is always desirable[1−2]; however, the removal of boron is still a challenge during refining. It is very difficult to vaporize boron by vacuum process because its vapor pressure is very low compared with that of silicon (10−4 Pa for boron and 10−1 Pa for silicon)[3−4]. Another difficulty regarding boron extraction is that its segregation coefficient in silicon is 0.8 which results in the fact that there is no removal effect by unidirectional solidification process[5−7]. The process usually used for the boron removal is plasma melting in an oxidizing atmosphere (O2, CO2 or H2O), during which boron is transformed into oxide forms, increasing its vapor pressure[8−9]. However, the plasma equipment and operation require a large initial investment.

Slag refining is an option for the removal of boron from molten silicon, and effective removal may be obtained for a certain slag composition. The technical viability of the slag refining process is confirmed, but the result is based on laboratory scale, and the refining time in static theoretical research is very long. The value of partition ratio (LB) obtained from experiments varies between 1.5 and 2.5[10−15]. The partition ratios of boron between SiO2-CaO-Na2O or SiO2-CaO-Al2O3 slag systems and liquid Si melt at 1 823 K were simulated using an assessed thermochemical databank together with the FACT oxide thermodynamic database by BALE et al[16]. The calculated values are approximately two times higher than the experimental ones, which indicates that the reaction kinetic barriers might play important roles in the refining processes. In the present study, pilot scale and dynamic slag experiments were carried out by using electromagnetic induction slag melting (EISM). The LB value between the slag systems and silicon phases was measured and the metallic impurities removal effects were analyzed. The mechanism of boron removal from silicon under EISM was discussed. Additionally, a detailed analysis for the thermodynamics and kinetics of boron removal were carried out. Impurity contents and microanalysis were confirmed by inductively coupled plasma atomic emission spectrometer (ICP-AES) and electron probe microanalysis (EPMA).
2 Experimental

The schematic diagram of experimental devices is shown in Fig. 1. An inductive furnace with 200 kW and 3,000 Hz was used for melting. The silicon was loaded in a quartz ceramic crucible with a size of $d_{120} \times 220$ mm. The crucible was surrounded by a graphite heater which was not a conductor at room temperature. The induction melting of silicon was carried out through water-cooled copper coil under protective gas. Three slag systems were chosen according to previous studies and the mass ratios of CaO/\(\text{SiO}_2\) in all slag systems were 1.21. Silicon material used in this study was treated by acid leaching. Metal impurities in silicon were reduced significantly, while non-metallic impurities such as B and P did not change after acid treatment. Silicon of 3 kg and slag of 0.3 kg were used in each experiment. The sample was withdrawn from the furnace after the test. Both the silicon phase and the slag phase were analyzed using ICP-AES to quantify boron and metal impurities contents. The partition ratio of boron between the slag and the silicon phase was defined as:

$$L_B = \frac{w_{\text{slag}}(B)}{w_{\text{Si}}(B)}$$  \hspace{1cm} (1)

where \(w_{\text{slag}}(B)\) and \(w_{\text{Si}}(B)\) are the concentration of boron in slag and in silicon, respectively. The experimental conditions and parameters are listed in Table 1.

3 Results

3.1 Effect of slag system on boron removal

Four types of typical slag systems were chosen for comparative study according to previous research \([11-14]\). The photograph of silicon ingots after test is shown in Fig. 2. From Fig. 2(a) it could be found that most of slag freezes at the bottom of silicon ingots after test and a small amount covers the side of silicon ingot. Slag deposits to the bottom of the crucible and then solidifies because the density of slag is greater than that of silicon melt. Thus, the purified silicon and the slag could be separated very well. Sodium hydroxide solution with concentration of 20% (mass fraction) is used to remove the surface slag of ingot and then the silicon ingots was cut off from the center. From Fig. 2(b) it could be found that the internal silicon ingot is very bright and there is no slag, which further illustrates that the slag and silicon melt could be separated very well.

The \(L_B\) values with different types of slag after melting at 1,773 K for 1 h are shown in Fig. 3. It could be seen that boron removal is significantly improved by EISM compared to previous static test results\([10-12]\).
Although CaO/SiO$_2$ ratios are the same in different slag systems, the values of $L_B$ are very different by adding different oxides to the CaO/SiO$_2$ slag system. The values of $L_B$ are significantly reduced by adding CaF$_2$ but significantly enhanced by adding Na$_2$O and Al$_2$O$_3$. Therefore, this work focuses on the removal of boron at different refining parameters in SiO$_2$-CaO-Na$_2$O and SiO$_2$-CaO-Al$_2$O$_3$ slag systems.

![Partition ratio $L_B$ in different types of slag systems](image)

### 3.2 Effect of refining process parameters on boron removal

#### 3.2.1 Refining time

Figure 4 shows the change of boron removal with time during refining at 1823 K in SiO$_2$-CaO-Na$_2$O and SiO$_2$-CaO-Al$_2$O$_3$ slag systems. It is found that $L_B$ is significantly improved compared to previous results in which $L_B$ was between 1.5 and 2.5 by EISM, although the variation tendency of $L_B$ under the two kinds of slag systems is different. EISM could reduce the diffusion resistance of impurity elements near the boundary layer and enhance the diffusion by increasing the melt flow rate, which could greatly speed up the removal rate of boron. Therefore, the required refining time is substantially reduced. The removal effect in SiO$_2$-CaO-Al$_2$O$_3$ slag systems is obviously better than that in SiO$_2$-CaO-Na$_2$O systems, and $L_B$ gradually increases with increasing time in SiO$_2$-CaO-Al$_2$O$_3$ systems, which indicates that the increase of refining time is conducive to the removal of boron. But $L_B$ increases and then reduces with increasing time in SiO$_2$-CaO system because the use of Na$_2$O might increase the basicity and decrease the melting point of the slag. However, Na$_2$O could be easily reduced to the silicon phase and becomes volatile at high temperature, which makes it difficult to work for a prolonged period [13].

#### 3.2.2 Refining temperature

Figure 5 shows the change of boron removal with temperature during refining for 1 h in SiO$_2$-CaO-Na$_2$O and SiO$_2$-CaO-Al$_2$O$_3$ slag systems. The value of $L_B$ gradually increases with the increase of refining temperatures in SiO$_2$-CaO-Al$_2$O$_3$ slag systems, which indicates that the increase of refining temperature is conducive to the removal of boron. Because the viscosity of slag reduces as the temperature increases, the mobility of slag and the silica activity in slag increase. All of these are conducive to the removal of boron. However, boron removal at low temperature is better than that at high temperature in the SiO$_2$-CaO-Na$_2$O system. This is because Na$_2$O could be easily reduced to the silicon phase and become volatile at high temperature [13].

![$L_B$ at different temperatures after refining for 1 h](image)

#### 3.2.3 Slag composition

Figure 6 shows the changes of boron removal with the content of Na$_2$O and Al$_2$O$_3$ in slag. $L_B$ has the same change trend with the contents of Na$_2$O and Al$_2$O$_3$ in SiO$_2$-CaO-Na$_2$O and SiO$_2$-CaO-Al$_2$O$_3$ slag systems, it increases as the proportion of Na$_2$O and Al$_2$O$_3$ in slag increases. It is apparent that if compounds with a basicity higher than that of CaO (or CaF$_2$) is used, a better partition ratio and a higher value for capacity can be obtained. This is because not only the basicity of slags could be greatly improved but also the activity of silica in slag could also be greatly increased by adding alkaline oxide into slag[13].
3.3 Removal of other impurity elements

Not only boron but also other elements such as Ca, Al and Mg could be easily removed by EISM. Table 2 shows impurities changes in silicon before and after refining. Al, Ca and Mg elements were well removed by slag refining and their removal rates reached 85.0%, 50.2% and 66.7%, respectively. The EPMA analysis of metal impurity elements in silicon and slag is shown in Fig.7 after refining for 2 h at 1823 K in SiO₂-CaO-Al₂O₃ system. It could be clearly seen that the distribution of Ca, Al and Mg elements is all on the slag side between silicon and slag, and these elements all concentrated in slag phase. Although the slag contains much Ca and Al, they do not contaminate silicon melt because they exist in slag phase with a relatively stable state and they contact with silicon melt in the form of molten oxide, thus they would not cause silicon pollution. As the oxygen content in slag phase is relatively high, Al and Mg are more inclined to enrich in slag phase because the affinity of slag to these two elements is greater than that of silicon phase.

Table 2 Impurity content in silicon before and after slag refining at 1823 K for 2 h (mass fraction, 10⁻⁶)

<table>
<thead>
<tr>
<th>Impurity content</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before refining</td>
<td>233</td>
<td>207</td>
<td>42</td>
</tr>
<tr>
<td>After refining</td>
<td>35</td>
<td>103</td>
<td>14</td>
</tr>
</tbody>
</table>

Fig.6 $L_{B}$ with contents of Na₂O and Al₂O₃ in slag after refining at 1823 K for 1 h

Fig.7 SEM image (a) and EPMA analysis (b–d) of metal impurity elements in silicon and slag after refining at 1823 K for 2 h
4 Analysis and discussion

4.1 Thermodynamic analysis of boron removal

The reaction of removal of boron from Si by using basic fluxes could be expressed as:

\[ B + \frac{3}{4} \text{SiO}_2 = \frac{3}{4} \text{Si} + \text{BO}_{1.5} \] (2)

The boron dissolved in the liquid silicon reacts with silica in the slag. Boron is oxidized and enters the slag, while the silica is reduced and enters the liquid melt. The distribution coefficient of boron is given as the ratio between the boron content in the slag and the boron content in the silicon as:

\[ L_B = \frac{w_{\text{slag}}(B)}{w_{\text{Si}}(B)} = \frac{K_{f_B}^{\gamma}}{\gamma_{\text{BO}_{1.5}}} \left( \frac{a(\text{SiO}_2)}{a(\text{Si})} \right)^{3/4} \] (3)

where \( K \) is the equilibrium constant of Eq. (2), \( k_{x \rightarrow y} \) is the coefficient for the transition from molar fraction to mass fraction, \( \gamma_{\text{BO}_{1.5}} \) and \( f_B \) are the activity coefficients of \( \text{BO}_{1.5} \) and \( B \) in slag and silicon phases, respectively.

From Fig.3 it is known that the removal effect of boron in \( \text{SiO}_2-\text{CaO}-\text{Na}_2\text{O} \) and \( \text{SiO}_2-\text{CaO}-\text{Al}_2\text{O}_3 \) slag systems is better than that in \( \text{SiO}_2-\text{CaO}-\text{CaF}_2 \) system. The activity coefficient of boron oxide calculated for \( \text{CaO}/\text{SiO}_2 \) based slag at 1 723−1 873 K could be approximately expressed as:

\[ \ln \gamma_{\text{BO}_{1.5}} = -4.00x(\text{CaO})/x(\text{SiO}_2) + 3.67 \] (4)

When \( \text{CaF}_2 \) is added in the slag, \( \text{CaO} \) could be generated after \( \text{CaF}_2 \) reacts with silica, thereby increases the basicity of slags. Although the addition of \( \text{CaF}_2 \) provides a broader basicity range compared to the binary system, the content of \( \text{SiO}_2 \) in slag reduces and the oxygen partial pressure \( (a(\text{SiO}_2)/a(\text{Si}))^{3/4} \) also significantly reduces. Meanwhile, the increased ratio of \( \text{CaO}/\text{SiO}_2 \) in Eq.(4) results in the decrease of \( \gamma_{\text{BO}_{1.5}} \).

But the change degree of \( \gamma_{\text{BO}_{1.5}} \) is smaller than that of \( (a(\text{SiO}_2)/a(\text{Si}))^{3/4} \). Therefore, \( L_B \) would be reduced according to Eq.(3)[13]. It is apparent that when \( \text{Na}_2\text{O} \) and \( \text{Al}_2\text{O}_3 \) are added in slag, a better partition ratio could be obtained, because not only the basicity of slag but also the oxygen partial pressure of slag could be greatly increased by adding alkaline oxide into slag. In this case, the oxygen partial pressure \( (a(\text{SiO}_2)/a(\text{Si}))^{3/4} \) and the ratio of \( x(\text{CaO})/x(\text{SiO}_2) \) in Eq.(4) also significantly increase, which results in the reduction of \( \gamma_{\text{BO}_{1.5}} \). So \( L_B \) would increase according to Eq.(3). In addition, the use of \( \text{Al}_2\text{O}_3 \) might decrease the melting point of the slag and the mobility and affinity of slag are also improved markedly[14]. \( L_B \) value gradually increases with temperature during EISM. The activity coefficient of boron \( (f_B^0) \) in dilute solution between 1 723 and 1 923 K silicon can be expressed as[11]:

\[ \lg f_B^0 = -\frac{1.11 \times 10^4}{T} + 5.82 \] (5)

\( f_B^0 \) and the equilibrium constant \( K \) increase with temperature. The effect of temperature on \( \gamma_{\text{BO}_{1.5}} \) is very small, so it could be ignored. The activity coefficient of boron oxide is affected by the incorporation between boron and silicate network. Further decrease of \( \gamma_{\text{BO}_{1.5}} \) with increasing silica content is not necessary for the amount of boron incorporated in the network might be related to the degree of polymerization of the slag structure. So \( L_B \) increases according to Eq.(3) in \( \text{SiO}_2-\text{CaO-\text{Al}_2\text{O}_3} \) slag system, but it decreases with increasing temperature in the \( \text{SiO}_2-\text{CaO-\text{Na}_2\text{O}} \) slag system because \( \text{Na}_2\text{O} \) could easily become volatile at high temperature[13]. Because boron is in micro scale in the silicon, it takes a certain time to diffuse from silicon into slag phase.

4.2 Kinetic analysis of boron removal

When a dissolved element is refined by slag treatment, it goes through the following five steps: 1) the impurity element transfers from the bulk metallic phase to the metal boundary layer; 2) the impurity element diffuses through the metal boundary layer; 3) the metal is oxidized at the interphase between metal and slag; 4) the impurity element diffuses through the slag boundary layer; 5) the impurity elements transfer from the slag boundary layer to slag bulk phase. Steps 1) and 5) depend on the stirring and mixing in silicon fluid and slag. Stirring is often done by gas bubbling or mechanical devices to increase the mass transfer in the bulk phases. Hence, slag properties such as viscosity are important. A high-viscosity would lead to low velocities in the slag and hence a low mass transfer of the impurity element. High-viscosity also lowers the diffusivity of the impurity element. Steps 2) and 4) depend on the mass transfer coefficients in the metal (\( \beta \)) and in the slag (\( \beta_s \)), respectively. A serious difficulty with refining silicon by extraction to a second (slag) phase is the problem of mixing in the slag phase. Often, the slag phase is relatively viscous, so it is difficult to mix the impurity element throughout the slag.

Electromagnetic induction slag refining method is used in this experiment. Figure 8 illustrates the movement of melt in the crucible under electromagnetic force which is formed by the interaction between the magnetic field in the medium frequency induction coil and the induction eddy current in melt. Because the electrical conductivity of silicon fluid and slag is different, slag would follow the silicon fluid movement and they could contact fully in the crucible, which is
conducive to the removal of impurities. And electromagnetic induction melting is superior to gas mixing and mechanical agitation, since the mixing process would not contact with the silicon fluid and would not introduce new impurities.

According to boundary layer theory, the effective boundary layer thickness (units) could be expressed as:

$$\delta = \left( \frac{c - c^*}{\frac{dc}{dx}} \right)_{x=0}$$  \hspace{1cm} (6)

where $c^*$ is the concentration at the interface; $c$ is the concentration of the liquid bulk concentration outside the boundary layer, and $c^* > c$. In addition, it is also known by the surface renewal theory that the mass transfer coefficient of impurity elements could be expressed as:

$$\beta = \sqrt{DS}$$  \hspace{1cm} (7)

where $D$ is the diffusion coefficient of impurity; $S$ is the surface renewal rate.

It is known by Eq.(6) that the larger the concentration gradient near the interface, the thinner the thickness of boundary layer. The concentration gradient here could become larger by increasing fluid flow, thereby reduces the thickness of boundary layer. When the flow rate continues to increase until the boundary layer thickness approaches zero, diffusion resistance disappears, and the flow at this time is called critical velocity. Therefore, it could reduce the diffusion resistance of impurity elements near the boundary layer and enhance the diffusion of them by increasing the melt flow rate. The mass transfer coefficient in the metal ($\beta$) and in the slag ($\beta_s$) were both enhanced, so it could improve and speed up the removal of boron. This indicates that EISM is a very effective method for removal the boron impurities in silicon.

5 Conclusions

1) MG-Si with $1.5 \times 10^{-5}$ B was successfully purified to $0.2 \times 10^{-5}$ B after EISM at 1 823 K for 2 h in SiO$_2$-CaO-Al$_2$O$_3$ slag systems. Al, Ca and Mg elements in MG-Si were also well removed and their removal efficiency reached 85.0%, 50.2% and 66.7%, respectively.

2) The $L_B$ value increased with temperature and refining time because the viscosity of slag reduced and the mobility of slag enhanced, and the silica activity in slag increased as temperature increased, which is conducive to the removal of boron.

3) The boron content in silicon was significantly improved compared to previous experimental results and it achieved the level required by EISM. Because EISM could reduce the diffusion resistance of impurity elements near the boundary layer and enhance the diffusion of them by increasing the melt flow rate. The mass transfer coefficient in the metal ($\beta$) and in the slag ($\beta_s$) were both enhanced, so it could improve and speed up the removal of boron. This indicates that EISM is a very effective method for removal the boron impurities in silicon.

References


应用电磁感应造渣法去除冶金级硅中杂质硼

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摘 要：提出一种新的提纯工艺即通过造渣与电磁感应熔炼相结合的方法来去除冶金级硅中的杂质硼。采用自行设计的真空感应熔炼炉进行不同造渣系条件下除硼的研究。结果表明，SiO2-CaO-Al2O3 渣系的除硼效果优于其它渣系，在 1 823 K 经过 2 h 精炼后，冶金级硅中的硼含量由原来的 1.5×10⁻⁵ 降到 0.2×10⁻⁵。同时冶金级硅中的 Al, Ca 和 Mg 杂质得到了精炼，去除率分别达到 85.0%，50.2% 和 66.7%。表明电磁感应造渣法是一种非常有效的去除冶金级硅中的硼和其他一些金属元素杂质途径。

关键词：冶金级硅；渣系；分配比

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