Boron removal from metallurgical silicon using CaO-SiO₂-CaF₂ slags

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Abstract: The removal of boron from metallurgical silicon in slag system of CaO-SiO₂-10%CaF₂ was investigated. The partition coefficient of boron (L_B) between slag and silicon phase was studied under different conditions of slag basicity (CaO/SiO₂ ratio), temperature, mass ratio of slag to silicon and gas blowing. The results show that L_B has a maximum value of 4.61 when the CaO/SiO₂ mass ratio is around 2 at 1 873 K. The logarithm of L_B is linear to the reciprocal of temperatures in the range of 1 773−1 973 K. L_B increases with the increase of mass ratio of slag to silicon, but it does not increase markedly when the ratio excesses 3. Gas blowing can significantly increase the removal of boron, and L_B increases with the increase of water vapor content.
Key words: solar grade silicon; slag treatment; boron removal; partition coefficient

1 Introduction

The total power capacity generated by solar cell usage reached 7.2 GW in 2009—an increase of 15% despite the international financial crisis. Accordingly, the supply of solar grade silicon (SOG-Si) experienced a rapid growth [1]. As the traditional Siemens method is complicated, and the investment is fairly large, the development of a metallurgical process for the production of SOG-Si has greater practical significance. Further, metallurgical silicon (MG-Si) is the main raw material for SOG-Si, which has a purity of approximately 99% (2N). In order to accord with the requirement of solar cell manufacture, it is necessary to purify the silicon to attain a purity of 6N−7N [2−4].

However, boron is difficult to extract by the traditional directional solidification or vacuum melting because of its high segregation coefficient and low vapor pressure [5−6]. The most effective approach to eliminate boron is slag treatment. Boron can react to form a boron oxide，such as B₂O₃, which is more stable in the basic slag phase as it is an acidic oxide. Therefore, it is predicted that the boron in MG-Si would transfer into basic slags. Further, these slags could then be easily removed, based on different densities from that of silicon,

after reaching thermodynamic equilibrium [7−9].

The calcium silicate system is the base for other slags [10−11]. In order to improve the boron-removal capacity of the slag, the partition coefficient of boron (L_B, boron concentration ratio between the slag and silicon phases) must be increased. The partition coefficient of boron, for a specified smelting duration, is influenced by three different factors: slag basicity—here, it refers to the CaO/SiO₂ mass ratio; reaction temperature; and the mass ratio of slag to silicon. This partition coefficient of boron can, further, be increased by gas blowing to improve the oxidation of boron.

2 Experimental

Different CaO-SiO₂-CaF₂ systems were prepared with CaF₂ content fixed at 10%, but with the CaO/SiO₂ ratio varying from 1.0 to 4.0. Experiments were carried out in the independently designed intermediate-frequency-induction melting furnace. A schematic diagram of the experimental apparatus is presented in Fig. 1, which comprises of vacuum, smelting and directional solidification systems. The vacuum system is composed of rotary vane mechanical and Roots pumps. The smelting system is designed to induce heating by an intermediate frequency influence and consists of an
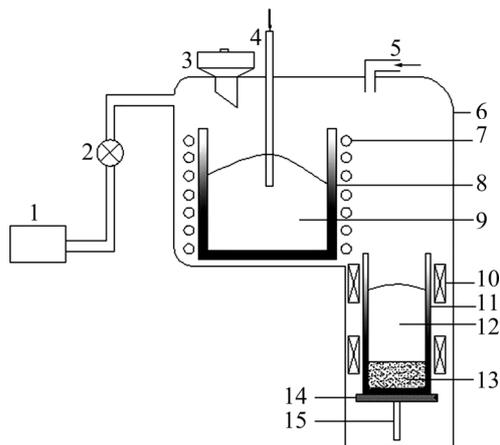
Fig. 1 Schematic drawing of experimental apparatus of slag treatment for boron removal: 1—Rotary vane mechanical pump; 2—Roots pump; 3—Feeding device; 4—Graphite rod; 5—Argon gas inlet; 6—Intermediate-frequency-induction melting furnace; 7—Induction coil; 8—High-strength graphite crucible; 9—Molten silicon; 10—Holding furnace; 11—Pouring crucible; 12—Silicon layer; 13—Slag layer; 14—Water cooled base; 15—Pull rod

induction coil, high-strength graphite crucible, feeding device and lifting graphite rod, which is used for gas blowing. The directional solidification system functions by lateral insulation of a pouring crucible with water cooling at the bottom.

  During the experiment, the rotary vane mechanical and Roots pumps were first started to begin evacuation. The power supply to the induction coil was switched on to heat the MG-Si in the graphite crucible at a vacuum degree of less than 100 Pa. Then, the slag was added by the feeding device after the silicon had melted completely. Smelting continued for 1 h under an argon atmosphere at temperatures between 1 773 and 1 973 K by increasing the electric power. The slag was poured out and settled in a slag layer below the silicon layer during directional solidification, separating easily due to a higher density. Samples were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after slag treatment to measure the boron content.

  The graphite rod for gas blowing should descend above the surface of molten silicon for preheating before its immersion in the melt to blow a reaction gas consisting of water vapor and argon gas.

3 Results and discussion

3.1 Effect of slag basicity on L_B

  The experimental results obtained from CaO-SiO$_2$-10%CaF$_2$ slags with different compositions are summarized in Table 1. The partition coefficient of boron (L_B) is expressed as

$$L_B = \frac{w(B)_{in\ slag}}{w(B)_{in\ Si}} \tag{1}$$

where $w(B)_{in\ slag}$ and $w(B)_{in\ Si}$ represent the boron contents in slag and silicon phases, respectively.

Table 1 ICP-AES analysis results of CaO-SiO$_2$-10％CaF$_2$ slags with CaO/SiO$_2$ ratio varying from 1.0 to 4.0 after 1 h of slag treatment at 1 873 K with slag-to-silicon mass ratio of 3

$w(CaO)/w(SiO_2)$	$w(B)_{in\ slag}/10^{-6}$	$w(B)_{in\ Si}/10^{-6}$	L_B
4.00	6.55	2.29	2.86
3.00	6.74	1.77	3.81
2.50	5.89	1.40	4.21
2.00	5.12	1.11	4.61
1.50	7.45	1.91	3.90
1.25	7.28	2.04	3.57
1.00	9.51	2.99	3.18

  Figure 2 depicts the relationship between L_B and slag basicity (CaO/SiO$_2$), together with the data obtained by TEIXEIRA and MORITA [12]. Contrary to the data published in the previous report in Ref. [12], the L_B increases at first with increasing the CaO/SiO$_2$ ratio and then decreases after reaching a maximum value. This accords with the result published by SUZUKI and SANO [13].
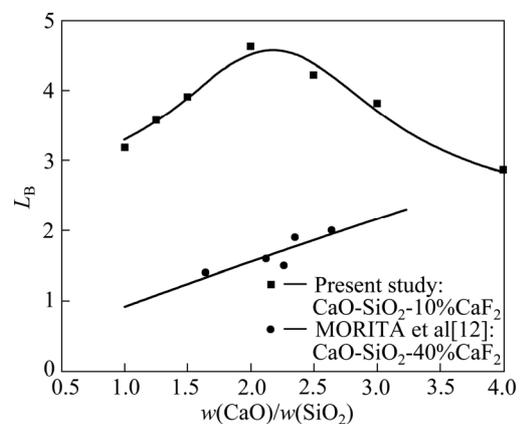

Fig. 2 Relationship between L_B and CaO/SiO$_2$ ratio for CaO-SiO$_2$-10％CaF$_2$ slags after 1 h of slag treatment at 1 873 K with slag-to-silicon mass ratio of 3

  The difference between the present study and the one reported by TEIXIERA and MORITA [12] was investigated by thermodynamic analysis. The oxidation reaction of the removal of boron from silicon to the slag is expressed as

$$[B]_{Si} + (3/4)SiO_2(l) = (BO_{1.5}) + (3/4)Si(l) \tag{2}$$

  The calculation of Gibbs free energy change $\Delta_r G$ of the abovementioned oxidation reaction by using the

Van't Hoff equation is presented as:

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln\left(\frac{(a(Si))^{3/4} \cdot a(BO_{1.5})}{(a(SiO_2))^{3/4} \cdot a(B)}\right) \quad (3)$$

where a_i is the activity of component i. The standard Gibbs free energy change $\Delta_r G^{\ominus}$ is constant at certain temperature and pressure. Therefore, it is necessary to decrease the values in brackets of Eq. (3) to ensure the reaction (2) occurs. The $BO_{1.5}$ is an acidic oxide that reacts with CaO, and is then incorporated into the slag phase to form stable calcium borosilicate [8]. Thus, the activity of $BO_{1.5}$ decreases with the increase of the amount of CaO. This is expected to promote the reaction (2), leading to an increase of L_B accordingly.

Considering $a_i = \gamma_i \cdot x_i$, where γ_i is the activity coefficient of component i, and x_i is the mole fraction of component i, then, the value in brackets of Eq. (3) can be further derived as follows:

$$K = \frac{(a(Si))^{3/4} \cdot a(BO_{1.5})}{a(SiO_2)^{3/4} \cdot a(B)}$$
$$= \left(\frac{a(Si)}{a(SiO_2)}\right)^{3/4} \cdot \frac{\gamma(BO_{1.5})}{\gamma(B)} \cdot \frac{x(BO_{1.5})}{x(B)} \quad (4)$$

where K is the equilibrium constant of reaction (2). In this study, the system is assumed to obey Henry's law, because the concentration of boron in molten silicon is very low. Therefore, the value of $a(Si)$ is considered to be approximately equal to 1, and the ratio of $x(BO_{1.5})$ and $x(B)$ can be replaced with L_B and Eq. (4) can be converted to

$$L_B = \frac{K \cdot \gamma(B) \cdot (a(SiO_2))^{3/4}}{\gamma(BO_{1.5})} \quad (5)$$

Based on the above assumption, K and $\gamma(B)$ are both temperature-dependent constants in dilute solution. With the increase in the CaO/SiO$_2$ ratio, the $\gamma(BO_{1.5})$ decreases, and further changes in the reaction are not apparent after the CaO/SiO$_2$ ratio exceeds 2 [14], whereas the value of $a(SiO_2)$ continues to fall constantly. Therefore, L_B cannot keep increasing, instead it follows a parabolic shape based on the numerator and denominator in Eq. (5).

In comparison with the binary system of CaO-SiO$_2$, the addition of CaF$_2$ constitutes an effective way to expand the range of basicity [15]. This development is attributed to the reaction between CaF$_2$ and SiO$_2$, as described in Eq. (6). The introduced F$^-$ can break the silica network, transforming bridging oxygen into free oxygen which then reacts to form CaO, and resulting in increased basicity [16].

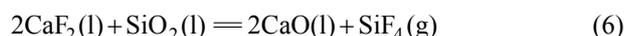$$2CaF_2(l) + SiO_2(l) = 2CaO(l) + SiF_4(g) \quad (6)$$

Figure 2 indicates that the partition coefficient of boron is markedly improved, as compared with the results reported by TEIXEIRA and MORITA [12]. As the content of CaF$_2$ is relatively low, the effective quantities of CaO and SiO$_2$ participating in the reaction are increased.

The maximum value of L_B was 4.61 when the CaO/SiO$_2$ ratio was approximately 2. This can be explained by [15]:

$$(4/3)[B]_{Si} + SiO_2(l) + 2O^{2-} = (4/3)(BO_3)^{3-} + Si(l) \quad (7)$$
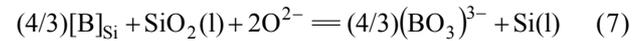
Theoretically, the reaction is conducted to the greatest extent when the molar ratio of CaO and SiO$_2$ is 2, which approximates to the mass ratio as these two have relative molecular mass of 56 and 60, respectively. This indicates optimal boron removal can be facilitated with a CaO/SiO$_2$ ratio of 2.

3.2 Effect of reaction temperature on L_B

The CaF$_2$ reduces the melting temperature of the slag. The reaction (7) can occur at temperatures higher than 1 687 K when free oxygen is released after the formation of the liquid phase, as seen in the phase diagram of the CaO-SiO$_2$-10%CaF$_2$ system [17]. Further, the reaction occurs more easily with increasing temperature, according to Ellingham's diagram [18].

The temperature dependence of L_B between 1 773 and 1 973 K was studied for the 60%CaO-30%SiO$_2$-10%CaF$_2$ slag system. As shown in Fig. 3, the logarithm of L_B varies linearly with the reciprocal of temperature. This indicates that boron removal is enhanced because the higher temperature induces an increased L_B.
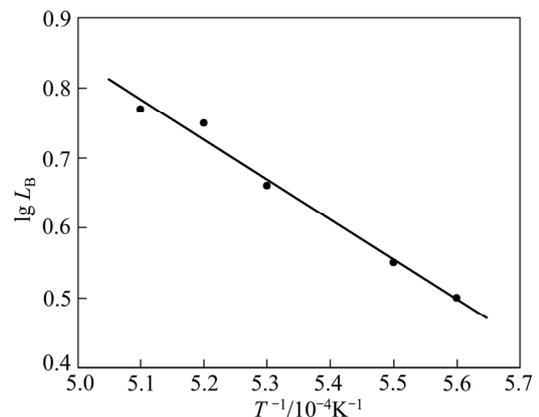

Fig. 3 Temperature dependence of L_B for 60%CaO-30%SiO$_2$-10%CaF$_2$ slag after 1 h of slag treatment with slag-to-silicon mass ratio of 3

3.3 Effect of mass ratio of slag to silicon on L_B

Figure 4 indicates the effect of different amounts of slags, with the mass ratio of slag to silicon (η) varying from 0.1 to 5, on boron removal. With increasing η, L_B increases; however, the trend becomes weaker when η excesses 3.
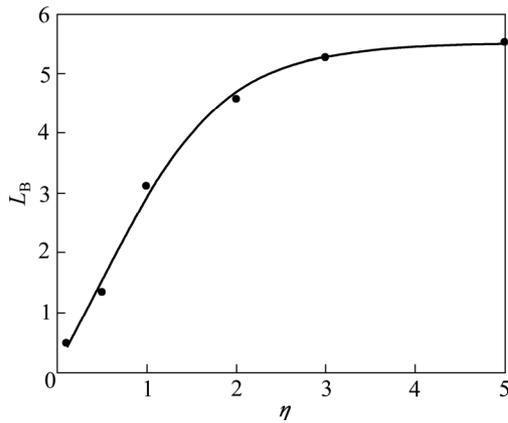
Fig. 4 Relationship between L_B and mass ratio of slag to silicon (η) for 60%CaO-30%SiO$_2$-10%CaF$_2$ slag after 1 h of slag treatment at 1 873 K

Based on the law of conservation of mass, the following relationship can be expressed, while ignoring the loss of silicon and slag after reaction.

$$m(\text{Si}) \cdot w(\text{B})^0_{\text{in Si}} + m(\text{slag}) \cdot w(\text{B})^0_{\text{in slag}} = m(\text{Si}) \cdot w(\text{B})_{\text{in Si}} + m(\text{slag}) \cdot w(\text{B})_{\text{in slag}} \quad (8)$$

where $m(\text{Si})$ and $m(\text{slag})$ represent the amount of silicon and slag, respectively; $w(\text{B})^0_{\text{in Si}}$ and $w(\text{B})_{\text{in Si}}$ indicate the contents of boron in silicon before and after the reaction; $w(\text{B})^0_{\text{in slag}}$ and $w(\text{B})_{\text{in slag}}$ depict the contents of boron in slag before and after the reaction, respectively. By combining the expression of L_B, Eq. (8) can be rewritten as

$$w(\text{B})_{\text{in Si}} = \frac{w(\text{B})^0_{\text{in Si}} + \dfrac{m(\text{slag})}{m(\text{Si})} \cdot w(\text{B})^0_{\text{in slag}}}{1 + \dfrac{m(\text{slag})}{m(\text{Si})} \cdot L_B} \quad (9)$$

When the mass ratio of slag to silicon approaches infinity, that is,

$$\eta = \frac{m(\text{slag})}{m(\text{Si})} \to \infty \quad (10)$$

then, the limit of boron content $w(\text{B})_{\text{in Si}}$ is calculated as $w(\text{B})^0_{\text{in slag}}/L_B$, which correlates with the initial boron content in slag. Therefore, the purity of slag needs to be controlled precisely. From Fig. 4, it is apparent that there is no obvious improvement of L_B even when η is very high. However, a large amount of slag easily causes contamination, and this does not meet the requirement of low-cost industrialization.

3.4 Effect of gas blowing on L_B

Refining gas comprising of a mixture of Ar and H$_2$O, was blown into the molten silicon during slag treatment for 60%CaO-30%SiO$_2$-10%CaF$_2$ slag with a slag-to-silicon mass ratio of 3 at 1 873 K. Gas blowing lasted for 1 h, and three gases were used: pure Ar, 0.5% H$_2$O+99.5%Ar, and 1.5% H$_2$O+98.5%Ar. From Fig. 5, it can be seen that L_B increases with the increase of H$_2$O content.
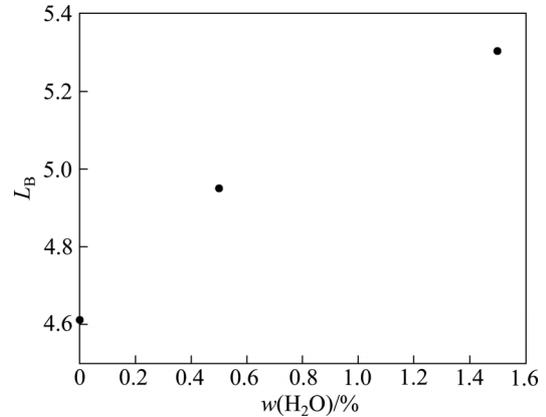

Fig. 5 Effect of H$_2$O content on L_B for 60%CaO-30%SiO$_2$-10%CaF$_2$ slag after 1 h of gas blowing at 1 873 K with slag-to-silicon mass ratio of 3 (refining gas: Ar+H$_2$O)

The addition of H$_2$O increases the concentration of OH$^-$, which improves the formation of BOH. The BOH can easily be eliminated by volatilization because it has a saturated vapor of 740 Pa [19]. Meanwhile, gas blowing provides a stronger agitation, which ensures molten slag disperse more fully and evenly in the melt. Therefore, the enhanced oxidation of boron leads to an increase of the partition coefficient of boron.

4 Conclusions

1) The partition coefficient of boron L_B was calculated at 1 873 K for CaO-SiO$_2$-10%CaF$_2$ slags with a CaO/SiO$_2$ ratio between 1.0 and 4.0. There was a parabolic relationship between the CaO/SiO$_2$ ratio and L_B, and the maximum value of L_B was 4.61 when the CaO/SiO$_2$ ratio was approximately 2.

2) The L_B increased with increasing temperature, and the logarithm of L_B was linear with the reciprocal of temperatures in the range of 1 773−1 973 K. With regard to the energy consumption, the temperature was set at 1 873 K.

3) The L_B increased with increasing mass ratio of slag to silicon, but there was no apparent increase in L_B when the ratio exceeded 3. The initial boron content of slag specified the limit of boron removal. A slag-to-silicon mass ratio of 3 was employed.

4) The effect of boron removal was improved by gas blowing with a gas mixture of Ar and H$_2$O to facilitate the concentration of OH$^-$ and also to enhance the dispersion of molten slag by agitation. The L_B was increased with the increase in H$_2$O content.

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采用 $CaO\text{-}SiO_2\text{-}CaF_2$ 渣系去除硅中杂质硼

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摘 要：采用 $CaO\text{-}SiO_2\text{-}10\%CaF_2$ 渣系，对工业硅进行造渣除硼研究。研究不同工艺条件下，渣系碱性、反应温度 T、渣金比和通气搅拌对硼在渣相和硅液中分配系数 L_B 的影响。结果表明，在 1 873 K 下，当 CaO/SiO_2 质量比为 2 时硼的分配系数可达最大值 4.61。在 1 773~1 973 K 下，$\lg L_B$ 与 $1/T$ 成线性关系。随着渣金比的增大，硼的分配系数也相应增大，但当渣金比大于 3 时，硼的分配系数并无明显增加。通气可显著提高硼的去除效果，硼的分配系数随气体中 H_2O 含量的增加而增大。

关键词：太阳能级多晶硅；造渣；除硼；分配系数

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