Boron removal from molten silicon using sodium-based slags

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Abstract: Slag refining, as an important option for boron removal to produce solar grade silicon (SOG-Si) from metallurgical grade silicon (MG-Si), has attracted increasing attention. In this paper, Na_2CO_3–SiO_2 systems were chosen as the sodium-based refining slag materials for boron removal from molten silicon. Furthermore, the effect of Al_2O_3 addition for boron removal was studied in detail, which showed that an appropriate amount of Al_2O_3 can help retention of the basicity of the slags, hence improving the boron removal rate.

Key words: polysilicon; boron removal; slag refining; sodium-based slag; Al_2O_3

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1. Introduction

The boom in photovoltaic (PV) power generation has caused a global shortage of solar grade silicon (SOG-Si). Refining metallurgical grade silicon (MG-Si) could be a promising way to solve this problem. However, it is difficult to remove boron from molten silicon because of the relatively high equilibrium partition coefficient[1] and low partial pressure[2] of boron.

Numerous approaches, such as plasma melting oxidation[3–6], oxidizing refining[7, 8] and slag refining[8–11], have been developed to refine MG-Si. The mechanism of boron removal from molten silicon has been deeply studied and the kinetic study of boron oxidation and removal by the plasma melting method has shown that the chemical reactions between boron and oxygen in molten silicon is the rate determining step[6]. For slag refining, the basic fluxes (such as calcium-based slags) used to remove boron from molten silicon have been widely studied, however, sodium-based slags are rarely reported, mainly due to the highly volatile characteristics of sodium compounds[9, 10, 12, 13].

In the present study, Na_2CO_3–SiO_2 systems were chosen for their high basicity as the refining sodium-based slag materials. To improve the thermal stability of the slags, Al_2O_3 was introduced and the effect of the added Al_2O_3 on boron removal was studied in detail.

2. Experimental procedure

MG-Si was chosen as raw silicon, with the B content varying from 6.0 to 8.0 mass ppm. 10 kg of raw silicon was melted in a graphite crucible using a medium-frequency induction furnace around the crucible. The temperature range of the molten silicon was 1873–1923 K. To insure sufficient contact between the slag and the silicon, the silicon melt was covered uniformly with the slag powder. The slag-silicon ratio varied from 0.1 to 0.5. A blender was used in one case.

Induced coupled plasma atomic emission spectrometry (ICP-AES) was used to measure the boron concentration in the silicon before and after the slag refining. A small amount of slag was intermittently sampled to identify the time dependence of the slag basicity. The slag samples were crushed then hydrolyzed and the basicity (indicated by Na_2O content) was determined by acid-base titration.

3. Results and discussion

3.1. Mechanism of boron removal with binary sodium-based slag

To provide a reference or guideline for the sodium-based slag refining application of metallurgical grade silicon, thermodynamic equilibrium analysis was adopted by calculating the Gibbs free energy of the silicon-slag system, based on the handbook of the thermochemical data of pure substances[14]. The boron dissolved in molten silicon, expressed as [B], would be oxidized (preferentially into B_2O_3[7]) and then absorbed by the slag materials[9, 10]. The reactions are expressed as:

$$3SiO_2(l) + 4[B] = 2B_2O_3(l) + 3Si(l), \tag{1}$$

$$Na_2CO_3(l) + B_2O_3(l) = 2NaBO_2(l) + CO_2(g), \tag{2}$$

$$Na_2CO_3(l) + 2B_2O_3(l) = Na_2B_4O_7(l) + CO_2(g). \tag{3}$$

Therefore, the two possible overall reactions of the boron removal process in this study are expressed as:

$$Na_2CO_3(l) + \frac{3}{2}SiO_2(l) + 2[B] = 2NaBO_2(l) + \frac{3}{2}Si(l) + CO_2(g), \tag{4}$$

$$Na_2CO_3(l) + 3SiO_2(l) + 4[B] = Na_2B_4O_7(l) + 3Si(l) + CO_2(g). \tag{5}$$

The relationship between the Gibbs free energy change (ΔG^{Θ}) of the chemical compound (B_2O_3, SiO_2, Na_2CO_3, $NaBO_2$, $Na_2B_4O_7$) and temperature (T) was calculated and shown in Fig. 1.

According to Fig. 1, both reactions are thermodynamically feasible in the temperature range of 1873–1923 K. However,

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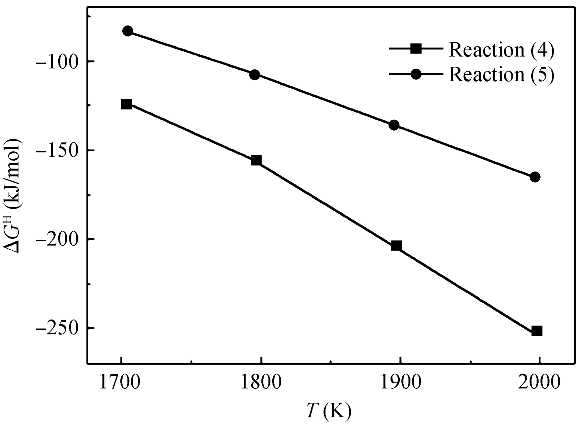

Fig. 1. ΔG^{Θ} of chemical compound versus temperature for the Na_2CO_3–SiO_2 system.

reaction (4) would be the main reaction in this slag-silicon system for the lower ΔG^{Θ}. Furthermore, compared to reaction (4), reaction (5) was hindered dynamically, as the higher boron content demand (the mole ratio of [B] to Na_2CO_3 of reaction (5) was double that of reaction (4), however, the boron content in this slag-silicon system was lower than 15 mass ppm. The mechanism of slag refining is considered to include two main steps: the oxidation of [B] and the absorption of boron oxide by slag materials. In this paper, the oxidant involved in reactions (4) and (5) was SiO_2, and the mole ratio of [B] to SiO_2 of the two reactions were the same (4 : 3), furthermore, the chemical valences of boron in $NaBO_2$ and $Na_2B_4O_7$ were the same too (+3). Therefore, both of the boron oxidations in the two reactions were the same and could be expressed as:

$$3SiO_2(l) + 4[B] = 2B_2O_3(l) + 3Si(l). \qquad (6)$$

Therefore, it could be inferred that the difference in the reaction products from reactions (4) and (5) was not caused by the oxidation step, hence, it was caused by the absorption step. Comparing reactions (4) and (5), it could be found that the mole ratio of [B] to Na_2CO_3 of reaction (5) was the double that of reaction (4), which means that reaction (5) demands a relatively higher boron content. Therefore, for the low boron content system, reaction (4) would be the main reaction.

It is noteworthy that both the boiling point and the decomposition temperature of $NaBO_2$ are relatively low (1747.4 K), therefore, some boron may escape from the slag-silicon system in the form of $NaBO_2$ or its decomposition products with the assistance of the volatilization of sodium compounds when the temperature of the silicon-slag system is high enough.

The reagent compositions of binary sodium-based slag are shown in Table 1. Table 2 shows the B content of the materials before and after slagging for 30 min with the binary sodium-based slag (the slag-silicon ratio = 0.1). It could be found that the B content of the silicon decreased after the binary sodium-based slag treatment, which demonstrated that boron could be removed from molten silicon by the binary sodium-based slag, and different B removal rates were obtained by changing the slag compositions.

Table 1. Reagent compositions of binary sodium-based slag.

Serial number	Na_2CO_3 (mass%)	SiO_2 (mass%)
1	30	70
2	40	60
3	50	50
4	55	45
5	60	40
6	65	35

Table 2. B content of binary sodium-based slag materials and silicon melt (ppm).

Serial number	Raw silicon	Silicon melt	Silicon melt before casting	Na_2CO_3	SiO_2	Slag	Rate of boron removal
1	7.81	14.69	12.93	0.3	0.6	1.2	12.0%
2	6.88	15.63	13.13	0.3	0.6	1.8	16.0%
3	8.42	14.81	11.55	0.3	0.6	2.6	22.0%
4	9.20	16.25	12.51	0.3	0.6	2.9	23.0%
5	7.59	14.66	11.36	0.3	0.6	3.1	22.5%
6	8.40	15.38	12.15	0.3	0.6	3.0	21.0%

Slag-silicon ratio = 0.1

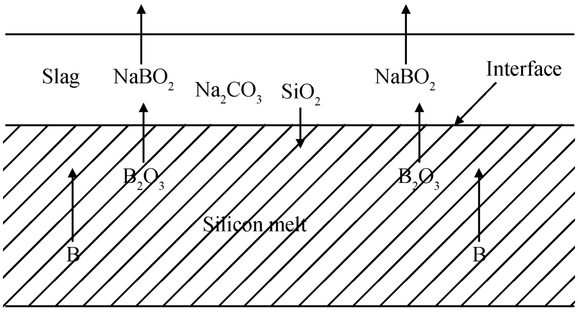

Fig. 2. Speculated deboronization mechanism.

It could also be found from Table 2 that before slagging, the B content in the silicon melt was higher than that in the raw silicon, which could be attributed to the contamination of B from the graphite crucible into the molten silicon during the melting process, even the B content of the raw silicon was more than 9.0 mass ppm. Hence, it could be inferred that the B content of the graphite crucible was quite high and the apparent diffusion of B from the molten silicon into the graphite crucible could be ignored.

In view of the decrease of the total amount of B in the slag-silicon system before and after slagging, we could conclude that some boron had escaped from the silicon-slag system by volatilization, supported by the low boiling point and decomposition temperature of $NaBO_2$. The speculated reaction mechanism of boron removal is schematically shown in Fig. 2.

3.2. Effect of Al_2O_3 addition on boron removal rate

To suppress the volatilization of sodium-based slag, Al_2O_3 was added to a slag with a composition similar to that employed when the best boron removal rate was obtained for the sodium-based slag (Na_2CO_3/SiO_2 = 55/45). Four kinds of samples were prepared, as shown in Table 3, the slagging time of the

Table 3. Reagent compositions of ternary sodium-based slag.

Serial number	Na_2CO_3 (mass%)	SiO_2 (mass%)	Al_2O_3 (mass%)
1	55.0	44.5	0.5
2	55.0	44.0	1.0
3	55.0	43.5	1.5
4	55.0	42.0	2.0

Slag-silicon ratio = 0.5.

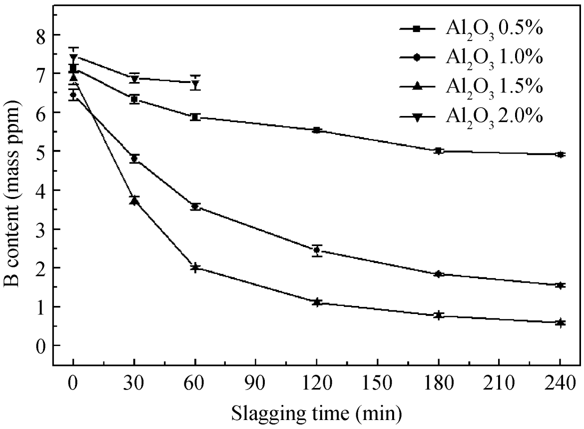

Fig. 3. Time dependence of the boron content on Al_2O_3 addition.

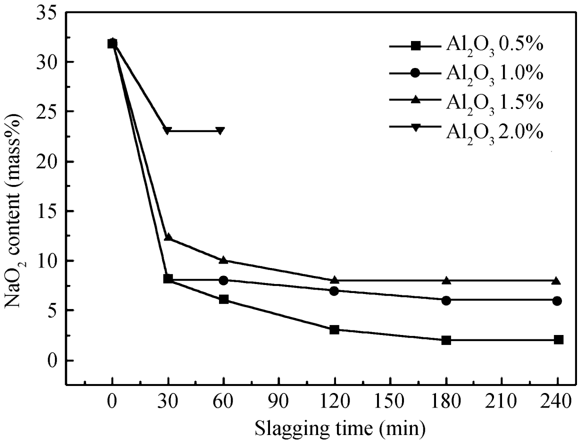

Fig. 4. Time dependence of slag basicities.

experiment was prolonged to 4 h, while the ratio of slag to silicon was increased to 0.5.

Figure 3 shows the time dependence of the boron content with different Al_2O_3 addition, from which it could be found that the boron content in the silicon was apparently reduced during the initial stage of slagging, although the reduction became slow when the slagging time was prolonged. With the Al_2O_3 addition of mass 1.5%, the boron was removed from 6.88 to 0.59 mass ppm, as the slagging time was increased to 4 h.

Figure 4 shows the time dependence of slag basicities with different Al_2O_3 addition, which revealed that the basicities decreased apparently at the initial slagging stage. As slagging time prolonged, different basicities were obtained with the changes of Al_2O_3 addition, which could be attributed to the formation of $NaAlO_2$. Compared with Na_2CO_3 and most kinds of sodium silicate, $NaAlO_2$ possesses a higher decomposition temperature (1900 K). Therefore, the formation of $NaAlO_2$ could increase the thermodynamic stability of the slag, hence, maintaining the basicity of the slag-silicon system, which was considered as one of the main effective factors in boron removal by slag refining[10].

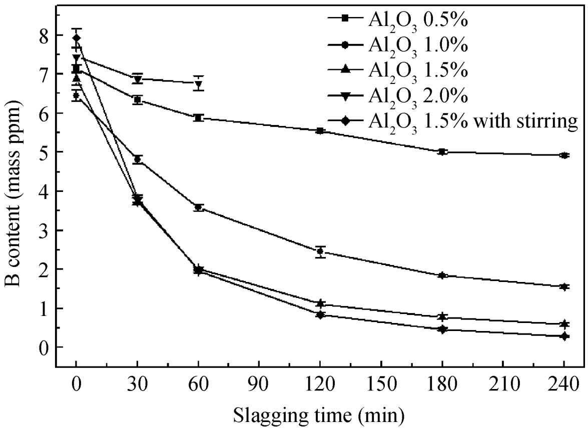

Fig. 5. Time dependence of the boron content on Al_2O_3 addition with and without stirring.

All these facts suggest that the boron removal was quite a complex process, which involved types of chemical reactions and the chemical reactions were affected by the slag composition and boron content of molten silicon. For slag refining, when the boron content of the molten silicon was higher than 2.0 mass ppm, the chemical reactions were the rate determining steps, which could mainly be attributed to the attenuation of the oxidant content or the basicity near the slag-silicon interface. However, the diffusion of boron from the molten silicon to slag-silicon interface, which was mainly caused by the concentration gradient of [B], would restrict the chemical reactions, especially when the boron content in the molten silicon was lower than 2.0 mass ppm.

To prove this, an extra experiment was conducted with a stirring process to homogenize the slag instantaneously and to keep fresh oxidant content or the basicity near the slag-silicon interface and the Al_2O_3 addition was 1.5%.

Figure 5 shows the time dependence of the boron content with and without the stirring process. It could be found that a better boron removal rate was obtained with stirring than that without stirring when the Al_2O_3 addition was 1.5%. The boron content was removed from 7.93 to 0.29 mass ppm, as shown in Fig. 5, which showed a better boron removal effect with the stirring process. It could be found from Fig. 5 that the boron content decreased rapidly at the initial slagging stage, which could be attributed to keeping fresh oxidant content or the basicity near the silicon-slag interface by stirring. When the slagging time was further prolonged, the boron removal rate decreased, which was similar to the results for without stirring (with the same turning point at 60 min). This indirectly supports the conclusion that when the boron content was lower than 2.0 mass ppm, the chemical reactions would be restricted by the diffusion of boron.

The better boron removal effect could be attributed to the homogenization of the molten silicon by stirring. The boron concentration gradient of the slag-silicon interface would be maintained by stirring, therefore, improving the boron removal effect.

4. Conclusions

Slag refining is an important option for boron removal from molten MG-Si in the sequential metallurgical process to produce high-purity SOG-Si. In this paper, the boron removal behavior with sodium-based slags has been investigated.

(1) Boron was removed from a slag-silicon system by sodium-based slags in the form of $NaBO_2$ or its decomposition.

(2) The appropriate amount of Al_2O_3 could maintain the basicity of the slag, hence improving the boron removal rate.

(3) The boron content was consistently reduced to less than 0.3 mass ppm, which was the permissible boron content for SOG-Si.

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