Application of slag refining technique to metallurgical grade silicon purification process: A review

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The photovoltaic generates electricity through direct conversion of sunlight, has fast-growing recently due to high global energy demand. Photovoltaic main material is silicon which needs refining process to fulfill the requirements. In this paper, the principle of silicon-slag refining was introduced and several types of imposing slag were reviewed. Boron removal from silicon using Si-based alloy and novel slag with active component were mentioned, and effects of slag refining processing parameters were discussed. According to the investigations, slag refining technique can remove a large amount of boron from MG-Si, and the potential industrial applications of slag refining technique were proposed.

Keywords: solar grade silicon, metallurgical grade silicon, slag refining, B removal.

Представлен принцип переработки кремниевого шлака, рассмотрены несколько типов шлака. Было упомянуто об удалении бора из кремния с использованием сплава на основе кремния (Si) и нового шлака с активным компонентом, обсуждается эффект от процесса рафинирования шлака. Согласно исследованиям, процесс рафинирования шлака может удалить большое количество бора из MG-Si (металлургического кремния), а также предложена потенциальная промышленная технология рафинирования шлака.

Технологія переробки шлаку для металургійного процесу очищення кремнію: огляд. *Rowaid Al-khazraji, Yaqiong Li, Lifeng Zhang*

Представлено принцип переробки кремнієвого шлаку, розглянуто кілька типів шлакових систем. Розглядається видалення бору з кремнію з використанням сплаву на основі кремнію (Si) та нового шлаку з активним компонентом, обговорюються наслідки від параметрів рафінування шлаку. За даними досліджень, технологія рафінування шлаку дозволяє видалити велику кількість бору з MG-Si (металургійного кремнію), запропоновано потенційне застосування у промисловості технологій рафінування шлаку.

1. Introduction

Application of solar energy comprises 0.24% of the global energy resource and 4.67% of renewable energy resource and wich raises up rapidly [1]. The solar cell has big attention currently and the need for solar grade silicon (SOG-Si, purity of 99.9999%) feedstock has been growing rapidly. Boron impurity in Si solar cells plays a major role in reducing photoelectric conversion efficiency through accelerating auger recombination and reducing the lifetime of minority carriers, and moreover, the metastable defects (BO_n), deep energy levels boric, and ferrous compounds are the main factors for cell decay. Most common routes to produce SOG-Si from metallurgical grade silicon

(MG-Si, purity of 98~99%) is still based on Siemens technology, which is considered an energy-intensive method and generates significant amounts of chemical wastes. In recent years, more economic effective metallurgical processes for SOG-Si production have been studied and developed, such as directional solidification [2, 3], acid leaching [4, 5], solvent refining [6, 7], plasma refining, vacuum process [8, 9], and slag refining [10, 11].

For solar cell application, the impurity level for elements should not exceed 1 ppmw [12]. Most impurities in MG-Si, especially metal elements, can be eliminated to the required content by directional solidification. However, this method is useless for the impurity with large segregation coefficient, such as B [13]. Moreover vacuum refining treatment shows no effect on B because of its low vapor pressure (10^{-6} Pa at 1773 K) [14]. It is noting that the molten slag like CaO–SiO$_2$ based systems (i.e. CaO–SiO$_2$, CaO–SiO$_2$–CaF$_2$, CaO–SiO$_2$–Al$_2$O$_3$, CaO–SiO$_2$–Na$_2$O, and so on) are efficient agents for B removal, which are common used in steel making industry. This current paper extensively reviews relevant theoretical and experimental studies in this field.

2. Basic principle

2.1 Principle of slag refining

Slag refining is one of the metallurgical methods used to remove B impurity from MG-Si. It includes melting MG-Si in the presence of a slag to remove B impurity. Slag refining has lower equipment cost with less energy consumption. It can be brief in reacting slag with MG-Si to oxidize impurities at Si/slag interface in the first step, and draw it from the interface to slag phase in the second step. The B impurity can be oxidized to BO, B$_2$O$_3$, B$_2$O, BO$_2$, and B$_2$O$_2$ gas by slag treatment and evaporated at 1685-2500 K [14]. From Ellingham oxides diagram [15], B has higher Gibbs free energy (ΔG) than Si which means B removal is a little hard. The major attempts in the purification of MG-Si using slag have been focused on determining equilibrium conditions between Si and slag and optimizing slag chemistry, including its basicity (CaO/SiO$_2$) and oxygen potential (P$_{O2}$), so that the removal efficiency of these elements maximized. The B oxidation reaction at the Si/slag interface can be expressed by the following chemical reaction:

$$B + \frac{3}{4}O_2 = \frac{1}{2}B_2O_3 \qquad (1)$$
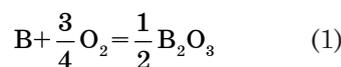
The slag absorbs B oxide (B$_2$O$_3$) in form of borate (BO_3^{3-}) as following reaction:

$$\frac{1}{2}B_2O_3 + \frac{3}{2}O^{2-} = BO_3^{3-} \qquad (2)$$
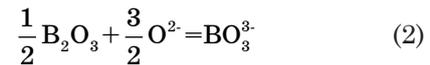
Oxide ion (O^{2-}) in the above reaction is provided by the slag through dissociation of basic oxides such as CaO, BaO, or Na$_2$O as expressed in reaction (3), while under equilibrium conditions the oxygen potential is established through reaction (4) as the dominant metal/oxide phases.

$$CaO = Ca^{2+} + O^{2-} \qquad (3)$$

$$SiO_2 = Si + O_2 \qquad (4)$$
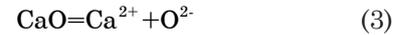
The distribution coefficient of B (L_B) used to evaluate the B removal from Si is expressed by equation (5):

$$L_B = \frac{(\%B)\text{in slag}}{[\%B]\text{in Si}} \qquad (5)$$

2.2 Thermodynamic analysis of slag treatment

Oxidation reaction of B at the interface between Si and slag can be given by equation (1). For slag containing silica, oxygen is generated as shown in equation (4). Combining equation (1) and (4) gives the total equation (6):

$$\frac{3}{4}(SiO_2) + [B] = (BO_{1.5}) + \frac{3}{4}Si \qquad (6)$$
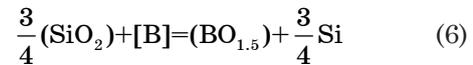
Therefore, the equilibrium constant for this reaction is obtained by equations (7):

$$K = \frac{\alpha_{BO_{1.5}}\alpha_{Si}^{3/4}}{\alpha_{SiO_2}^{3/4}\alpha_B} \qquad (7)$$

Where α is the activity of the component i, and it is expressed by the mole fraction and the activity coefficient of component i (γ_i) as shown in the following equation:

$$\alpha_1 = \gamma_1 x_1 \qquad (8)$$

Equation (7) can be re-written as the following equations:

$$K = \frac{\alpha_{BO_{1.5}}(\alpha_{Si})^{3/4}}{\alpha_B(\alpha_{SiO_2})^{3/4}} = \frac{\gamma_{BO_{1.5}}X_{BO_{1.5}}}{\gamma_B X_B} \cdot (\frac{\alpha_{Si}}{\alpha_{SiO_2}})^{3/4} \qquad (9)$$

$$L_B = \frac{X_{BO_{1.5}}}{X_B} = \frac{K\gamma_B}{\gamma_{BO_{1.5}}} \cdot (\frac{\alpha_{SiO_2}}{\alpha_{Si}})^{3/4} \qquad (10)$$

where $X_{BO1.5}$ and X_B are the B contents in slag and Si after slag treatment, respectively; α_i and γ_i are the activity and activity coefficient of the component i, respectively; K is the equilibrium constant of the reaction; and L_B is the partition coefficient of B. From equation (10), it can be seen that L_B is affected by the activ-

ity coefficient of B in the Si phase, the activity coefficient of $BO_{1.5}$ in the slag phase, the oxygen partial pressure, temperature, and the slag composition.

3. Different slags used for MG-Si refining

Several slag systems have been proposed for MG-Si treatment, including $CaO–SiO_2$ [16-18], $Na_2O–SiO_2$ [19, 20], $CaO–SiO_2–CaF_2$ [16, 21, 22], $BaO–SiO_2–Al_2O_3$ [10], $CaO–SiO_2–Al_2O_3–MgO$ [10], and so on. Different experiments and researches of slag refining using different experimental conditions have been reviewed and discussed below.

3.1 MG-Si purification by slag refining using binary slag system

Generally, $CaO–SiO_2$ slag system is used for the removal of B individually or combined with other additives, which made the $CaO–SiO_2$ system more important and basic. The changes in the composition of this binary system could affect the B removal efficiency. The amount of B removal by slag treatment is a function of CaO/SiO_2 ratio (basicity), oxygen contents in slag, and free oxygen ions. Teixeira et al. [16], Wu et al. [17], and Wei et al. [18] studied the B removal from MG-Si using $CaO–SiO_2$ slag. Wu et al. [17] worked to refine MG-Si using SiO_2. The result shows that the process needs quite high temperature and the final B content in Si is above the SOG-Si level. The B removal efficiency is greatly improved with the addition of basic oxide CaO to SiO_2, because the high oxygen contents are necessary to oxidize B as B_2O_3, and the high basicity provides free oxygen ions to absorb B_2O_3 into the slag phase. Additionally, the $CaO–SiO_2$ phase diagram shows that increasing the SiO_2 content appropriately is beneficial to decrease the melting point of the slag. When the content of SiO_2 is 42.3%~61.3%, the melting point of slag is ranging from 1710 K to 1813 K, which is higher than that of Si. Therefore, the slag treatment needs high heating temperature above 1710 K.

Compared to the commonly used $CaO–SiO_2$ slag system, the $Na_2O–SiO_2$ slag [19] shows relatively low melting point, density, surface tension, and viscosity. The removal rate of B increases with increasing Na_2O concentration in slag, and the B is removed at the slag/gas interface in the form of $Na_2B_2O_4$, which is a volatile compound. Finally, 91 % of B was removed by using 50%NaO–SiO_2 slag at 1823 K. Fang et al. [20] investigated the B removal by multiple slag operations with $Na_2O–SiO_2$ slag. The B content decreased from 10.6 to 10.6 ppmw by one slag treatment and the removal efficiency

of B with slag refining in once, twice and three times was 93.87 %, 96.96 %, and 98.68 %, respectively.

3.2 MG-Si purification by slag refining using ternary slag system

In order to promote B removal, enhancing slag chemistry is considered an important factor, such as slag basicity, viscosity, and melting point. This leads to the modification of the binary slag system to ternary slag system by adding active agents. Wu et al. [23] and Li et al. [24] studied the effect of K_2CO_3 addition to $CaO–SiO_2$ slag during the purification process. Their results show that the addition of high basic K_2CO_3 can improve the mass transfer of B in slag, and therefore increased the removal efficiency of B. Teixeira et al. [16], Luo et al. [21], and Jing et al. [22] added CaF_2 to $CaO–SiO_2$. The CaF_2 addition provided a broader of basicity range compared to the binary systems, but it did not obviously improve the LB. CaF_2 is neither as acidic as silica nor as basic as CaO and hence it dilutes both compounds in the slag phase. The addition of CaF_2 leads to de-polymerization of silicate network by F- which has the ability to move between silicate anions and free the O_2 from the SiO_2, thereby decreasing the electrostatic bound and lowering the viscosity of the slag. The obtained O_2 facilitates the removal of B in the Si/slag interface. Furthermore, the reaction between CaF_2 and SiO_2 can form CaO, resulting in a higher basicity. So the addition of CaF_2 can expand the range of basicity and facilitate the removal of B. In case of using lithium compounds with slag, Wu et al. [25], Ding et al. [26], and Lai et al. [27] investigated the $SiO_2–CaO–Li_2O$ and $SiO_2–CaO–LiF$ ternary slag systems. LiF can lower the slag's viscosity, and Li_2O can react with many metal oxides, (i.e. CuO, Fe_2O_3) and non-metal oxides, (i.e. B_2O_3 and P_2O_5). It is worth noting that the addition of Li_2O or LiF to $SiO_2–CaO$ constitute more effective ways for the B removal. With increasing Li_2O content, the basicity of slag increases, which reinforces the slag ability to absorb B oxides and increase L_B value. Nishimoto et al. [28] proposed to optimize B removal by combining $CaO–SiO_2$ slag treatment with Cl_2 gaseous at 1823 K, resulting in the reduction and removal of B content as B–O–Cl form. Wang et al. [29] and Lu et al. [30] added $CaCl_2$ to $CaO–SiO_2$ slag, which reduced the melting point and viscosity of slag. B can react with the slag at the slag/Si interface, and then enter into the slag as $BO_{1.5}$. And $BO_{1.5}$ can react with $CaCl_2$ in the molten slag to form B–O–Cl with a high vapor pressure resulting in the evaporation of B from the slag. Lu et al. [31] used $CaO–SiO_2$ slag system with intermit-
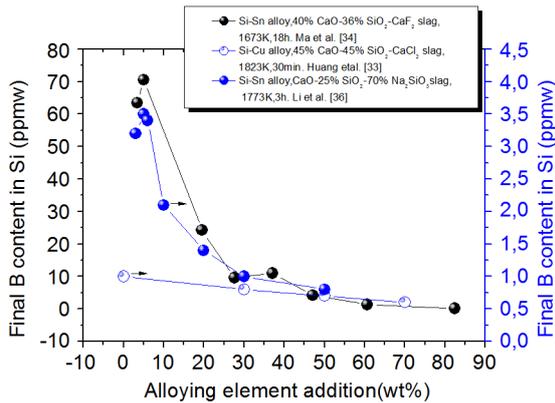
Fig. 1. Effect of alloying element on the final B content in Si

tent $CaCl_2$ addition. The results showed that the intermittent $CaCl_2$ addition promotes the elimination of B. Wu et al. [32] studied the combined method consisting slag treatment and gas blowing. The B concentration decreased from 22 ppmw to 0.75 ppmw by using 42.5%CaO–SiO_2–15%$CaCl_2$ slag and 40%Ar–20%O_2–H_2O gas composition. They found it is helpful to remove B by adding water vapor into the oxygen, because the partial pressure of the gaseous boric hydrate species is much higher than that of gaseous boric oxide species. Luo et al. [21] used CaO–SiO_2–(Na_2O, Al_2O_3) slag for the slag refining. The CaO–SiO_2–(Na_2O, Al_2O_3) ternary slag showed better results compared to the CaO–SiO_2 binary slag under the same experimental conditions. The L_B was 2.1 after CaO–SiO_2 slag treatment, while the L_B in the CaO–SiO_2–Na_2O and CaO–SiO_2–Al_2O_3 can respectively increase to 4 and 6.5.

3.3 MG-Si purification by slag refining using quaternary slag system

More attempts were used to enhance the slag refining efficiency by using quaternary slag. Johnston et al. [10] investigated Al_2O_3–CaO–MgO–SiO_2 slag. They found that L_B reached the maximum value of about 1.5 when the basicity was 0.8. It shown that the slag with strongly basic and oxidizing features would be useful for B removal from Si. Yuan et al. [33] studied slag refining using SiO_2–CaO–Na_3AlF_6–CaSiO$_3$ slag, and the B content decreased from 14 ppmw to 0.436 ppmw by using 23.12%SiO_2–CaO–16.83%Na_3AlF_6–49.61%$CaSiO_3$ slag. The B contents in Si are strongly affected by slag composition and addition of Na_3AlF_6–CaO to $CaSiO_3$ slag. Table 1 summarizes the slag refining with different slag systems results.

3.4 Si-based alloy refining using slag system

With the development of slag treatment, the B content in MG-Si decreased gradually, which

resulted in the lack of mass transfer, reaction process, and the low activity of B. Although the increase of melting temperature can increase the activity of B in Si phase, but the refining cost increased. In order to improve the L_B and B removal efficiency, MG-Si can be alloy with another element as the first step and treated it with slag in the following step. Huang et al. [34] reported the purification of Si–Cu alloy by using CaO–SiO_2–$CaCl_2$ slag. The B contents reduced from 3.12 ppmw to 0.35 ppmw, and B contents decreased from 3.12 to 1.01 ppmw without the addition of Cu in the experiment under the same conditions. Ma et al. [35, 36] investigated a sequential refining process of MG-Si composed of Si–Sn solvent refining, slag treatment, and acid leaching. In their work, the prepared Si–Sn alloy was treated with CaO–SiO_2–CaF_2 slag with different slag to alloy mass ratio. B content was found to be decreased from 33 ppmw to 0.3 ppmw, and there was an increasing in LB with increasing Sn contents in Si–Sn alloy due to the increasing B activity coefficient and oxygen partial pressure. Li et al. [37] combined Si–Cu solvent refining and CaO–SiO_2–Na_2O–Al_2O_3 slag treatment. When the Si alloyed with Cu or Sn, the B removal efficiency after slag refining can be improved remarkably. Fig. 1 shows the relationship between alloying element and final B content in Si. As shown in this figure, the B removal is favorable with higher metal compositions. According to equation (10), alloying metal such (as Cu and Sn) has the ability to decrease the activity of silicon or/and increase the activity coefficient of $BO_{1.5}$. This resulted in an increase in the L_B. Although the Cu content in the refined Si increased, it can be removed in the following refining step. For example, directional solidification is an unavoidable refining step for SOG-Si production through any integrated metallurgical route, Cu and Sn can be removed in this step.

4. Influencing factors on slag refining process

MG-Si treated by slag refining with various temperatures, holding time, and heating methods could exhibit different refining results. For instance, increasing the temperature leads to reduce in B contents as shown in Fig. 2(a), because the high temperature can reduce slag viscosity and increase the silica activity in the slag. Additionally, holding time is an important parameter affecting B removal, as shown in Fig. 2(b). In the first 30 min, the B content was significantly reduced, but as time continued to increase, the B content did not change significantly and only slightly decreased. This is because as the content of B in Si decreases,

Table 1. MG-Si refining using various slag systems

Slag system	Author	Main work	Refining results	Ref.
Binary slag system	Teixeira et al.	B removal from MG-Si using CaO–SiO$_2$ slag at 1823 K for 18 h, CaO:SiO$_2$=1.21:1, and slag:MG-Si=2.2:1	B:150 → 10.4 ppmw, L_B=5.5	[16]
	Wei et al.	B removal from MG-Si using 50%CaO–SiO$_2$ slag at 1823 K for different time, and slag: MG-Si=1:1	B:22 →5.1 ppmw for 1 h, R.E.=76.8% B:22 →4.73 ppmw for 3 h, R.E.=78.5%	[18]
	Wu et al.	B removal from MG-Si using 50%CaO–SiO$_2$ slag at 1823 K for 1.5 h, and slag:MG-Si=1:1	B:22 → 5 ppmw, R.E.=77%	[23]
	Wu et al.	B removal from MG-Si using 60%CaO–SiO$_2$ slag at 1873 K for 3 h, and slag:MG-Si=2.5:1	B: 18 → 1.8 ppmw, R.E.=90%	[17]
	Safarian et al.	B removal from Si using Na$_2$O–SiO$_2$ slag at 1823 K for 15 min, and slag:MG-Si=2:1	R.E.=90% using 50%Na$_2$O–SiO$_2$	[19]
	Fang et al.	Multiple slag operation using Na$_2$O–SiO$_2$ slag to remove B from MG-Si at 1973 K for 0.5 h, Na$_2$O:SiO$_2$ =2:1, and slag:MG-Si=2:1	B:10.6→ 0.3 (1 run),→ 0.15 (2 run)→12 ppmw(3 run)	[20]
	Lai et al.	B removal from MG-Si using 60%Li$_2$O–SiO$_2$ at 1973 K for 0.5 h, and slag:MG-Si=3:1	B:8.6→0.4ppmw, R.E.=95.3%	[27]
	Wu et al.	B removal from MG-Si using 40%CaO–40%SiO$_2$–K$_2$CO$_3$ slag at 1823 K for 3.8 h, and slag: MG-Si=1:1	B:22 → 1.8 ppmw, R.E.=91.8%	[23]
	Li et al.	B removal from MG-Si using 20%K$_2$CO$_3$–44%SiO$_2$–CaO slag at 1873 K for 4 h, and slag: MG-Si=1:1	B:22 → 1.8 ppmw, R.E.=91.8% L_B=12.2	[24]
	Luo et al.	B removal from MG-Si using CaO-SiO$_2$–10%(CaF$_2$, Al$_2$O$_3$,Na$_2$O) slag, CaO/SiO$_2$ =1.21, and slag:MG-Si=1:10	–CaF$_2$, L_B=1.5 –Al$_2$O$_3$, L_B=6.5 –Na$_2$O, L_B=4	[21]
	Jing et al.	B removal from MG-Si by 60%CaO–30%SiO$_2$–CaF$_2$ slag at 1873 K for 1 h and slag:MG-Si=3:10	B: → 1.1 ppmw, L_B=4.61	[22]
Ternary slag system	Wu et al.	B removal from MG-Si by CaO–20%Li$_2$O–44%SiO$_2$–CaO slag at 1873 K for 2 h, and slag: MG-Si=4:1	B:18 → 1.3 ppmw, R.E.=92.7%	[25]
	Ding et al.	B removal at 1823 K for 0.5-4 h, CaO/SiO$_2$=0.8,using: - CaO–SiO$_2$–2wt%Li$_2$O - CaO–SiO$_2$–5wt%LiF	–L_B=1.98 –L_B=2.77	[26]
	Lai et al.	B removal from MG-Si using 54%Li$_2$O–36%SiO$_2$–CaF$_2$ at 1973 K for 0.5 h and slag:MG-Si=2:1	B:8.6 → 0.46 ppmw, R.E.=94.6%	[27]
	Wang et al.	B removal from MG-Si by oxidized chlorination and evaporation using 23%SiO$_2$–47%CaO–CaCl$_2$ slag at 1723 K for 12 h, and slag:MG-Si=2:1	B:150 → 30 ppmw, L_B=2.4,	[29]
	Lu et al	B removal from MG-Si using 10%CaCl$_2$–10%CaO–SiO$_2$ slag, slag:MG-Si=1:1, and 0.5h	B:3.8 → 1.4 ppmw, R.E.=63%	[31]
	Nishimoto et al.	B removal from MG-Si using 55%CaO–SiO$_2$ slag with introducing Cl$_2$ gas at 1823 K	B:400 → 300 ppmw, R.E.=25%	[28]
	Wu et al.	B removal from MG-Si using 42.5%CaO–42.5%SiO$_2$–CaCl$_2$ slag, 40%Ar–20%O$_2$–H$_2$O gas at 1823K for 3h and slag:MG-Si=1:1	B:22 → 0.75 ppmw, R.E.=96.5%	[32]
	Johnston et al.	B removal from MG-Si by 35%Al$_2$O$_3$–25%CaO–3%MgO–SiO$_2$ slag at 1773K for 2h and slag:MG-Si=1.36:1	L_B=1.6	[10]
Quaternary slag system	Yuan et al.	B removal from MG-Si using 23.12%SiO$_2$–10.4%CaO–16.83%Na$_3$AlF$_6$–CaSiO$_3$ slag at 1823 K for 1 h, and slag:MG-Si= 1:1	B:14 → 0.436 ppmw, R.E.=96.9%	[33]
	Sun et al.	B removal from MG-Si by CaO–SiO$_2$–15%BaO–20%CaF$_2$ slag at1873 K for1 h, and slag:MG-Si=1:4	B:3.5 → 0.37 ppmw, R.E.=89.4%	[39]

the kinetic behavior of the B hindered, which results in longer time for B removal by the slag treatment. It could be concluded that B oxidation reached equilibrium after 30 min.

Slag refining can also be affected by the heating manner. Wu et al. [38] in their work investigated the effect of heating method on B removal. The results shown that when the slag refining is performed using an resistance furnace, the boron removal efficiency reaches 42.1%, while when slag refining is performed using an electromagnetic induction furnace, the boron removal efficiency reaches 83.15%. Obviously, the heating manner of electromagnetic induction accelerates the refining reaction, which causes a sharp increase of efficiency of B removal.

5. Conclusion

Slag refining is the main refining method for removing boron impurities in silicon. It uses slag to oxidize B impurity to reduce its content in Si. According to literature review, the conclusions were summarized as follows.

Changing the slag basicity shows a big influence on B removal from Si, where SiO_2 provides oxygen potential to oxidize B and CaO provides the oxygen ions to absorb B oxide into the slag. Therefore a suitable balance ratio between these two oxides is needed to enhance B removal.

Additive agents are quite helpful for the slag process, because it added to $CaO-SiO_2$ slag can decrease melting point, viscosity and adjust slag basicity, which aims to enhance B removal. It is worth mentioning that CaF_2 can reduce the liquidus temperature of the slag and enhance the mass transfer process, and $CaCl_2$ can be used to promote B removal as gas product.

Slag refining of Si alloy has shown very large L_B and the B removal efficiency because of the increasing the activity coefficient of B and the decreasing activity of SiO_2. It provided a favorable condition for removal of alloy phase by selective acid leaching.

The slag refining application for Si–alloy has a high potential for better B removal from MG-Si. Although it can not avoid the introduction of alloying metal as impurities into the refined Si, it can be removed through directional solidification refining step. Therefore, this process is considered as a low-cost treatment comparing to Siemens process.

Acknowledgments
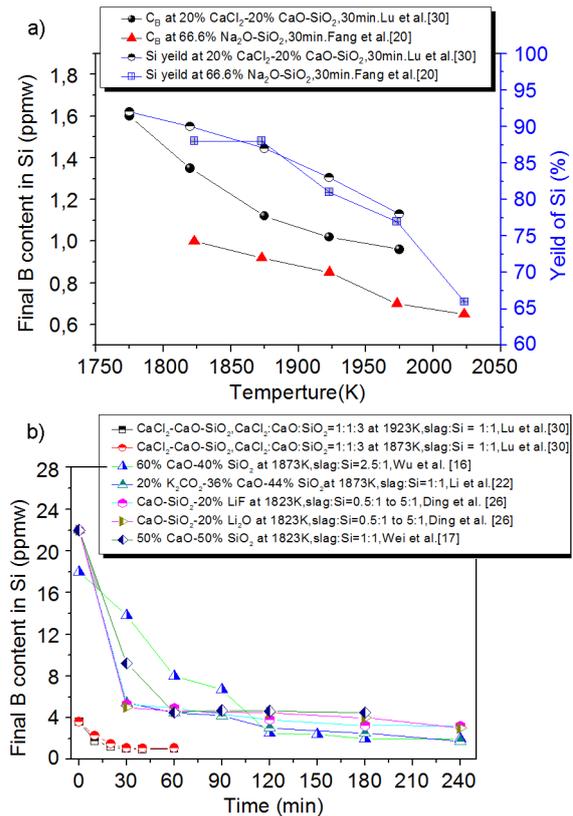
Fig. 2. (a) Effect of temperature on the final B content and Si yield, and (b) effect of holding time on final B content after slag refining.

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