

Boron removal for solar-grade silicon production by metallurgical route

A review

Chen, Hui; Morita, Kazuki; Ma, Xiaodong; Chen, Zhiyuan; Wang, Ye

DOI

[10.1016/j.solmat.2019.110169](https://doi.org/10.1016/j.solmat.2019.110169)

Publication date

2019

Document Version

Final published version

Published in

Solar Energy Materials and Solar Cells

Citation (APA)

Chen, H., Morita, K., Ma, X., Chen, Z., & Wang, Y. (2019). Boron removal for solar-grade silicon production by metallurgical route: A review. *Solar Energy Materials and Solar Cells*, 203, Article 110169. <https://doi.org/10.1016/j.solmat.2019.110169>

Important note

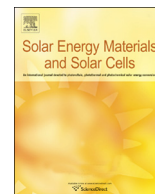
To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.



Boron removal for solar-grade silicon production by metallurgical route: A review

Hui Chen^{a,b}, Kazuki Morita^b, Xiaodong Ma^c, Zhiyuan Chen^d, Ye Wang^{a,*}

^a School of Chemical Engineering, Sichuan University, Chengdu, 610065, Sichuan, PR China

^b Department of Materials Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, 113-8654, Japan

^c School of Chemical Engineering, University of Queensland, Brisbane, Queensland, 4072, Australia

^d Department of Materials Science and Engineering, Delft University of Technology, Delft, 2628, CD, the Netherlands

ARTICLE INFO

Keywords:

Solar-grade silicon
Boron removal
Slag treatment
Solvent refining
Gas injection

ABSTRACT

Solar energy has received considerable attention over the past few decades, due to its importance as a green and renewable energy. Low-cost solar-grade silicon production is critical for the widespread use of solar cells. Conventional routes (e.g., modified Siemens process: chlorosilane and hot filament) have still dominated the production of solar-grade silicon. The metallurgical route offers benefits in the productivity and cost, but efficient removal of boron is one of the most daunting challenges in front of us. This paper reviews thermodynamic and kinetic properties (solubility, diffusivity, diffusion coefficients, mass transfer rate, and activity coefficient) of boron and recent research topics (slag treatment, solvent refining, gas injection, plasma treatment, and acid leaching) for boron removal.

1. Introduction

With an energy crisis and environmental degradation, the demand for photovoltaic (PV) installation rises from 7.7 GW in 2009 to 72.9 GW in 2017 [1]. Silicon-based solar cells account for more than 94% of the PV market due to the low cost, high photoelectric conversion efficiency, and stability [2].

According to the purity and industrial application, silicon (Si) material can be divided into 3 grades: metallurgical-grade silicon (MG-Si, purity: 99% (2N)), solar-grade silicon (SOG-Si, purity: 99.9999% (6N)), and electronic-grade silicon (EG-Si, purity: 99.9999999% (9N)). The concentrations of impurities in SOG-Si are listed in Table 1 [3]. Impurities can be divided into 3 main categories: Dopants (e.g., P and B) that affect resistivity, light elements (e.g., O, C, and N) that can form inclusions (e.g., SiO₂, SiC, and Si₃N₄) above the solubility limits and can create structure loss in the Czochralski (CZ) Process and instability in the MC process, and metals (e.g., Fe, Ti, Cu, Cr, and Al) that can reduce the lifetime of carriers and cell efficiency.

SOG-Si and EG-Si can be used to produce solar cells, while MG-Si is always as the raw material for the SOG-Si and EG-Si production. Scrap, or offcut, rejected and non-prime material from the EG-Si, was the main supply route for SOG-Si production previously. Because of the fast growth of the PV market in the past few decades, scrap is insufficient and the main source today is non-prime polysilicon, which is

deliberately produced by operating conventional processes (e.g., modified Siemens process: chlorosilane and hot filament, The Union Carbide and Komatsu process: monosilane and hot filament, and The Ethyl Corporation Process: silane and fluidized bed reactor) with more economical parameters (e.g., higher production efficiency, lower energy consumption, and higher impurity grades) [4].

With the break of key technologies and the decrease in energy consumption, the contract price of SOG-Si by the modified Siemens process declines from 100 USD/kg in 2009 to 10 USD/kg today [5]. However, the doping process is always required for the following solar module production by using polycrystalline Si to ensure a high concentration of carrier, which wastes purity and increases cost doubtless [6].

An alternative is the metallurgical route with many advantages, such as energy-saving, environmentally-friendly, and continuous. Life cycle assessments (LCAs) have also been carried out to the polysilicon production by the metallurgical route. Compared to the 30–70 gCO₂-eq/kWh of global warming potential (GWP) of modified Siemens process, the metallurgical route in China has only 20 gCO₂-eq/kWh [7], and environmental LCA study performed on the Elkem solar metallurgical process route shows the same value (23 gCO₂-eq/kWh) too [8]. The equivalent energy consumption for the production of SOG-Si via the metallurgical route is 20 kWh per kilogram polysilicon, 3 times lower than that for conventional processes [4,9]. As for the grid-

* Corresponding author.

E-mail address: wangye@scu.edu.cn (Y. Wang).

Table 1
Maximum concentrations of impurities in MG-Si, SOG-Si, and EG-Si.

Elements		Al	Fe	Ca	Mg	Mn	Cr	Ti	V	Zr	Cu	B	P	C	O
MG-Si	%	2	5	1	0.1	0.05	0.05	1.6	0.01	0.01	0.01	0.08	0.05	0.6	3
SOG-Si	ppmw	0.1	0.1	0.3	0.1	0.1	0.1	0.01	0.1	0.1	0.1	0.3	0.1	3	10
EG-Si	ppbw	0.8	0.2	0.01	0.2	0.2	0.2	3	0.2	0.2	0.2	0.2	0.8	0.5	–

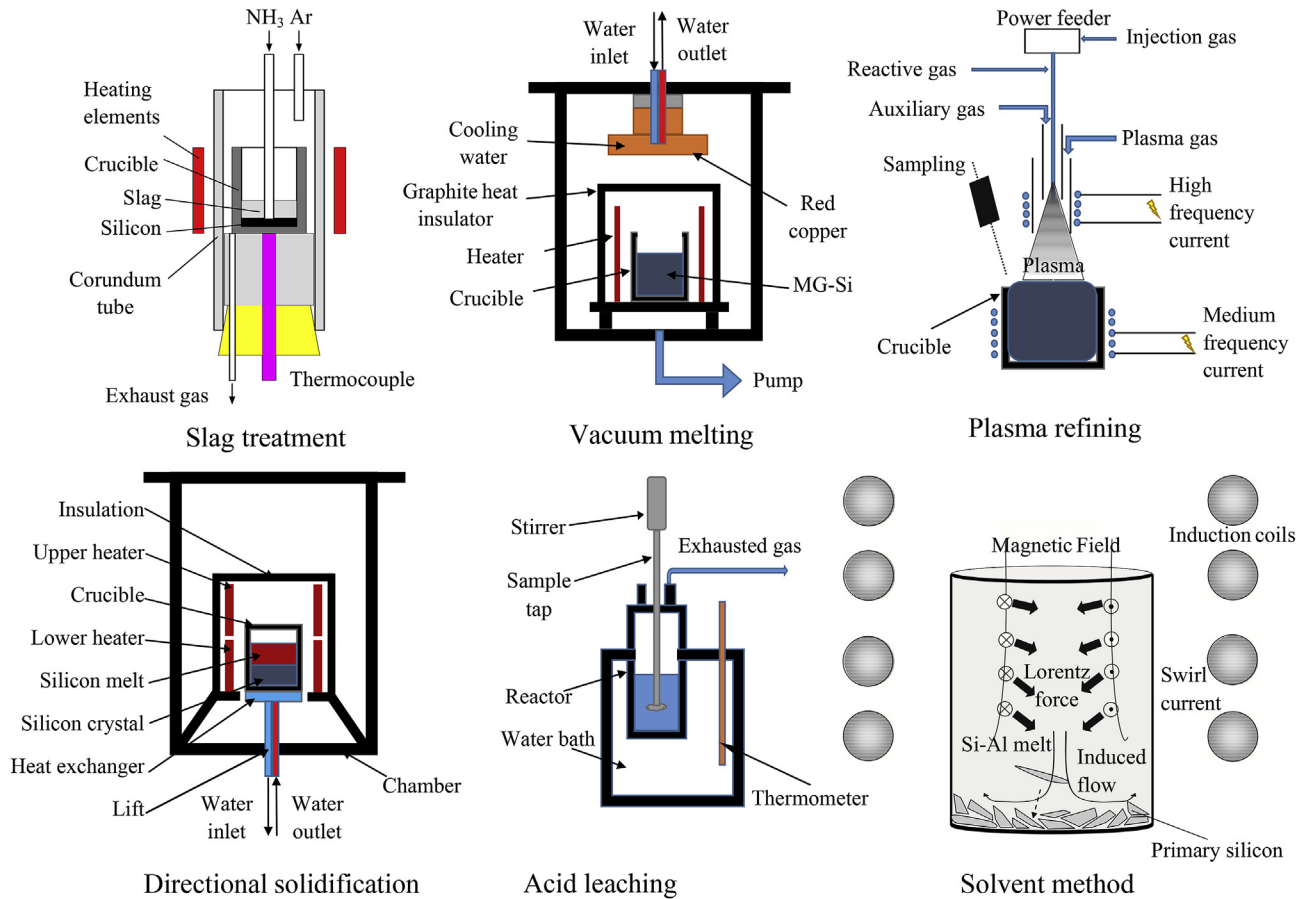


Fig. 1. Various metallurgical purification processes for Si.

connected power generation system (including PV system manufacture, PV system transportation and installation, PV station operation and maintenance, PV power transmission, and PV station retirement) supported by the polycrystalline Si in the metallurgical route, the comprehensive environmental impact for China is 6.92×10^{-14} based on ECER-125 index, which is about 56–66% of that for other nations (Italy, Japan, Australia, and the USA) [7]. Lower environmental impacts (e.g., human toxicity, freshwater eutrophication, and freshwater eco-toxicity) are also from the use of Si feedstock by the metallurgical route based on the environmental LCA analysis of the Passivated Emitter and Rear Cell (PERC) technology [10].

Fig. 1 shows various metallurgical purification processes in the metallurgical route, including slag treatment [11], hydrometallurgical leaching [12], vacuum evaporation [13], directional solidification [14], electron beam [15], and plasma method [16], and MG-Si is the raw material for SOG-Si production. *Dongmeng method*[®], a representative method proposed by Dongmeng energy Co., Ltd, is shown in Fig. 2. According to this method, metal impurities can be removed by acid leaching [17] and electron beam is an effective method to vaporize P and O [18]. However, the biggest difficulty of this method is the first step (the acquisition of Si with low boron (B) concentration), B removal from Si is most difficult by metallurgical route due to the low vapour partial

pressure and high segregation coefficient.

The level of B tolerated in the process of solar cell production is becoming less stringent with the development of solar cells. In fact, once the B concentration is higher than 0.3 ppmw, the minority carrier lifetime shortens sharply with B–O defects, which determines the photoelectric conversion efficiency [19]. Directional solidification and vacuum melting cannot remove B effectively. Nowadays, slag refining, low-temperature Si-based solvent refining, gas blowing, high-temperature plasma, and acid leaching are the main processes for B removal. To effectively diminish B concentration for large-scale SOG-Si production, it is important to review the development of refining processes for B removal.

2. Properties of boron in silicon

2.1. Solubility of boron in silicon

A thermochemical database that covers 33 elements has been developed by Tang et al. [20]. The Si–B binary system is illustrated in Fig. 3, and the composition range of B in SOG-Si generally ranges from ppm to a few percents [21–25]. However, considering their verification in the binary alloy systems, it should be careful when using these data.

Dongmeng method

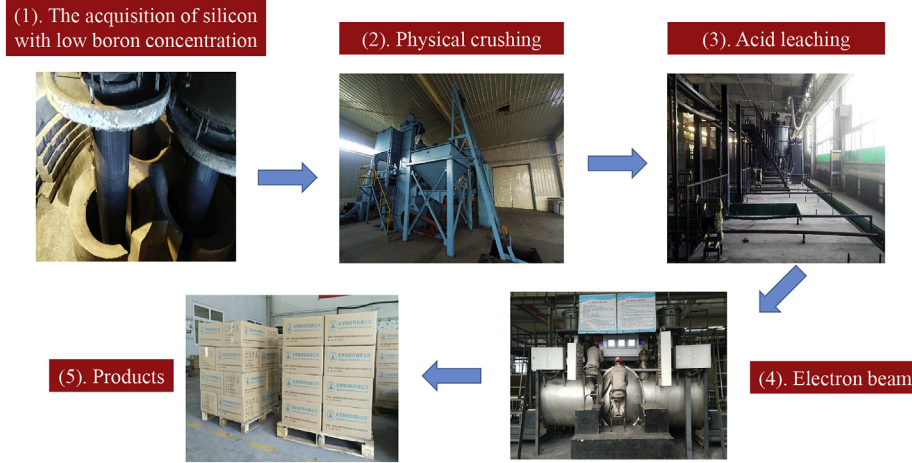


Fig. 2. Dongmeng method. (1), The acquisition of Si with low B concentration, which is produced by Submerged-arc furnaces or Intermediate-frequency furnaces; (2), Physical crushing to expose grain boundaries where purities gather; (3), Acid leaching to remove metal impurities on the surfaces; (4), Electron beam to supplement electrons and to vaporize P, Fe, and O in a high vacuum.

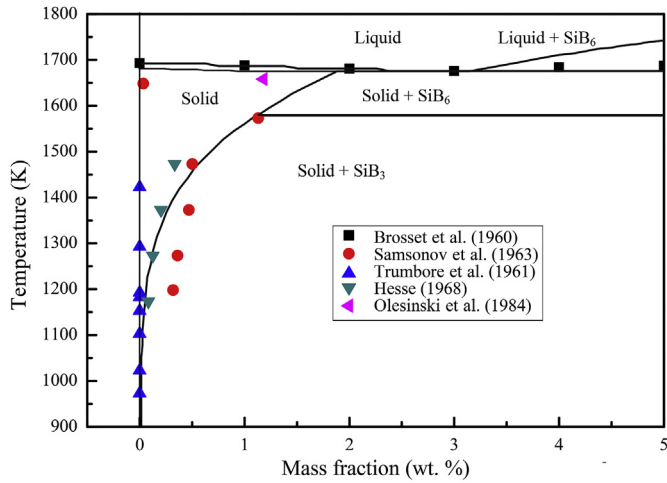


Fig. 3. Phase equilibria in the Si-rich Si-B system.

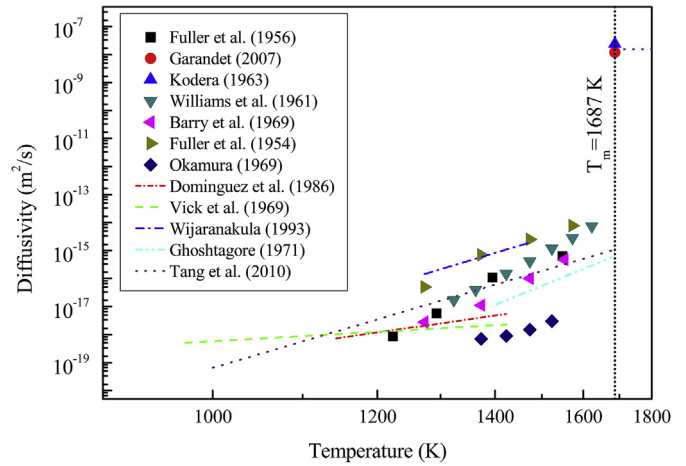


Fig. 4. Diffusion coefficients of B in Si.

2.2. Diffusivity of boron in silicon

Refining Si for solar cell applications, the dissolved B will be at a ppb-ppm level. The mass transfer of B from the bulk phase of Si to the reacting surface/interface is, therefore, an important step in the refining process, so diffusion coefficients, especially evaluated by experimental measurements, are very necessary for the discussion of kinetics and the achievement of modelling. Fig. 4 shows the assessed diffusivities of B as a function of temperature in both solid and liquid Si [26–36]. Here, we recommend the result from Tang et al. [37] and give a relation between the diffusivity of boron and temperature, as shown in Eq. (1).

$$\lg D = \begin{cases} \frac{-10373}{T} - 8.81, & 1000 \text{ K} < T < 1678 \text{ K} \\ -7.77(\pm 0.15), & 1687 \text{ K} < T \end{cases} \quad (1)$$

2.3. Diffusion coefficients and mass transfer coefficients of boron in silicon and slags

Slag treatment can remove B from MG-Si with a relatively high removal efficiency. However, the single-stage slag treatment is unable to yield Si with an enough-low B concentration, and the rate of removal depends on the reactor/process design. It is therefore of interest to determine the rate-limiting step(s) of B removal from MG-Si by slag treatment. During the slag refining process, the mass transfers of both

boron [B] in molten Si and boron oxide (BO_{1.5}) in the slag, as shown in Table 2, can affect the rate of B removal.

2.4. Activity coefficients of B in Si and slags

In the field of B removal, it is very important to clarify the mechanism and kinetics of the removal process for the improvement of removal efficiency. The activity is also one of the thermodynamic properties for the achievement of numeral simulation and model construction.

The activity coefficient of B is expressed as Eq. (2), by using the first-order interaction coefficients.

$$\lg \gamma_B = \lg \gamma_B^0 + \sum_1^{i=n} \epsilon_B^i x_i \quad (2)$$

where γ_B^0 is the activity coefficient of B in molten Si for an infinite dilute solution relative to the pure liquid state; x_i and ϵ_B^i are the mole fraction of i species and the interaction coefficient between i species and B in molten Si, respectively.

Noguchi et al. [49] reported the activity coefficient in Si melt determined by equilibrating solid BN and liquid Si under a N₂ atmosphere from 1723 to 1923 K, as shown in Eq. (3).

$$\lg \gamma_B^0 = -\frac{11100}{T} + 5.82, \quad (1723 \text{ K} < T < 1923 \text{ K}) \quad (3)$$

Tanahashi et al. [50] measured the activity coefficient in molten Si

Table 2

Diffusion coefficients and mass transfer rates. D_{Si} and D_S are the diffusion coefficients of B in Si and $BO_{1.5}$ in slag, respectively. β_{Si} and β_S are the mass transfer coefficients of B in Si and $BO_{1.5}$ in slag, respectively. δ_{Si} and δ_S are boundary layer thicknesses in Si and slag, respectively.

Slags (mass fraction)	D_{Si}	D_S	β_{Si}	β_S	δ_{Si}	δ_S	Temp.	Ref.
Unit	$10^{-8} m^2 s^{-1}$	$10^{-9} m^2 s^{-1}$	$10^{-6} m s^{-1}$	$10^{-7} m s^{-1}$	mm	mm	K	–
0.37CaO–0.63SiO ₂		5.24		62		0.85	1723	Wang et al. (2018) [38]
0.5CaO–0.5SiO ₂	1.46		170	31.6	0.086		1823	Wu et al. (2015) [39]
0.4CaO–0.4SiO ₂ –0.2K ₂ CO ₃				243			1823	Wu et al. (2016) [40]
0.55CaO–0.45SiO ₂				14			1823	Nishimoto et al. (2012) [41]
0.63Na ₂ O–0.37SiO ₂				3.66			1973	Fang et al. (2014) [42]
0.20CaO–0.17SiO ₂ –0.63CaCl ₂		8.46		250		0.34	1723	Wang et al. (2015) [43]
0.4CaO–0.4SiO ₂ –0.2MgO				43			1923	Krystad et al. (2012) [44]
0.2CaO–0.6SiO ₂ –0.1CaF ₂ –0.1Al ₂ O ₃			6.85	1.01			2073	Zhang et al. (2013) [45]
–	2.7						1687	Tang et al. (2009) [46]
–	2.4 ± 0.7						1687	Kodera (1963) [47]
–	1.2						1687	Garandet (2007) [48]

by equilibrating the Si–B melt with solid BN and/or Si₃N₄ at 1723 and 1773 K, as shown in Eq. (4).

$$\ln \gamma_B^0 = \begin{cases} 2.5 \pm 0.2, & (1723 \text{ K}) \\ 2.3 \pm 0.2, & (1773 \text{ K}) \end{cases} \quad (4)$$

Inoue et al. [51] studied the effect of calcium on the thermodynamic properties of B in molten Si, and got the activity coefficient in Eq. (5).

$$\ln \gamma_B^0 = 2.27(\pm 0.01), \quad (1723 \text{ K}) \quad (5)$$

Yoshikawa et al. [52] determined the activity coefficient by equilibrating molten Si with solid Si₃N₄ and BN at 1693 and 1923 K, as shown in Eq. (6). Eq. (7) is the activity coefficient of B in solid Si measured by the segregation behaviour of B between solid Si and Si–Al melt [53].

$$\lg \gamma_B^0 = \frac{289(\pm 450)}{T} + 1.19(\pm 0.25), \quad (1693 \text{ K} < T < 1923 \text{ K}) \quad (6)$$

$$\ln \gamma_B^0 = \frac{14073(\pm 276.6)}{T} - 5.73(\pm 0.19), \quad (1273 \text{ K} < T < 1473 \text{ K}) \quad (7)$$

Khajavi et al. [54] used activity coefficients of B in Si–Fe alloy to evaluate that in solid Si, as shown in Eq. (8).

$$\ln \gamma_B^0 = \frac{16317(\pm 282)}{T} - 7.06(\pm 0.18), \quad (1483 \text{ K} < T < 1583 \text{ K}) \quad (8)$$

The results mentioned above are shown in Fig. 5. A possible reason why the data from Noguchi et al. [49] deviate from those from other researchers is that they did not take the formation of Si₃N₄ into

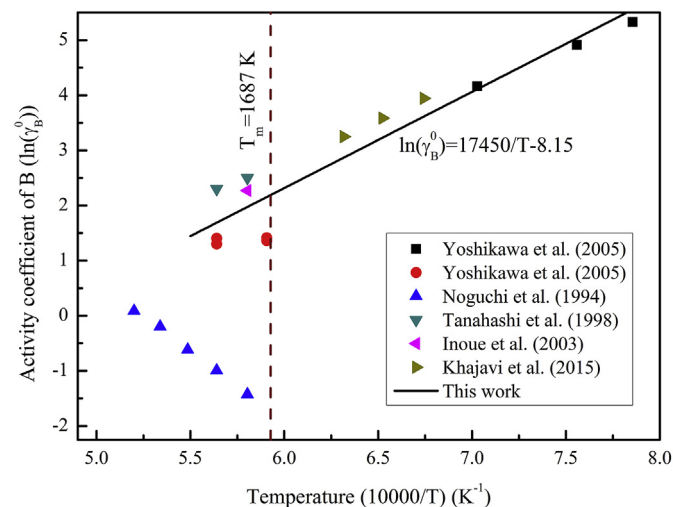


Fig. 5. Activity coefficients of B in Si.

consideration, and when ignored these data, the activity coefficient of B can be represented by Eq. (9).

$$\ln \gamma_B^0 = \frac{17450}{T} - 8.15, \quad (1173 \text{ K} < T < 1923 \text{ K}) \quad (9)$$

Interaction coefficients between various species and B in molten Si are listed in Table 3, and the self-interaction coefficients of B in Si can be fitted by Eq. (10).

Teixeira et al. [56] investigated the basicity (the ratio of mass fraction between CaO and SiO₂, denoted as R) and the activity coefficients of BO_{1.5} for CaO–SiO₂ and CaO–SiO₂–CaF₂ slags at 1823 K, as shown in Eq. (11).

$$\ln \gamma_{BO_{1.5}} = -4.00R + 3.67, \quad (1823 \text{ K}) \quad (11)$$

2.5. Segregation coefficients of B between solid silicon and solvent

In the solidification process, there will be a clearly defined interface observed between solid Si and liquid eutectics. At the solid/liquid interface, the concentration of B in the solidified Si is in equilibrium with that in solvent. As for the solidification of Al–45mol%Si melt, for example, the first phase precipitated is solid Si, as called primary Si. B has a higher solubility in the liquid than in solid Si and can, therefore, be removed effectively by the solvent refining. Primary Si, of course, is saturated with Al, which has to be removed at a later stage.

The segregation coefficient of B (k_B) can be expressed as Eq. (12).

$$k_B = \frac{x_B^S}{x_B^L} = \frac{\gamma_B^L}{\gamma_B^S} \exp\left(\frac{\Delta G_B^0}{RT}\right) \quad (12)$$

where x_B^S and x_B^L are the molar fractions of B in the solid and liquid phase, respectively. γ_B^S and γ_B^L are the corresponding activity coefficients. ΔG_B^0 refers to the Gibbs energy of the fusion of B. Eq. (13) shows the k_B between the solid Si and Si–Al melt measured by Temperature-Gradient Zone Melting method [52]. The values of k_B for various solvents are listed in Table 4.

$$\ln k_B = 4.23 - 7300/T \quad (13)$$

3. Recent research topics

There are 5 main processes for B removal: slag treatment, solvent refining, gas blowing, plasma, and acid leaching [61].

3.1. Slag treatment

Multi-component slag consisting of oxides can absorb or gather impurities in the refining process, and can prevent Si from contamination and heat loss. B can be oxidized by slag at phase boundaries,

Table 3
Interaction coefficients between various species and boron in silicon.

$$\epsilon_B^B = \frac{2153860}{T} - 1435.47, \quad (1273 \text{ K} < T < 1773 \text{ K}) \quad (10)$$

Interaction coefficients	Results	Ref.
ϵ_B^{Ca}	-3.08 ± 0.84 (1723 K)	Inoue et al. (2003) [51]
ϵ_B^B	370 ± 140 (1273 K), 120 ± 40 (1373 K), and 67 ± 20 (1473 K); -159 ± 45 (1483 K), -111 ± 28 (1533 K), and -96 ± 12 (1583 K); -164 ± 8 (1723 K), and -105 ± 8 (1773 K)	Yoshikawa et al. (2005) [53], Khajavi et al. (2015) [54], and Tanahashi et al. (1998) [50]
ϵ_B^{Al}	1313 (1173 K), 970 (1273 K), 610 K (1373 K), and 400 (1473 K)	Yoshikawa et al. (2005) [53]
ϵ_B^{Sn}	2506 ± 143 (1173 K)	Xu et al. (2014) [55]
ϵ_B^N	240 (1723 K), 80 ± 20 (1723 K), 73 ± 1 (1773 K)	Noguchi et al. (1994) [49], and Tanahashi et al. (1998) [50]

Table 4
Segregation coefficients of boron between solid silicon and eutectics.

Alloys	Results	Ref.
Si	0.8	Hall (1953) [57]
Si–Al	0.22 (1273 K), 0.32 (1373 K), and 0.49 (1473 K)	Yoshikawa et al. (2005) [54]
Si–17 wt% Fe	0.07 (1480 K)	Esfahani et al. (2011) [58]
Si–20 wt% Fe	0.33 (1483 K), 0.41 (1533 K), and 0.49 (1583 K)	Khajavi et al. (2015) [54]
Si–Sn	0.038 (1500 K, calculated)	Zhao et al. (2011) [59]
Si–34 wt% Ni	20–65	Yin et al. (2011) [60]

and after a sufficient amount of refining time, interfacial reactions will reach equilibrium. Si with lower impurity level can be purified by separating it from refining slags. In the CaO–SiO₂ slag treatment process, for example, the B removal process, detailed in Fig. 6, can be divided into 5 steps: (1) mass transfer from Si bulk phase to the metal boundary layer, (2) diffusion through the metal boundary layer to interface, (3) interfacial reaction at the interface between metal and slag, (4) diffusion through the slag boundary layer from the interface, and (5) mass transfer from the slag boundary layer to slag bulk phase [62].

The interfacial reaction is shown as Eq. (14), and its equilibrium constant *K* is given by Eq. (15).



$$K = \frac{\gamma_{(BO_{3/2})} x_{(BO_{3/2})} a_{[Si]}^{3/4}}{\gamma_{[B]} x_{[B]} a_{(SiO_2)}^{3/4}} \quad (15)$$

where *x_i*, *a_i*, and *γ_i* are the molar fraction, activity, and activity coefficient of *i* species, respectively.

Distribution coefficient (*L_B*) is always used to present the removal efficiency, as shown in Eq. (16).

$$L_B = \frac{x_{(BO_{1.5})}}{x_{[B]}} = K \cdot \frac{\gamma_{[B]} a_{(SiO_2)}^{3/4}}{\gamma_{(BO_{1.5})} a_{[Si]}^{3/4}} \quad (16)$$

It should be noted that this value is only available when reactions achieve equilibrium, and it only depends on the components of slag, temperature, and atmosphere. The *L_B* should be as high as possible to minimize the amount of slag needed for refining, because twice or more times slag treatments are unfavorable for industrial application. Unfortunately, typical values of *L_B* range from 1 to 2, and the highest value of *L_B* reported by Teixeira et al. [56] is around 5.5. It means that a large ratio of amount between slag and silicon (*μ*) is needed to refine Si. The maximum *L_B* constraint leads to the development of ternary or multi-components slag systems with suitable thermodynamic and kinetic properties (e.g., low viscosity, low melting point, and high basicity). For example, viscosity, density, and surface tension can affect the separation of metal from slag.

There are many types of slag for B removal from Si, such as CaO–SiO₂–CaF₂, CaO–SiO₂–TiO₂ [63], SiO₂–CaO–Al₂O₃ [64], Al₂O₃–BaO–SiO₂ [65], CaO–SiO₂–Na₂O–Al₂O₃ [66], as shown in Table 5.

Khattak et al. [83] described that B concentration in MG-Si decreases from 18 to 1 ppmw using the CaO–SiO₂ slag. Johnston et al. [84] and Cai et al. [85] studied the effects of basicity of Al₂O₃–CaO–MgO–SiO₂, Al₂O₃–BaO–SiO₂, CaO–SiO₂–CaF₂, and CaO–SiO₂–Al₂O₃ slag on B removal.

The efficiency of B removal from molten Si by slag treatment is dependent on several parameters (e.g., reaction kinetics, diffusivity, and partition ratio), which are determined by the structure of slag [86]. According to the solid-state ¹¹B NMR analysis and quantum chemical calculation [4], B–4Si–Ca is the most possible structure to represent the boron incorporation in the silicate network [87,88]. Five structural forms of B (i.e. [3], B–3Si [3], B–2Si–1NBO, BO₃ (non-ring), BO₄ (1B, 3Si), and BO₄ (0B, 4Si)) in the borosilicate network were detected by

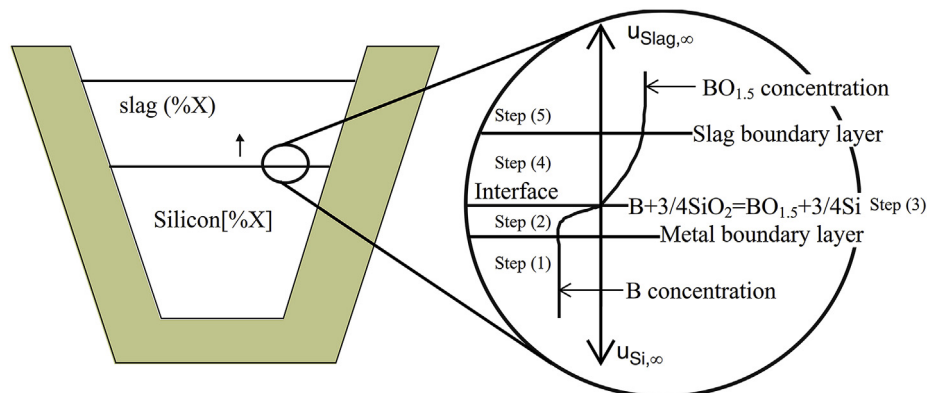


Fig. 6. Reaction mechanism of boron removal using CaO–SiO₂ slag.

Table 5
Different slag systems for boron removal.

Slags	Results	Ref.
CaO–SiO ₂ , CaO–SiO ₂ –MgO	→ < 3 ppmw	Liaw et al. (1983) [67]
CaO–SiO ₂ –MgO	$L_B = 1.7$ ($R = 0.95$)	Noguchi et al. (1990, 1994) [49]
CaO–SiO ₂ –CaF ₂	$L_B = 1.6$ ($R = 2$)	
CaO–SiO ₂	7.6→0.3 ppmw	Fujiwara et al. (2003) [68]
CaO–SiO ₂	$L_B = 5.5$ –4.3 ($R = 0.55$ –1.21)	Teixeira et al. (2009) [69]
CaO–SiO ₂	18→1.8 ppmw ($R = 1.5$, $\mu = 2.5$, 1873 K, 3 h); $L_B = 1.57$	Wu et al. (2014) [70]
CaO–SiO ₂	22→4.73 ppmw; $L_B = 0.72$ –1.58	Wei et al. (2015) [71]
SiO ₂ –NaO	10.6→0.65 ppmw ($R = 0.8$, 1973 K, 0.5 h); 0.4→0.2 ppmw ($R = 2$, 1973 K, 0.5 h)	Fang et al. (2014) [42]
CaO–SiO ₂ –Al ₂ O ₃	1.5→0.2 ppmw (1823 K, 2 h)	Luo et al. (2011) [72]
CaO–SiO ₂ –Al ₂ O ₃	$\lg(L_B) = 0.66$ –1.8	Jung et al. (2014) [64]
CaO–SiO ₂ –Al ₂ O ₃	$L_B = (2.1-2.4) \cdot \{x(\text{SiO}_2)/[x(\text{Al}_2\text{O}_3) + x(\text{SiO}_2)]\}$	Jakobsson et al. (2014) [73]
CaO–SiO ₂ –NaO	30→5 ppmw ($R = 1.1$, 1873 K, 1 h)	Safarian et al. (2015) [74]
CaO–SiO ₂ –K ₂ CO ₃	22→1.8 ppmw (1823 K, 6 h); $L_B = 2.08$	Wu et al. (2016) [40]
Li ₂ O–SiO ₂ –CaF ₂	8.6→0.46 ppmw (1973 K, 0.5 h)	Lai et al. (2016) [75]
CaO–SiO ₂ –ZnO	12.94→2.18 ppmw (1823 K, 1 h)	Wang et al. (2016) [76]
CaO–SiO ₂ –Li ₂ O	18→1.3 ppmw ($R = 1.5$, $\mu = 4$, 1873 K, 3 h)	Wu et al. (2012) [77]
CaO–SiO ₂ –LiF	22→1.3 ppmw ($R = 0.8$, $\mu = 4$, 1823 K, 2 h); $L_B = 1.6$ –2.7	Ding et al. (2012) [78]
CaO–SiO ₂ –Al ₂ O ₃ –CaF ₂	25→4.4 ppmw ($\mu = 1$, 2073 K, 2 h); product: B ₂ O ₃	Li et al. (2014) [79]
CaO–MgO–Al ₂ O ₃ –SiO ₂	$L_B = 1$ –1.8 (1873 K)	Johnston et al. (2010) [80]
CaO–SiO ₂ –CaCl ₂	148→21 ppmw ($R = 1.3$, $\mu = 3$, 1723 K, 0.5 h); 75→5 ppmw ($R = 1.3$, $\mu = 2$, 1823 K, 0.5 h)	Wang et al. (2014, 2015) [43,81,82]

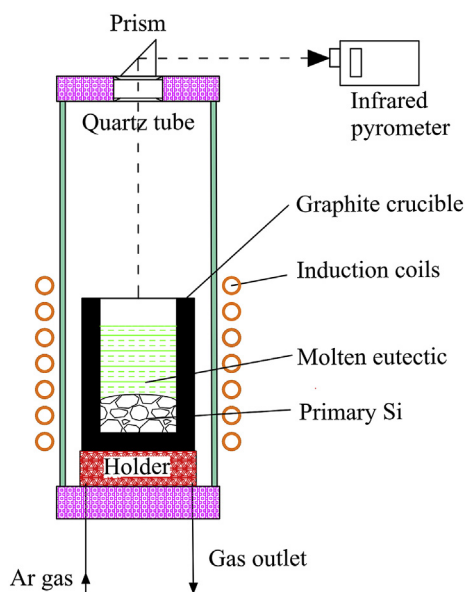


Fig. 7. Schematic of the experimental apparatus for solvent refining.

NMR spectroscopy of the CaO–SiO₂–Na₂O slag [89]. BO_{1.5} (1B, 3Si) was the main structure contributing to the incorporation of B into the Si network, and BO₃ (non-ring) plays an important role in suppressing the oxidation of B [90].

The L_B in Eq. (16), the determinant of the removal efficiency, is dependent on the activity coefficient and reaction temperature. There is a maximum value of L_B , because chemical equilibrium and steady state can always reach in the treatment process for nearly all slag systems without volatiles. How to improve L_B and/or break the steady state is the key to B removal. There are 3 ways to achieve it: (1) adding volatile substances, (2) partly or totally replacing CaO with other oxides with higher abilities of oxidation, and (3) gas blowing. As for the first, the introduction of volatile substances can facilitate the removal of boron oxides from the slag into gaseous phase. The representative one of volatile substances is CaCl₂, and Mellström et al. [91] proposed this idea firstly in 1989, by which the B concentration decreased from 17 to 5 ppmw after 0.5 h. Wang et al. [92,93] researched this ternary CaO–SiO₂–CaCl₂ slag system comprehensively, followed by Lu et al. [94,95] and Huang et al. [96]. The introduction of chlorination can

transform BO_{1.5} in the slag to BOCl/BCl₃ that can be evaporated at high temperatures.

According to the definition of L_B (see Eq. (16)), γ_B and a_{Si} are nearly independent on the properties of slag. Introducing Na₂O/K₂O, the representative oxides with higher abilities of oxidation than CaO, as well as Na₂CO₃/K₂CO₃, can increase the oxygen potential of slag (a_{SiO_2}) and thus L_B . In addition, the large volatilization of slag helps the gasification of BO_{1.5} in the form of Na₂B₂O₄ [97–99].

Although slag treatment has obvious advantages, such as low cost and large-scale, considering the limitation of B removal, we can comprehensively utilize this process combined with gas injection for the improvement in kinetics. The gas injection process will be discussed later.

3.2. Solvent refining

Solvent refining is on the basis of fractional crystallization. At a temperature about 1473 K, eutectics form when silicon mixes with metals with low melting points (e.g., Al, Sn, Cu, and Zn), and in the process of directional solidification, impurity of B gathers in molten eutectic phases (e.g., Si–Al [100], Si–Sn [101], Si–Cu [102], and Si–Al–Sn [103]) because the liquid melt has a higher solubility than solid Si. In the directional solidification process with a slightly convex front (instead of a planar front), there is a clearly defined interface observed between solid Si and liquid melt, as shown in Fig. 7. By definition, ideal solvents are those with low melting points and/or high solubilities of B.

According to Aluminum Company of America and Union Carbide Corporation's patents, Cu, Cu–Al, or Al solvent can be used to upgrade MG–Si [104,105]. They predicted an effective removal of metallic impurities, but did not reveal an opportunity for B removal. Since 2003, thermodynamics on SOG–Si refining with the Si–Al melt at a low temperature has been intensively investigated by Yoshikawa et al. [106], and a novel concept of low-temperature solidification refining of Si with a Si-based solvent has accordingly been proposed [107]. In particular, B cannot be effectively removed by conventional directional solidification, while its concentration decreased from 56 ppmw to 0.88 ppmw when using Al–Si alloy treatment [108].

Over the past few years, many papers have been published regarding the purification of Si using solvent refining [109,110]. Research data from various researchers are listed in Table 6.

Table 6 sees that the addition of precipitation agents (e.g., Zr, Hf, and Ti) to Si–Al solvent is the research hotspot. The reason for the

Table 6
Different alloy systems for boron removal.

Alloys	Results	Ref.
Si–Al	→0.8–1.9 ppmw; $RE^a = 95\%$	Yoshikawa et al. (2003, 2005, 2009) [107,111]
Si–Al	$RE = 74.3\%$	Li et al. (2015) [112]
Al–Si (with rotating magnetic field)	65→4.67 ppmw	Zou et al. (2015) [113]
Si–Al (additive: Ti)	170→1.1 ppmw; precipitate: TiB_2	Yoshikawa et al. (2005) [114]
Si–Al (additive: 575 ppm Ti)	295→12 ppmw; precipitate: TiB_2	Ban et al. (2016) [115]
Si–Al (additive: Zn)	14.8→2.4 ppmw	Li et al. (2014) [116]
Si–Al (additive: Hf)	→1.2 ppmw	Lei et al. (2016) [117]
Si–Al (additive: Zr, Hf, and Ti)	12→1.2 ppmw	Lei et al. (2018) [118]
Si–Al (additive: V)	506→74 ppmw	Chen et al. (2018) [119]
Si–Sn (twice refining)	15→0.12 ppmw	Zhao et al. (2011) [59]
Si–Al–Sn	14.8→3.9 ppmw	Li et al. (2014) [103]
Si–Cu (additive: Ca)	$RE = 44.4\%$	Fang et al. (2013) [120]
Si–Cu (with acid leaching)	$RE = 58.7\%$	Huang et al. (2016) [121]
Si–Fe	27→2 ppmw	Esfahani et al. (2011) [58]
Si–Na	9.1→0.3 ppmw	Morito et al. (2012) [122]
Si–Ga	$RE = 83.3\%$	Li et al. (2015) [123]

^a RE is the abbreviation of Removal efficiency.

determination of Si–Al is that the k_B between solid Si and Si–Al eutectic is lowest. The final concentration of B could reach around 1 ppmw.

According to the thermodynamic calculation [124], the precipitates (e.g., ZrB_2 , HfB_2 , and TiB_2) are more likely to be formed, because the values of the standard free energy of formation of these precipitates are much lower than other borides (e.g., AlB_2 , AlB_{12} , and SiB_6). However, only the existence of TiB_2 and ZrB_2 in Si–Al alloy has been experimentally confirmed [114,115,125,126].

There is a controversy about the precipitation mechanism. Some papers reported that precipitates can be enriched in the liquid phase [124,126], while the other opinion is that TiB_2 particles are precipitated at the beginning of the formation of primary Si and absorbed by the purified Si phase [114]. It seems that the phase, where a great amount of precipitates remain, is independent on the solidification direction (the direction of gravitational force or the opposite) [127]. Therefore, the mechanism of the precipitation still needs to be fully investigated.

The only advantage of the solvent refining process is the low-temperature operation in terms of cost reduction. Further investigation is still necessary for the search of other optimal solvents and the recycle of solvents.

3.3. Gas injection

The gas injection can be defined as the process, in which oxidizing gases (e.g., H_2O , O_2 , and H_2) are blown into liquid Si (or the slag phase when combined with slag treatment) at high temperatures, as shown in Fig. 8, and B contained in Si is oxidized to oxides (e.g., BO, B_2O_3 , B_2O , BO_2 , and B_2O_2), or hydroxide gases (e.g., BHO, BHO_2 , BH_2O_2 , and BH_3O_3) formed under a humid atmosphere ($Ar-H_2O-O_2$). These gaseous products can be easily vaporized because their equilibrium partial pressures are 10^5 – 10^{10} times than the oxidizing gases mentioned above.

Generally speaking, the oxidants needed for oxidative refining reactions can be introduced either as a gas (in the form of air by gas-blowing through a nozzle, or a lance installed on the top of a crucible, or plugged in the bottom), or the slag containing $CaO-SiO_2$. Gas-blowing is usually combined with the addition of some kinds of slags (e.g., CaO , MgO , and CaF_2), which also act as oxidizing agents. In a broad sense, plasma treatment can also be regarded as an oxidative refining process.

From the equilibrium point of view, the oxidation of Si is more favourable than that of B, and SiO vapour is more likely to be formed

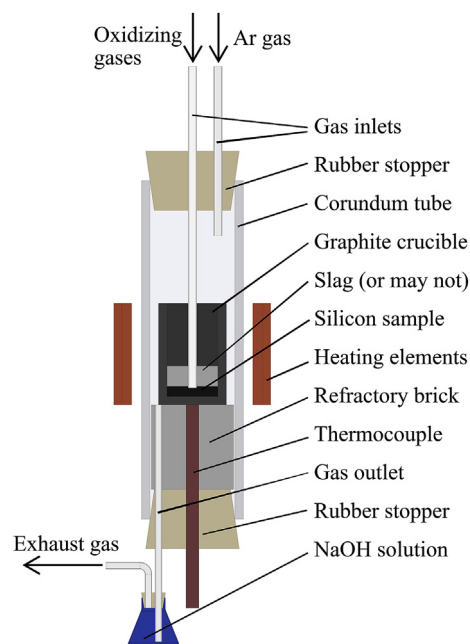


Fig. 8. The cross-sectional configuration of experimental setup for gas injection.

above 873 K, which makes the refining process more complicated. By thermodynamic calculation, the main products when B in liquid Si reacts with the water vapour are BOH, BH_2 , BO, and B_2O_2 [128]. One problem for gas injection is that Si can also be oxidized by the water vapour, which may cause some loss of Si.

Since the work published by Theuerer in 1956 [129], it has been known that liquid Si can be purified with respect to B when brought in contact with a gas mixture of $Ar-H_2-H_2O$. After that, various gas systems have been studied, including Cl_2 [41], O_2 [130], H_2 , HCl [131], and H_2O [132].

Kondo et al. [133] applied a process, in which reaction gases (H_2 , H_2O , and O_2) were blown to the bottom of the liquid Si to oxidize B, and the B concentration decreased from 25 to 5 ppmw.

The sole role of H_2 and H_2O assisting the slag treatment has been emphasized by several authors, such as Khattak et al. [134,135], whereas Amouroux et al. [136] and Suzuki et al. [137,138] have underlined the benefit of using an oxidative plasma in the presence of moisture and hydrogen. Amouroux et al. [139] have also shown that B elimination was enhanced when fluorides (e.g., CaF_2) were injected with the plasma gas. Schei [140] from Elkem AS of Norway has described a counter-flow solid-liquid reactor to remove B by fractional extraction in a semi-continuous process. Research data of various researchers are listed in Table 7.

As we all have seen, different researchers have obtained different data, and it is obvious that the injection of $H_2O(g)$, H_2 , and O_2 can improve the removal efficiency. However, saturated vapour pressures of nearly all compounds of B are very low, and this limits the reaction rate of B removal.

3.4. Plasma treatment

Although B is less volatile than Si, however, B can react with O, Cl, and H at high temperatures to form volatile species, such as BHO, BO, and BH_2 . To increase the temperature of Si melt, plasma heating has been employed in laboratory experiments.

The plasma treatment using thermal plasma can increase the dynamics of B removal from liquid Si. In the plasma treatment, gaseous boron oxides (e.g., BO, B_2O , B_2O_3) are expected to form at the temperature higher than 2300 K, and among these boron oxides, BO has a

Table 7
Different gas systems for boron removal.

Gases	Results	Ref.
HCl-H ₂ O	20-60→0.3 ppmw	Khattak et al. (1999, 2002) [141,142]
H ₂ O	24.8→2.01 ppmw; product: HBO	Safarian et al. (2014) [143]
H ₂ O	10→2 ppmw (solar furnace, 3473 K, 50 min); product: BOH	Flamant et al. (2006) [144]
O ₂	35→1.8 ppmw	Wu et al. (2013) [145]
H ₂ O-O ₂	35→1.8 ppmw	Wu et al. (2014) [146]
H ₂ O-O ₂ , O ₂	18→2 ppmw; product: B ₂ O ₃ /B ₂ O ₃ H ₂	Wu et al. (2009) [130]
H ₂ -H ₂ O	< 1 ppmw (induction heating, 2–3 h); product: BH ₂ /BOH	Nordstrand et al. (2012) [132]
H ₂ -H ₂ O	64→0.5 ppmw	Sortland et al. (2014) [147]
H ₂ -H ₂ O	10-25→about 0.1 ppmw	Safarian et al. (2016) [148]
NH ₃ -N ₂	120→ < 1 ppmw (1823 K, 6 h)	Chen et al. (2016) [149]

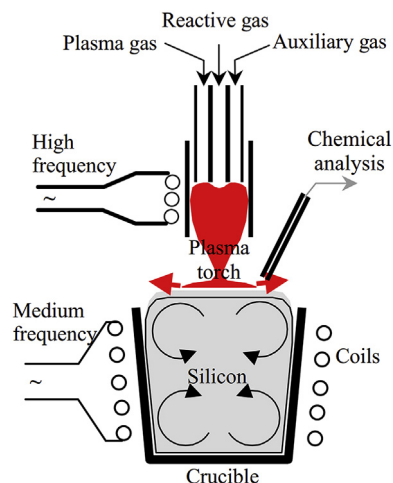


Fig. 9. Schematic diagram of plasma process.

relatively high vapour pressure. Ar-H₂O [138], Ar-CO₂ [150], Ar-H₂-H₂O [129], Ar-H₂-O₂ [151], and Ar-He-H₂O [152] were chosen as plasma gases to oxidize and/or hydrogenate B in liquid Si. The schematic diagram of plasma process is shown in Fig. 9 [153].

The advantages of high-temperature plasma treatment are high refining temperature, high activities of chemical reactions, and high abilities to degas. Lee et al. [16] reported that the plasma of Ar-H₂-H₂O can remove B in the forms of BO and HBO. Yuge et al. [154] diminished the B concentration in MG-Si from 10 to 0.1 ppmw by 50.6% H₂-4.6% H₂O plasma refining. Obviously, the results of plasma treatment shown in Table 8 are much better than that of normal gas injection, but there are also many disadvantages limiting its development of the industrial application, such as expensive equipment for production, high energy consumption, and intermittent production.

3.5. Acid leaching

Metallic impurities, which can form intermetallic phases (e.g. silicides, and silicates) with Si, always segregate at the grain boundaries, Hydrometallurgical upgrading of Si by acid leaching has a long history.

Table 8
Different plasma systems for boron removal.

Plasma systems	Results	Ref.
Ar + H ₂ O	12→1 ppmw	Ikeda et al. (1996) [155]
Ar + H ₂ O	22→0.2 ppmw	Cai et al. (2013) [156]
Ar + H ₂ O; additive: CaF ₂	37.5→4 ppmw	Suzuki et al. (1992) [138]
H ₂ + H ₂ O	5-10→0.1 ppmw	Nakamura et al. (2004) [157]
Ar + H ₂	10→0.1 ppmw	Nakamura et al. (2003) [158]
H ₂ + O ₂	15→2 ppmw	Aleman et al. (2002) [128]
Ar + H ₂ + O ₂ ; DC bias	64→0.3 ppmw	Rousseau et al. (2007) [159]

Elkem Silgrain process® still produce MG-Si commercially; the powders of 90FeSi alloy (90% Si) are immersed in an acid solution of HCl-FeCl₃, in which continuous grain boundaries react with the acid mixture and then disintegrate [160]. This process is particularly efficient in the removal of transition metal (e.g., Fe, Cu) because these impurities have very low segregation coefficients in Si.

Surface treatment (or leaching) by HF acid or HCl/HF mixture is also well-known to wash out the residual impurities presented as oxides or silicates. Grinding Si prior to acid leaching to increase the surface exposure is a way to enhance the purification [161,162]. The brief flowchart of acid leaching is shown as Fig. 10.

Sun et al. [163] reported the effects of the concentration of HF acid and particle size of Si on the removal efficiency. After the calcination treatment at 1273 K for 2 h, quenching at 373 K for 2 h under vacuum, and HNO₃ + HF acid leaching at 323 K for 80 min, the B concentration of Si powders (particle size: 44–74 μm) decreased from 128 to 10.9 ppmw. In addition, the B concentration of Si powders (particle size: 74–154 μm) decreased from 8.6 to 3.0 ppmw for the duration (2 h) of HF + H₂O₂ + (CH₂OH)₂ acid leaching at 328 K [12].

However, it must be emphasized that this method cannot in practice refine Si with the B concentration below its dissolution limit at the corresponding solidification composition. But fortunately, B in solidified MG-Si presents as additional phases at grain boundaries, which can be removed by crushing and subsequent etching, giving the Si grain at approximately 2 mm [164].

3.6. Combined process

The hotspot of research is the combined process, for example, slag treatment combined with the solvent method listed in Table 9. It can be concluded that the combination of different refining processes is a better choice.

For the development of slag treatment, as discussed above, the introduction of CaCl₂/Na₂O/K₂O and/or gas injection can be a common way. As for the former, the high evaporation rate of CaCl₂/Na₂O/K₂O at a custom temperature (1723–1923 K) in the process of slag treatment cannot be neglected, so this promotes a combination of slag treatment and solvent refining. When combined with solvent refining, the reaction temperature drops from about 1873 to 1273 K, and this decrease in temperature reduces the evaporation rate during the whole refining process.

Gas blowing is used to break the steady state reached at the interface between Si and slag, and thus to improve the reaction rate on the aspect of kinetics. Attempts for combined methods have been succeeded, as shown in Fig. 11. Xia et al. [172] used 0.55Ar-0.3H₂O-0.15O₂ and CaO-CaCl₂ slag to refine MG-Si, and B concentration diminished from 21 to 2.1 ppmw after 3 h.

4. Conclusion and outlook

Slag treatment is still the main refining method for removing B from

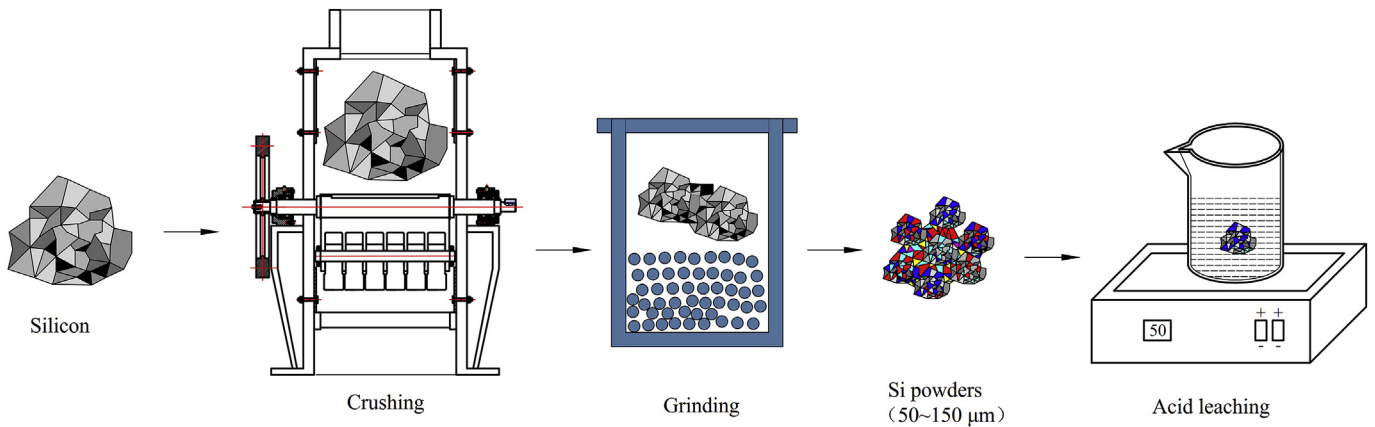


Fig. 10. Flow chart of acid leaching.

Table 9
Different combined processes for boron removal.

Processes	Results	Ref.
CaO-SiO ₂ -Na ₂ O slag + Si-Sn alloy	12.92→0.98 ppmw	Li et al. (2016) [165]
CaO-SiO ₂ -CaCl ₂ slag + Si-Cu alloy	3.12→0.35 ppmw	Huang et al. (2016) [96]
CaO-SiO ₂ -Na ₂ O-Al ₂ O ₃ slag + Si-Cu alloy	600→10 ppmw	Li et al. (2014) [66]
CaO-SiO ₂ -CaF ₂ slag + Si-Sn alloy	33→0.3 ppmw	Ma et al. (2013) [101]
CaO-SiO ₂ slag + Cl ₂ gas	350→146 ppmw	Nishimoto et al. (2012) [41]
CaO-CaF ₂ flux + O ₂ gas	14→7.6 ppmw (1773 K, 0.1 h)	Tanahashi et al. (2014) [166]
CaO-SiO ₂ -CaCl ₂ slag + H ₂ O-O ₂ gas	22→0.75 ppmw (4 h)	Wu et al. (2017) [167]
CaO-SiO ₂ -Al ₂ O ₃ + electrical potential difference of 3 V	375→1 ppmw	Islam et al. (2014) [168]
CaO-SiO ₂ + mechanical agitation	440→60 ppmw	White et al. (2015) [169]
Si-Al + supergravity separation	63% of separation efficiency	Li et al. (2015) [170]
CaO-SiO ₂ -CaF ₂ + Si-Sn + HCl solution leaching	33→0.3 ppmw (μ = 0.45, 1673 K, 0.5 h for slag treatment)	Ma et al. (2014) [171]

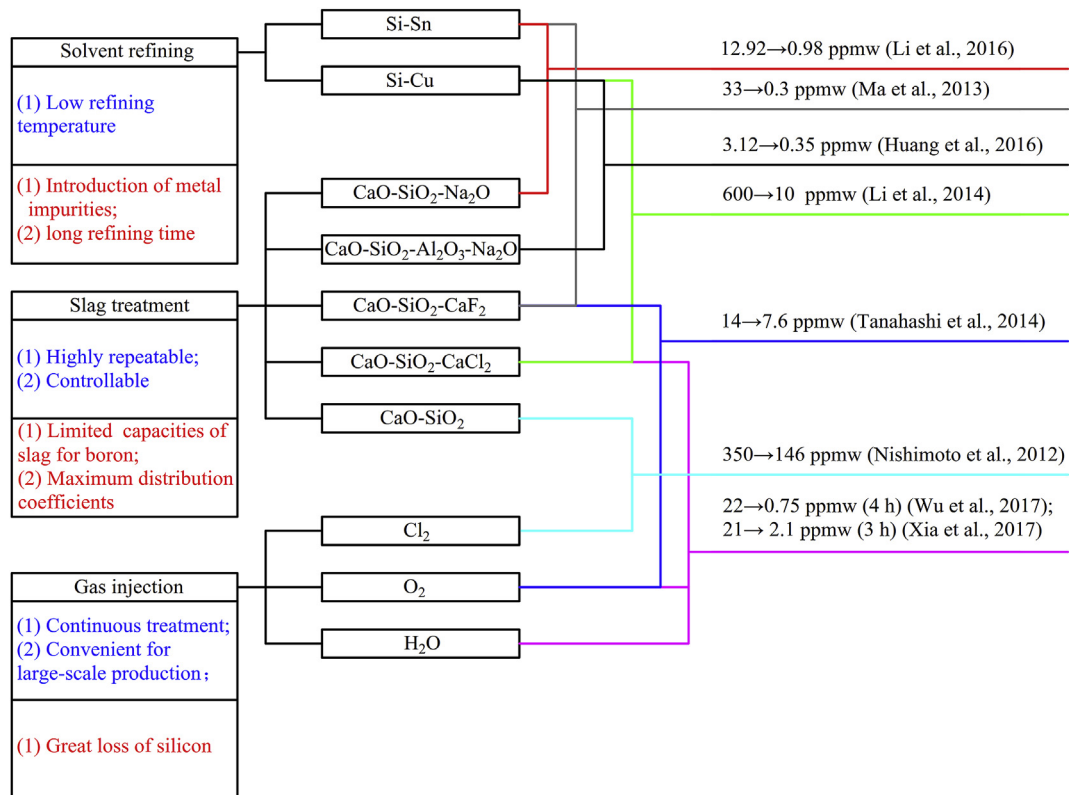


Fig. 11. Different combined processes for boron removal.

Si. For the slag treatment, the oxidation is the principal mechanism of B removal, though there are CaCl_2 -contained slag systems. As we all know, the basis of the slag is the silicate, and the tertiary or multiple components (e.g., MgO , Li_2O , Al_2O_3 , and CaF_2) only can change its properties. To develop the slag treatment, the introduction of $\text{Na}_2\text{O}/\text{K}_2\text{O}/\text{CaCl}_2$, and the coupling with other methods are very efficient. Many data in this direction have been obtained, but it is still far from our goal (B concentration less than 0.3 ppmw).

As for solvent refining, the biggest problem is the separation of primary Si and eutectics. Of course, there are seemingly many ways to solve this, such as supergravity, the addition of electromagnetic field, and directional solidification. However, all these cannot be called as effective ways for Si separation. In addition, the introduction of metal impurities may overload the directional solidification process with more refining task. The recycle of solvent is also a tricky problem in front of researchers.

The lack of repeatability is also a source of difficulty. The data from various researchers differ from each other, so there are also many ambiguities in the achievement of the goal. Perhaps this problem arises from the limits of detection (LoDs). As for the advanced detection instruments (e.g. ELAN DRC II ICP-MS produced by *PerkinElmer*), the LoDs for boron are near 10 ng/L, with the background equivalent concentrations of 24 ng/L [173], but for some instruments (e.g. ICP-MS2000B produced by *Jiangsu Skyray Instrument Co., Ltd.*), the LoDs for boron are only 300 ng/L. In addition, if we consider the B concentration the inorganic acid used in the process of sample preparation, data analysis will be very complex because it is not a simple addition and subtraction problem. For example, we always used the mixture of HF/HNO_3 acid for Si dissolving, but different ratios may lead to the change in the volume of their mixture. To measure the B concentration accurately, setting off-peak correction points and background correction for complex background structures are required, and for this, Agilent Technologies, Inc. supplies two different algorithms for ICP-OES background correction: Fitted Background Correction (FBC) and Fast Automated Curve Fitting Technique (FACT) [174].

On the other hand, perhaps too much attention to the level decrease in B concentration have been given, and if the effects of B and/or borides on the performance of solar cells and on the production process of solar modules have been clear, inclusions or clusters containing B (e.g., SiB_6) in Si can be modified to form less harmful inclusions, which is similar to the calcium treatment for steel production. This opinion may give us a new way to deal with the exceeded B concentration of SOG-Si.

Acknowledgements

This work was supported by the National Natural Science Foundation of China [No. 51604176]; the Science and Technology Benefiting Project of Chengdu, China [No. 2016-HM01-00399-SF]; the Science and Technology Cooperation Program of Sichuan University and Panzhihua, China [No. 2018CDPZH-24]; and the Key Research and Development Program of Sichuan, China [No. 18ZDYF]. We thank for Dr. Wen Tian (Experimental teaching center for Engineering, School of chemical engineering, Sichuan University) for technical assistance.

References

- [1] L.P. Bloomberg Finance, Q4 2016 Global PV Market Outlook, (2016), pp. 1–3.
- [2] I.S.E. Fraunhofer, Photovoltaics Report, Fraunhofer ISE, Freiburg, 2017, pp. 19–20.
- [3] F. Chigondo, From metallurgical-grade to solar-grade silicon: an overview, *Silicon India* 10 (2018) 789–798.
- [4] G. Bye, B. Ceccaroli, Solar grade silicon: technology status and industrial trends, *Sol. Energy Mater. Sol. Cells* 130 (2014) 634–646.
- [5] ITRPV Working Group, International Technology Roadmap for Photovoltaic (ITRPV) 2017 Results Including Maturity Report 2018 Processes, ninth ed., (2018) September.
- [6] X. Li, J.H. Lee, A.N. Sprafke, R.B. Wehrspohn, Black metallurgical silicon for solar energy conversion, *Semicond. Sci. Technol.* 31 (2015) 09–14.
- [7] Z. Yu, W. Ma, K. Xie, G. Lv, Z. Chen, J. Wu, J. Yu, Life cycle assessment of grid-connected power generation from metallurgical route multi-crystalline silicon photovoltaic system in China, *Appl. Energy* 185 (2017) 68–81.
- [8] R. Glöckner, J.O. Odden, G. Halvorsen, R. Tronstad, M.J. de Wild-Scholten, Environmental Life Cycle Assessment of the Elkem Solar Metallurgical Process Route to Solar Grade Silicon with Focus on Energy Consumption and Greenhouse Gas Emissions, *Silicon for the Chemical and Solar Industry IX*, (2008) Oslo, Norway.
- [9] M.J. De Wild-Scholten, R. Glöckner, J.O. Odden, G. Halvorsen, R. Tronstad, LCA comparison of the Elkem Solar metallurgical route and conventional gas routes to solar silicon, *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, Valencia, Spain, 2008, pp. 1–5 Sep.
- [10] M.M. Lunardi, J.P. Alvarez-Gaitan, N.L. Chang, R. Corkish, Life cycle assessment on PERC solar modules, *Sol. Energy Mater. Sol. Cells* 187 (2018) 154–159.
- [11] M.D. Johnston, L.T. Khajavi, M. Li, S. Sokhanvaran, M. Barati, High-temperature refining of metallurgical-grade silicon: a review, *J. Occup. Med.* 64 (2012) 935–945.
- [12] H. Lai, L. Huang, C. Gan, P. Xing, J. Li, X. Luo, Enhanced acid leaching of metallurgical grade silicon in hydrofluoric acid containing hydrogen peroxide as oxidizing agent, *Hydrometallurgy* 164 (2016) 103–110.
- [13] Q. Wang, W. Dong, Y. Tan, D. Jiang, C. Zhang, X. Peng, Impurities evaporation from metallurgical-grade silicon in electron beam melting process, *Rare Met.* 30 (2011) 274.
- [14] S. Hu, Y. Dai, A. Gagnoud, Y. Fautrelle, R. Moreau, Z. Ren, Z. Ren, K. Deng, X. Li, Effect of a magnetic field on macro segregation of the primary silicon phase in hypereutectic Al-Si alloy during directional solidification, *J. Alloy. Comp.* 722 (2017) 108–115.
- [15] J.C.S. Pires, J. Otubo, A.F.B. Braga, P.R. Mei, The purification of metallurgical grade silicon by electron beam melting, *J. Mater. Process. Technol.* 169 (2005) 16–20.
- [16] B.P. Lee, H.M. Lee, D.H. Park, J.S. Shin, T.U. Yu, B.M. Moon, Refining of MG-Si by hybrid melting using steam plasma and EMC, *Sol. Energy Mater. Sol. Cells* 95 (2011) 56–58.
- [17] P.R. Mei, S.P. Moreira, E. Cardoso, A.D.S. Côrtes, F.C. Marques, Purification of metallurgical silicon by horizontal zone melting, *Sol. Energy Mater. Sol. Cells* 98 (2012) 233–239.
- [18] S.S. Zheng, T.A. Engh, M. Tangstad, X.T. Luo, Separation of phosphorus from silicon by induction vacuum refining, *Separ. Purif. Technol.* 82 (2011) 128–137.
- [19] T. Shimoda, T. Masuda, Liquid silicon and its application in electronics, *Jpn. J. Appl. Phys.* 53 (2014) 02B-A01.
- [20] K. Tang, E.J. Øvrelid, G. Tranell, M. Tangstad, A thermochemical database for the solar cell silicon materials, *Mater. Trans.* 50 (2009) 1978–1984.
- [21] G.V. Samsonov, V.M. Slepstov, Investigation of the solubility of boron in silicon, *J. Inorg. Chem.* 8 (1963) 1047–1048 (Crys Structure, Equi Diagram; Experimental).
- [22] C. Brosset, B. Magnusson, The silicon-boron system, *Nature* 187 (1960) 54.
- [23] F.A. Trumbore, P.E. Freeland, R.A. Logan, Distribution coefficient of antimony in silicon from solvent evaporation experiments, *J. Electrochem. Soc.* 108 (1961) 458–460.
- [24] J. Hesse, Löslichkeit und Ausscheidungskinetik von Bor in polykristallinem Silizium, *Z. Met.* 59 (1968) 499–503.
- [25] R.W. Olesinski, G.J. Abbaschian, The B-Si (boron-silicon) system, *Bulletin of alloy phase diagrams* 5 (1984) 478–484.
- [26] C.S. Fuller, J.A. Ditzenberger, Diffusion of donor and acceptor elements in silicon, *J. Appl. Phys.* 27 (1956) 544–553.
- [27] J.P. Garandet, New determinations of diffusion coefficients for various dopants in liquid silicon, *Int. J. Thermophys.* 28 (2007) 1285–1303.
- [28] H. Kodera, Diffusion coefficients of impurities in silicon melt, *Jpn. J. Appl. Phys.* 2 (1963) 212.
- [29] E.L. Williams, Boron diffusion in silicon, *J. Electrochem. Soc.* 108 (1961) 795–798.
- [30] M.L. Barry, P. Olofsen, Doped Oxides as diffusion sources I. Boron into silicon, *J. Electrochem. Soc.* 116 (1969) 854–860.
- [31] C.S. Fuller, J.A. Ditzenberger, Diffusion of boron and phosphorus into silicon, *J. Appl. Phys.* 25 (1954) 1439–1440.
- [32] M. Okamura, Boron diffusion into silicon using elemental boron, *Jpn. J. Appl. Phys.* 8 (1969) 1440.
- [33] E. Dominguez, M. Jaraiz, A non-Fickian model of the boron in silicon diffusion from BN sources, *J. Electrochem. Soc.* 133 (1986) 1895–1900.
- [34] G.L. Vick, K.M. Whittle, Solid solubility and diffusion coefficients of boron in silicon, *J. Electrochem. Soc.* 116 (1969) 1142–1144.
- [35] W. Wijaranakula, An anomalous enhanced tail diffusion of boron in directly bonded samples of heavily and lightly doped silicon, *Jpn. J. Appl. Phys.* 32 (1993) 3872.
- [36] R.N. Ghoshtagore, Donor diffusion dynamics in silicon, *Phys. Rev. B* 3 (1971) 397.
- [37] K. Tang, E.J. Øvrelid, G. Tranell, M. Tangstad, Thermochemical and Kinetic Databases for the Solar Cell Silicon Materials, *Crystal Growth of Si for Solar Cells*, Springer, Berlin, Heidelberg, 2009, pp. 219–251.
- [38] F. Wang, J. Wu, W. Ma, Y. Lei, K. Wei, B. Yang, Experimental determination of diffusion and mass transfer of boron oxide in molten slag for metallurgical grade silicon purification, *J. Chem. Thermodyn.* 118 (2018) 215–224.
- [39] J. Wu, F. Wang, Z. Chen, W. Ma, Y. Li, B. Yang, Y. Dai, Diffusion and mass transfer of boron in molten silicon during slag refining process of metallurgical grade silicon, *Fluid Phase Equilib.* 404 (2015) 70–74.
- [40] J. Wu, F. Wang, W. Ma, Y. Lei, B. Yang, Thermodynamics and kinetics of boron removal from metallurgical grade silicon by addition of high basic potassium carbonate to calcium silicate slag, *Metall. Mater. Trans. B* 47 (2016) 1796–1803.

- [41] H. Nishimoto, Y. Kang, T. Yoshikawa, K. Morita, The rate of boron removal from molten silicon by CaO-SiO₂ slag and Cl₂ treatment, *High Temp. Chem. Process* 31 (2012) 471–477.
- [42] M. Fang, C. Lu, L. Huang, H. Lai, J. Chen, X. Yang, J. Li, W. Ma, P. Xing, X. Luo, Multiple slag operation on boron removal from metallurgical-grade silicon using Na₂O-SiO₂ slags, *Ind. Eng. Chem. Res.* 53 (2014) 12054–12062.
- [43] Y. Wang, K. Morita, Reaction mechanism and kinetics of boron removal from molten silicon by CaO-SiO₂-CaCl₂ slag treatment, *J. Sustain. Metall.* 1 (2015) 126–133.
- [44] E. Krystad, K. Tang, G. Tranell, The kinetics of boron transfer in slag refining of silicon, *J. Occup. Med.* 64 (2012) 968–972.
- [45] L. Zhang, Y. Tan, J. Li, Y. Liu, D. Wang, Study of boron removal from molten silicon by slag refining under atmosphere, *Mater. Sci. Semicond. Process.* 16 (2013) 1645–1649.
- [46] K. Tang, E.J. Øvrelid, G. Tranell, M. Tangstad, Critical assessment of the impurity diffusivities in solid and liquid silicon, *J. Occup. Med.* 61 (2009) 49–55.
- [47] H. Koderu, Diffusion coefficients of impurities in silicon melt, *Jpn. J. Appl. Phys.* 2 (1963) 212.
- [48] J.P. Garandet, New determinations of diffusion coefficients for various dopants in liquid silicon, *Int. J. Thermophys.* 28 (2007) 1285–1303.
- [49] R. Noguchi, K. Suzuki, F. Tsukihashi, N. Sano, Thermodynamics of boron in a silicon melt, *Metall. Mater. Trans. B* 25 (1994) 903–907.
- [50] M. Tanahashi, T. Fujisawa, C. Yamauchi, Activity of boron in molten silicon, *J. Mining Mater. Process Inst. Jpn* 114 (1998) 807–812.
- [51] G. Inoue, T. Yoshikawa, K. Morita, Effect of calcium on thermodynamic properties of boron in molten silicon, *High Temp. Chem. Process* 22 (2003) 221–226.
- [52] T. Yoshikawa, K. Morita, Thermodynamic property of B in molten Si and phase relations in the Si-Al-B system, *Mater. Trans.* 46 (2005) 1335–1340.
- [53] T. Yoshikawa, K. Morita, Removal of B from Si by solidification refining with Si-Al melts, *Metall. Mater. Trans. B* 36 (2005) 731–736.
- [54] L.T. Khajavi, K. Morita, T. Yoshikawa, M. Barati, Thermodynamics of boron distribution in solvent refining of silicon using ferrosilicon alloys, *J. Alloy. Comp.* 619 (2015) 634–638.
- [55] F. Xu, S. Wu, Y. Tan, J. Li, Y. Li, Y. Liu, Boron removal from metallurgical silicon using Si-Al-Sn ternary alloy, *Separ. Sci. Technol.* 49 (2014) 305–310.
- [56] L.A.V. Teixeira, K. Morita, Removal of boron from molten silicon using CaO-SiO₂ based slags, *ISIJ Int.* 49 (2009) 783–787.
- [57] R.N. Hall, Segregation of impurities during the growth of germanium and silicon, *J. Phys. Chem. A* 57 (1953) 836–839.
- [58] S. Esfahani, M. Barati, Purification of metallurgical silicon using iron as impurity getter, part II: extent of silicon purification, *Met. Mater. Int.* 17 (2011) 1009–1015.
- [59] L. Zhao, W. Zhi, Z. Guo, C. Li, Low-temperature purification process of metallurgical silicon, *Trans. Nonferrous Metals Soc. China* 21 (2011) 85–1192.
- [60] Z. Yin, A. Oliazadeh, S. Esfahani, M. Johnston, M. Barati, Solvent refining of silicon using nickel as impurity getter, *Can. Metall. Q.* 50 (2011) 166–172.
- [61] R. Al-khazraji, Y. Li, L. Zhang, Application of slag refining technique to metallurgical grade silicon purification process: a review, *Met. Funct. Mater.* 25 (2018) 364–370.
- [62] J.A.T. Jones, B. Bowman, P.A. Lefrank, The Making, Shaping, and Treating of Steel-Steelmaking and Refining Volume, The AISE Steel Foundation, Pittsburgh, PA, 1998, pp. 281–304.
- [63] H. Bjerke, Removal of Boron from Silicon by Slag Treatment and by Evaporation of Boron from Slag in Hydrogen Atmosphere, Master's Thesis, Institutt for materialteknologi, 2012.
- [64] E.J. Jung, B.M. Moon, S.H. Seok, D.J. Min, The mechanism of boron removal in the CaO-SiO₂-Al₂O₃ slag system for SoG-Si, *Energy* 66 (2014) 35–40.
- [65] M.D. Johnston, M. Barati, Metallurgical Refining of Silicon for Solar Applications by Slagging of Impurity Elements, *Materials Challenges in Alternative and Renewable Energy*, (2011), pp. 207–224.
- [66] M. Li, T. Utigard, M. Barati, Removal of boron and phosphorus from silicon using CaO-SiO₂-Na₂O-Al₂O₃ flux, *Metall. Mater. Trans. B* 45 (2014) 221–228.
- [67] H.M. Liaw, F.S. d'Aragona, Purification of metallurgical-grade silicon by slagging and impurity redistribution, *Sol. Cells* 10 (1983) 109–118.
- [68] H. Fujiwara, R. Otsuka, K. Wada, T. Fukuyama, Silicon purifying method, slag for purifying silicon and purified silicon, U.S. Patent Application No. 10/503 (2005) 304.
- [69] L.A.V. Teixeira, Y. Tokuda, T. Yoko, K. Morita, Behavior and state of boron in CaO-SiO₂ slags during refining of solar grade silicon, *ISIJ Int.* 49 (2009) 777–782.
- [70] J. Wu, Y. Li, K. Wei, B. Yang, Y. Dai, Boron removal in purifying metallurgical grade silicon by CaO-SiO₂ slag refining, *T. Nonferr. Metal. Soc.* 24 (2014) 1231–1236.
- [71] K. Wei, H. Lu, W. Ma, Y. Li, Z. Ding, J. Wu, Y. Dai, Boron removal from metallurgical grade silicon by CaO-SiO₂ slag refining, *Rare Met.* 34 (2015) 522–526.
- [72] D. Luo, L. Ning, Y. Lu, G. Zhang, T. Li, Removal of boron from metallurgical grade silicon by electromagnetic induction slag melting, *T. Nonferr. Metal. Soc.* 21 (2011) 1178–1184.
- [73] L.K. Jakobsson, M. Tangstad, Distribution of boron between silicon and CaO-MgO-Al₂O₃-SiO₂ slags, *Metall. Mater. Trans. B* 45 (2014) 1644–1655.
- [74] J. Safarian, G. Tranell, M. Tangstad, Boron removal from silicon by CaO-Na₂O-SiO₂ ternary slag, *Metall. Mater. Trans. E* 2 (2015) 109–118.
- [75] H. Lai, L. Huang, C. Lu, M. Fang, W. Ma, P. Xing, J. Li, X. Luo, Reaction mechanism and kinetics of boron removal from metallurgical-grade silicon based on Li₂O-SiO₂ slags, *J. Occup. Med.* 68 (2016) 2371–2380.
- [76] F. Wang, J. Wu, W. Ma, M. Xu, Y. Lei, B. Yang, Removal of impurities from metallurgical grade silicon by addition of ZnO to calcium silicate slag, *Separ. Purif. Technol.* 170 (2016) 248–255.
- [77] J. Wu, W. Ma, B. Jia, B. Yang, D. Liu, Y. Dai, Boron removal from metallurgical grade silicon using a CaO-Li₂O-SiO₂ molten slag refining technique, *J. Non-Cryst. Solids* 358 (2012) 3079–3083.
- [78] Z. Ding, W. Ma, K. Wei, J. Wu, Y. Zhou, K. Xie, Boron removal from metallurgical-grade silicon using lithium containing slag, *J. Non-Cryst. Solids* 358 (2012) 2708–2712.
- [79] J. Li, L. Zhang, Y. Tan, D. Jiang, D. Wang, Y. Li, Research of boron removal from polysilicon using CaO-Al₂O₃-SiO₂-CaF₂ slags, *Vacuum* 103 (2014) 33–37.
- [80] M.D. Johnston, M. Barati, Distribution of impurity elements in slag-silicon equilibria for oxidative refining of metallurgical silicon for solar cell applications, *Sol. Energy Mater. Sol. Cells* 94 (2010) 2085–2090.
- [81] Y. Wang, X. Ma, K. Morita, Evaporation removal of boron from metallurgical-grade silicon using CaO-CaCl₂-SiO₂ Slag, *Metall. Mater. Trans. B* 45 (2014) 334–337.
- [82] H. Chen, Y. Wang, W. Zheng, Q. Li, X. Yuan, K. Morita, Model implementation of boron removal using CaCl₂-CaO-SiO₂ slag system for solar-grade silicon, *Metall. Mater. Trans. B* 48 (2017) 3219–3227.
- [83] C.P. Khattak, K.V. Ravi (Eds.), *Silicon Processing for Photovoltaics II*, vol 6, Elsevier, 2012.
- [84] M.D. Johnston, M. Barati, Effect of slag basicity and oxygen potential on the distribution of boron and phosphorus between slag and silicon, *J. Non-Cryst. Solids* 357 (2011) 970–975.
- [85] J. Cai, J. Li, W. Chen, C. Chen, X. Luo, Boron removal from metallurgical silicon using CaO-SiO₂-CaF₂ slags, *Trans. Nonferrous Metals Soc. China* 21 (2011) 1402–1406.
- [86] A. Hosseinpour, L.T. Khajavi, Slag refining of silicon and silicon alloys: a review, *Min. Proc. Ext. Met. Rev.* 39 (2018) 308–318.
- [87] L. Du, J.F. Stebbins, Solid-state NMR study of metastable immiscibility in alkali borosilicate glasses, *J. Non-Cryst. Solids* 315 (2003) 239–255.
- [88] L.A.V. Teixeira, Y. Tokuda, T. Yoko, K. Morita, Behavior and state of boron in CaO-SiO₂ slags during refining of solar grade silicon, *ISIJ Int.* 49 (2009) 777–782.
- [89] G. Qian, Z. Wang, X. Gong, L. Sun, The importance of slag structure to boron removal from silicon during the refining process: insights from Raman and nuclear magnetic resonance spectroscopy study, *Metall. Mater. Trans. B* 48 (2017) 3239–3250.
- [90] J. Kline, M. Tangstad, G. Tranell, A Raman spectroscopic study of the structural modifications associated with the addition of calcium oxide and boron oxide to silica, *Metall. Mater. Trans. B* 46 (2015) 62–73.
- [91] R. Mellström, O. Andersson, G. Åhlund, I. Johansson, Method for the purification of silicon, (1989) Intl. Patent. WO8902415 (A1). 1989-03-23.
- [92] Y. Wang, K. Morita, Measurement of the phase diagram of the SiO₂-CaCl₂ system and liquid area study of the SiO₂-CaO-CaCl₂ system, *Metall. Mater. Trans. B* 47 (2016) 1542–1547.
- [93] Y. Wang, K. Morita, Measurement of CaO-SiO₂-CaCl₂ slag density by an improved Archimedeian method, *J. Min. Metall. B* 51 (2015) 113–116.
- [94] C. Lu, L. Huang, H. Lai, M. Fang, W. Ma, P. Xing, L. Zhang, J. Li, X. Luo, Effects of slag refining on boron removal from metallurgical-grade silicon using recycled slag with active component, *Separ. Sci. Technol.* 50 (2015) 2759–2766.
- [95] C. Lu, T. Tang, Z. Sheng, P. Xing, X. Luo, Improved removal of boron from metallurgical-grade Si by CaO-SiO₂-CaCl₂ slag refining with intermittent CaCl₂ addition, *Vacuum* 143 (2017) 7–13.
- [96] L. Huang, H. Lai, C. Gan, H. Xiong, P. Xing, X. Luo, Separation of boron and phosphorus from Cu-alloyed metallurgical grade silicon by CaO-SiO₂-CaCl₂ slag treatment, *Separ. Purif. Technol.* 170 (2016) 408–416.
- [97] C. Yin, B. Hu, X. Huang, Boron removal from molten silicon using sodium-based slags, *J. Semicond.* 32 (2011) 092003.
- [98] J. Safarian, G. Tranell, M. Tangstad, Thermodynamic and kinetic behavior of B and Na through the contact of B-doped silicon with Na₂O-SiO₂ slags, *Metall. Mater. Trans. B* 44 (2013) 571–583.
- [99] L. Zhang, Y. Tan, F.M. Xu, J.Y. Li, H.Y. Wang, Z. Gu, Removal of boron from molten silicon using Na₂O-CaO-SiO₂ slags, *Separ. Sci. Technol.* 48 (2013) 1140–1144.
- [100] T. Yoshikawa, K. Morita, Solid solubilities and thermodynamic properties of aluminum in solid silicon, *J. Electrochem. Soc.* 150 (2003) G465–G468.
- [101] X. Ma, T. Yoshikawa, K. Morita, Removal of boron from silicon-tin solvent by slag treatment, *Metall. Mater. Trans. B* 44 (2013) 528–533.
- [102] A.M. Mitrašinović, T.A. Utigard, Refining silicon for solar cell application by copper alloying, *Siliconindia* 1 (2009) 239–248.
- [103] Y. Li, Y. Tan, J. Li, Q. Xu, Y. Liu, Effect of Sn content on microstructure and boron distribution in Si-Al alloy, *J. Alloy. Comp.* 583 (2014) 85–90.
- [104] P.S. Kotval, H.B. Strock, Process for the Production of Improved Refined Metallurgical Silicon, U.S. Patent and Trademark Office, Washington, DC, 1980 U.S. Patent No. 4,193,975.
- [105] R.K. Dawless, Silicon Purification Method Using Copper or Copper-Aluminum Solvent Metal, U.S. Patent and Trademark Office, Washington, DC, 1989 U.S. Patent No. 4,822,585.
- [106] T. Yoshikawa, K. Morita, Removal of phosphorus by the solidification refining with Si-Al melts, *Sci. Technol. Adv. Mater.* 4 (2003) 531.
- [107] T. Yoshikawa, K. Morita, An evolving method for solar-grade silicon production: solvent refining, *J. Occup. Med.* 64 (2012) 946–951.
- [108] T. Yoshikawa, K. Morita, Refining of Si by the solidification of Si-Al melt with electromagnetic force, *ISIJ Int.* 45 (2005) 967–971.
- [109] J.L. Gumaste, B.C. Mohanty, R.K. Galgali, U. Syamaprasad, B.B. Nayak, S.K. Singh, P.K. Jena, Solvent refining of metallurgical grade silicon, *Sol. Energy Mater.* 16 (1987) 289–296.
- [110] R.K. Dawless, R.L. Troup, D.L. Meier, A. Rohatgi, Production of extreme-purity

- aluminum and silicon by fractional crystallization processing, *J. Cryst. Growth* 89 (1988) 68–74.
- [111] K. Morita, T. Yoshikawa, Thermodynamic evaluation of new metallurgical refining processes for SOG-silicon production, *T. Nonferr. Metal. Soc.* 21 (2011) 685–690.
- [112] Y. Li, Y. Tan, P. Cao, J. Li, P. Jia, Y. Liu, Study on redistribution of boron during silicon solidification refining process in Si-Al melts, *Mater. Res. Innov.* 19 (2015) 81–85.
- [113] Q. Zou, J. Jie, J. Sun, T. Wang, Z. Cao, T. Li, Effect of Si content on separation and purification of the primary Si phase from hypereutectic Al-Si alloy using rotating magnetic field, *Separ. Purif. Technol.* 142 (2015) 101–107.
- [114] T. Yoshikawa, K. Morita, Thermodynamics on the solidification refining of silicon with Si-Al melts, EPD Congress-TMS 2005 Annual Meeting and Exhibition. San Francisco, 2005, pp. 549–558.
- [115] B. Ban, J. Li, X. Bai, Q. He, J. Chen, S. Dai, Mechanism of B removal by solvent refining of silicon in a Si melt with Ti addition, *J. Alloy. Comp.* 672 (2016) 489–496.
- [116] Y. Li, Y. Tan, J. Li, K. Morita, Si purity control and separation from Si-Al alloy melt with Zn addition, *J. Alloy. Comp.* 611 (2014) 267–272.
- [117] Y. Lei, W. Ma, L. Sun, J. Wu, Y. Dai, K. Morita, Removal of B from Si by Hf addition during Al-Si solvent refining process, *Sci. Technol. Adv. Mater.* 17 (2016) 12–19.
- [118] Y. Lei, W. Ma, J. Wu, K. Wei, S. Li, K. Morita, Impurity phases and their removal in Si purification with Al-Si alloy using transition metals as additives, *J. Alloy. Comp.* 734 (2018) 250–257.
- [119] K. Chen, X. Chen, Y. Lei, W. Ma, J. Han, Z. Yang, Mechanism of enhancing B removal from Si with V addition using Al-Si as the refining solvent, *Separ. Purif. Technol.* 203 (2018) 168–177.
- [120] M. Fang, C. Lu, H. Lai, L. Huang, J. Chen, W. Ma, Z. Sheng, J. Shen, J. Li, X. Luo, Effect of solidification rate on representative impurities distribution in Si-Cu alloy, *Mater. Sci. Tech-Lond.* 29 (2013) 861–867.
- [121] L. Huang, H. Lai, C. Lu, M. Fang, W. Ma, P. Xing, J. Li, X. Luo, Enhancement in extraction of boron and phosphorus from metallurgical grade silicon by copper alloying and aqua regia leaching, *Hydrometallurgy* 161 (2016) 14–21.
- [122] H. Morito, T. Karahashi, M. Uchikoshi, M. Isshiki, H. Yamane, Low-temperature purification of silicon by dissolution and solution growth in sodium solvent, *Siliconindia* 4 (2012) 121–125.
- [123] J. Li, B. Ban, Y. Li, X. Bai, T. Zhang, J. Chen, Removal of impurities from metallurgical grade silicon during Ga-Si solvent refining, *Siliconindia* 9 (2017) 77–83.
- [124] J. Wu, D. Yang, M. Xu, W. Ma, Q. Zhou, Z. Xia, Y. Lei, K. Wei, S. Li, Z. Chen, K. Xie, Boron removal from silicon using secondary refining techniques by metallurgical method, *Separ. Purif. Rev.* 00 (2018) 1–21.
- [125] X. Bai, B. Ban, J. Li, Z. Fu, Z. Peng, C. Wang, J. Chen, Effect of Ti addition on B removal during silicon refining in Al-30%Si alloy directional solidification, *Separ. Purif. Technol.* 174 (2017) 345–351.
- [126] Y. Lei, P. Qiu, K. Chen, X. Chen, W. Ma, J. Wu, K. Wei, S. Li, G. Lv, J. Qiu, Mechanism of ZrB₂ formation in Al-Si alloy and application in Si purification, *ACS Sustain. Chem. Eng.* 7 (2019) 12990–12996.
- [127] Y. Ren, H. Wang, K. Morita, Growth control and enrichment of Si crystals from Si-Sn melt by directional solidification, *Vacuum* 158 (2018) 86–92.
- [128] C. Alemany, C. Trassy, B. Pateyron, K.I. Li, Y. Delannoy, Refining of metallurgical-grade silicon by inductive plasma, *Sol. Energy Mater. Sol. Cells* 72 (2002) 41–48.
- [129] H.C. Theuerer, Removal of boron from silicon by hydrogen water vapor treatment, *J. Occup. Med.* 8 (1956) 1316–1319.
- [130] J. Wu, B. Yang, Y. Dai, K. Morita, Boron removal from metallurgical grade silicon by oxidizing refining, *T. Nonferr. Metal. Soc.* 19 (2009) 463–467.
- [131] A. Yvon, E. Fourmond, C. Ndzogha, Y. Delannoy, C. Trassy, Inductive plasma process for refining of solar grade silicon, EPM 2003 4th International Conference on Electromagnetic Processing of Materials, Forum Editions, 2003, pp. 125–130 September.
- [132] E.F. Nordstrand, M. Tangstad, Removal of boron from silicon by moist hydrogen gas, *Metall. Mater. Trans. B* 43 (2012) 814–822.
- [133] N. Ito, J. Kondo, K. Okazawa, M. Okajima, Method for Producing High Purity Silicon, U.S. Patent and Trademark Office, Washington, DC, 2008 U.S. Patent Application No. 11/885,798.
- [134] H. Chen, X. Yuan, K. Morita, Y. Zhong, X. Ma, Z. Chen, Y. Wang, Reaction mechanism and kinetics of boron removal from molten silicon via CaO-SiO₂-CaCl₂ slag treatment and ammonia injection, *Metall. Mater. Trans. B* 50 (2019) 1–7.
- [135] F. Schmid, C.P. Khattak, Method for Purifying Silicon, vol 107, U.S. Patent and Trademark Office, Washington, DC, 1999, p. 972 U.S. Patent No. 5.
- [136] J. Amourox, D. Morvan, Heat and mass transfer phenomena during plasma slag interactions: applications in the production of ultrapure material, *High Temp. Chem. Process* 1 (1992) 537–560.
- [137] K. Suzuki, N. Sano, Thermodynamics for removal of boron from metallurgical silicon by flux treatment, Tenth EC Photovoltaic Solar Energy Conference, Springer, Dordrecht, 1991, pp. 273–275.
- [138] K. Suzuki, T. Kumagai, N. Sano, Removal of boron from metallurgical-grade silicon by applying the plasma treatment, *ISIJ Int.* 32 (1992) 630–634.
- [139] R. Combes, D. Morvan, J. Amourox, G. Picard, Boron elimination from silicon by inductive plasma with bias applied, *J. Phys.* 3 3 (1993) 921–943.
- [140] A. Schei, Method for Refining of Silicon, U.S. Patent and Trademark Office, Washington, DC, 1998 U.S. Patent No. 5,788,945.
- [141] C.P. Khattak, F. Schmid, D.B. Joyce, E.A. Smelik, M.A. Wilkinson, Production of solar-grade silicon by refining of liquid metallurgical-grade silicon, In AIP Conference Proceedings, 462 1999, pp. 731–736.
- [142] C.P. Khattak, D.B. Joyce, F. Schmid, A simple process to remove boron from metallurgical grade silicon, *Sol. Energy Mater. Sol. Cells* 74 (2002) 77–89.
- [143] J. Safarian, K. Tang, K. Hildal, G. Tranell, Boron removal from silicon by humidified gases, *Metall. Mater. Trans. E* 1 (2014) 41–47.
- [144] G. Flamant, V. Kurtcuoglu, J. Murray, A. Steinfeld, Purification of metallurgical grade silicon by a solar process, *Sol. Energy Mater. Sol. Cells* 90 (2006) 2099–2106.
- [145] J. Wu, W. Ma, Y. Li, B. Yang, D. Liu, Y. Dai, Thermodynamic behavior and morphology of impurities in metallurgical grade silicon in process of O₂ blowing, *T. Nonferr. Metal. Soc.* 23 (2013) 260–265.
- [146] J. Wu, Y. Li, W. Ma, K. Liu, K. Wei, K. Xie, B. Yang, Y. Dai, Impurities removal from metallurgical grade silicon using gas blowing refining techniques, *Siliconindia* 6 (2014) 79–85.
- [147] Ø.S. Sortland, M. Tangstad, Boron removal from silicon melts by H₂O/H₂ gas blowing: mass transfer in gas and melt, *Metall. Mater. Trans. E* 1 (2014) 211–225.
- [148] J. Safarian, K. Tang, J.E. Olsen, S. Andersson, G. Tranell, K. Hildal, Mechanisms and kinetics of boron removal from silicon by humidified hydrogen, *Metall. Mater. Trans. B* 47 (2016) 1063–1079.
- [149] Z. Chen, K. Morita, Iron-catalyzed boron removal from molten silicon in ammonia, *Metall. Mater. Trans. E* 3 (2016) 228–233.
- [150] K. Suzuki, K.S. akaguchi, T. Nakagiri, N. Sano, Gaseous removal of phosphorus and boron from molten silicon, *J. Jpn. Inst. Metals* 54 (1990) 161–167.
- [151] D. Morvan, J. Amourox, F. Sloomman, N. Madigou, T. Roger, Control of the Plasma Refining of Materials by Computer Analysis Using an Optical Fiber, Spectrometer and O.M.A., the 8th International Symposium on Plasma Chemistry, vol. 3, ISPC-8, Tokyo, Japan, 1987, pp. 1868–1873.
- [152] H. Baba, N. Yuge, Y. Sakaguchi, M. Fukai, F. Aratani, Y. Habu, Removal of boron from molten silicon by argon-plasma mixed with water vapor, Tenth EC Photovoltaic Solar Energy Conference, Springer, Dordrecht, 1991, pp. 286–289.
- [153] Y. Delannoy, C. Alemany, K.I. Li, P. Proulx, C. Trassy, Plasma-refining process to provide solar-grade silicon, *Sol. Energy Mater. Sol. Cells* 72 (2002) 69–75.
- [154] N. Yuge, H. Baba, Y. Sakaguchi, K. Nishikawa, H. Terashima, F. Aratani, Purification of metallurgical silicon up to solar grade, *Sol. Energy Mater. Sol. Cells* 34 (1994) 243–250.
- [155] T. Ikeda, M. Maeda, Elimination of boron in molten silicon by reactive rotating plasma arc melting, *Mater. Trans. JIM* 37 (1996) 983–987.
- [156] J. Cai, C. Lu, J. Li, W. Ma, X. Luo, Boron removal from metallurgical silicon by plasma melting using electromagnetic induction, *Chin. J. Nonferrous Metals* 12 (2012) 033.
- [157] N. Nakamura, H. Baba, Y. Sakaguchi, Y. Kato, Boron removal in molten silicon by a steam-added plasma melting method, *Mater. Trans.* 45 (2004) 858–864.
- [158] N. Nakamura, H. Baba, Y. Sakaguchi, S. Hiwasa, Y. Kato, Boron removal in molten silicon with steam added plasma melting method, *J. Jpn. Inst. Metals* 67 (2003) 583–589.
- [159] S. Rousseau, M. Benmansour, D. Morvan, J. Amourox, Purification of MG silicon by thermal plasma process coupled to DC bias of the liquid bath, *Sol. Energy Mater. Sol. Cells* 91 (20) (2007) 1906–1915.
- [160] M.D. Díez, M. Fjeld, E. Andersen, B. Lie, Validation of a compartmental population balance model of an industrial leaching process: the Silgrain® process, *Chem. Eng. Sci.* 61 (2006) 229–245.
- [161] S. Pizzini, Solar grade silicon as a potential candidate material for low-cost terrestrial solar cells, *Sol. Energy Mater.* 6 (1982) 253–297.
- [162] J. Dietl, Hydrometallurgical purification of metallurgical-grade silicon, *Sol. Cells* 10 (1983) 145–154.
- [163] Y. Sun, Q. Ye, C. Guo, H. Chen, X. Lang, F. David, Q. Luo, C. Yang, Purification of metallurgical-grade silicon via acid leaching, calcination and quenching before boron complexation, *Hydrometallurgy* 139 (2013) 64–72.
- [164] T. Shimo, T. Yoshikawa, K. Morita, Thermodynamic study of the effect of calcium on removal of phosphorus from silicon by acid leaching treatment, *Metall. Mater. Trans. B* 35 (2004) 277–284.
- [165] J. Li, P. Cao, P. Ni, Y. Li, Y. Tan, Enhanced boron removal from metallurgical grade silicon by the slag refining method with the addition of tin, *Separ. Sci. Technol.* 51 (2016) 1598–1603.
- [166] M. Tanahashi, T. Fujisawa, C. Yamauchi, Oxidative removal of boron from molten silicon by CaO-based flux treatment with oxygen gas injection, *Metall. Mater. Trans. B* 45 (2014) 629–642.
- [167] J. Wu, Y. Zhou, W. Ma, M. Xu, B. Yang, Synergistic separation behavior of boron in metallurgical grade silicon using a combined slagging and gas blowing refining technique, *Metall. Mater. Trans. B* 48 (2017) 22–26.
- [168] M.S. Islam, M.A. Rhamdhani, G.A. Brooks, Electrically enhanced boron removal from silicon using slag, *Metall. Mater. Trans. B* 45 (2014) 1–5.
- [169] J.F. White, D. Sichen, Mass transfer in slag refining of silicon with mechanical stirring: transient kinetics of Ca and B transfer, *Metall. Mater. Trans. B* 46 (2015) 135–144.
- [170] J. Li, Z. Guo, J. Li, L. Yu, Super gravity separation of purified Si from solvent refining with the Al-Si alloy system for solar grade silicon, *Siliconindia* 7 (2015) 239–246.
- [171] X. Ma, T. Yoshikawa, K. Morita, Purification of metallurgical grade Si combining Si-Sn solvent refining with slag treatment, *Separ. Purif. Technol.* 125 (2014) 264–268.
- [172] Z. Xia, J. Wu, W. Ma, Y. Lei, K. Wei, Y. Dai, Separation of boron from metallurgical grade silicon by a synthetic CaO-CaCl₂ slag treatment and Ar-H₂O-O₂ gas blowing refining technique, *Separ. Purif. Technol.* 187 (2017) 25–33.
- [173] J. Chen, W. You, J. Du, H. Pan, Ultra-trace interference-free analysis of solar-grade silicon wafers by ELAN DRC II ICP-MS, http://www.perkinelmer.com.cn/lab-solutions/resources/docs/APP_SolarGradeSiliconWafersbyELANDRCII.pdf.
- [174] ICP-OES background and interference removal, https://www.agilent.com/cs/library/flyers/public/5110_ICP-OES_5991-8452EN_background_correction.pdf.