



## Boron removal from molten silicon using CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> slag

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**Abstract:** The distribution coefficient ( $L_B$ ) of boron between CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> slag and silicon was investigated using electromagnetic induction melting for the purpose of improving the boron removal fraction. The dependence of the boron distribution coefficient between slag and silicon on the fundamental parameters of CaO to SiO<sub>2</sub> mass ratio and refining time and the additions of BaO and CaF<sub>2</sub> to the slag was discussed. The results show that  $L_B$  can be increased by adding BaO and CaF<sub>2</sub> to CaO–SiO<sub>2</sub> slag. The maximum value of  $L_B$  (6.94) is obtained when the CaO to SiO<sub>2</sub> mass ratio is 1.1:1 and the contents of BaO and CaF<sub>2</sub> are fixed at 15% and 20%, respectively. Increasing the refining time increases the  $L_B$ . After the slag treatment is performed twice, the boron content of the silicon is successfully reduced from  $3.5 \times 10^{-5}$  to  $3.7 \times 10^{-6}$ , and the removal fraction of boron reaches 89.4%.

**Key words:** metallurgical silicon; boron removal; CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub>

### 1 Introduction

Because of environmental pollution and the depletion of fossil fuels, solar energy is an option to provide renewable energy to adapt to the demands of sustainable development. Silicon has been used as a starting material in the photovoltaic industry. In recent years, metallurgical grade silicon (MG-Si) [1] has been used as a feedstock alternative to substitute electronic grade silicon to solve the problem of silicon feedstock shortage. The purity of metallurgical grade silicon is 2N. Therefore, to satisfy the purity requirements of solar grade silicon (SOG-Si), it is necessary to remove a variety of impurities, such as phosphorus and boron impurities.

These metallic impurities can be removed by directional solidification because of their low segregation coefficient. Phosphorus can be removed using vacuum refining because of its high vapor pressure. However, boron is difficult to remove using either directional solidification [2,3] or vacuum treatment [4,5] because of its high segregation coefficient [6] and low vapor pressure. Slag treatment is an effective method to remove boron from metallurgical silicon. Boron reacts with slag

to form boron oxides that transfer to the slag phase, whereas, refined silicon can easily be separated from the slag phase.

In recent years, various CaO–SiO<sub>2</sub>-based slag systems have been investigated to evaluate the removal of boron from metallurgical silicon [7–10]. TEIXEIRA et al [11,12] conducted systematic research to understand the thermodynamics of the CaO–SiO<sub>2</sub> slag system. JOHNSTON et al [13,14] discussed the effects of slag basicity, oxygen potential and the mass ratio of slag to silicon on the boron removal process. LUO et al [15] studied the kinetics of boron removal using an electromagnetic induction melting process.

Apparently, the boron removal fraction is strongly dependent on slag chemistry. BaO is one of the most basic fluxes, which is preferred to remove acidic impurities such as boron. Besides, the slag basicity of BaO is stronger than that of CaO, and BaO can decrease the melting point and viscosity of the slag [16,17].

CaF<sub>2</sub> can further reduce the viscosity and liquefaction temperature of the slag [18,19], promoting the mass transfer process. Therefore, BaO and CaF<sub>2</sub> were chosen in the present study to improve the boron removal fraction.

The extraction of boron from silicon using

CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> slag has not been systematically studied. SUZUKI et al [8] only investigated the effect of the CaO to SiO<sub>2</sub> mass ratio on extraction using CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> slag. Therefore, in the present study, comprehensive data on the fundamental parameters including CaO to SiO<sub>2</sub> mass ratio, refining time, additions of BaO and CaF<sub>2</sub> to the slag and repeated slag treatment have been investigated. The values of the boron distribution coefficient between slag and silicon ( $L_B$ ) of CaO–SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> and CaO–SiO<sub>2</sub> were compared.

## 2 Experimental

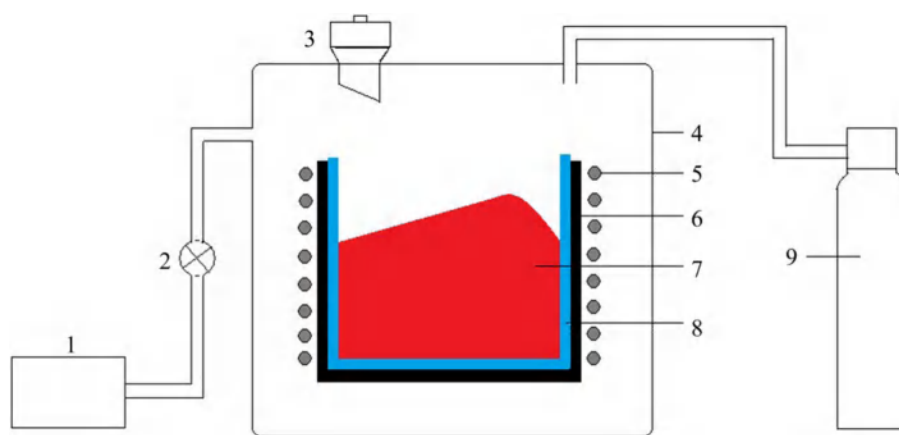
CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> slag was used to remove the boron. Although liquid slag is an ionic melt composed of cations and anions, the F<sup>-</sup> ions in the slag are assumed to exist with Ca<sup>2+</sup>, and this component is expressed as CaF<sub>2</sub>. All of the oxides and CaF<sub>2</sub> were reagent grade. The metallurgical grade silicon that was used as the raw material in this study was supplied by Xinlong Co., Ltd. The boron content of this MG-Si was  $3.5 \times 10^{-5}$ . The effects of varying the CaO to SiO<sub>2</sub> mass ratio, refining time, as well as the BaO and CaF<sub>2</sub> proportions were studied to obtain high values of  $L_B$ . The CaO to SiO<sub>2</sub> mass ratio was varied from 0.3:1 to 1.1:1 with the BaO and CaF<sub>2</sub> contents fixed at 5% and 10%, respectively. The refining time varied from 1200 to 6000 s. BaO content varied from 0 to 35%, and CaF<sub>2</sub> content varied from 0 to 40%. The  $L_B$  values of CaO–SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> slag and CaO–SiO<sub>2</sub> slag were also compared.

The experimental parameters are shown in Table 1. The experimental process consisted of the following steps. The metallurgical silicon was ground to a particle size of 0.1–0.2 mm. The metallurgical grade silicon was then washed with acetone in an ultra-sonic cleaner to remove possible solid residue from the surface. After

**Table 1** Experimental parameters used in this study

Parameter	Value
Initial boron content in silicon	$3.5 \times 10^{-5}$
Temperature/K	1873
Mass ratio of silicon to slag	4:1
Melting time/s	1200–6000
Filled argon pressure/kPa	10

drying, 0.3 kg of metallurgical silicon and 0.075 kg of slag (silicon to slag mass ratio of 4:1) were placed in a pure graphite cylindrical crucible (inner diameter: 0.06 m; outer diameter: 0.07 m; height: 0.16 m) that was surrounded by a graphite holder (inner diameter: 0.07 m; outer diameter: 0.09 m; depth: 0.16 m). The slag layer was placed in the middle of the graphite crucible. Then, the crucible was loaded into an intermediate frequency (2000 Hz) induction melting furnace. The schematic diagram of the apparatus is provided in Fig. 1. The basic equipment consisted of a rotary vane mechanical vacuum pump, a diffusion vacuum pump, a feeding device, an induction coil heating system and an argon gas inlet. Firstly, the rotary vane mechanical vacuum pump and the diffusion vacuum pump evacuated the furnace. When the absolute pressure was below 30 Pa, electric power was applied to melting the metallurgical silicon and slag, and argon gas was added to the furnace to maintain a pressure of approximately  $1.0 \times 10^4$  Pa. An infrared thermometer was used to measure the temperature. Two colors of pyrometer were used in the present experiments and the wavelength is 1.0  $\mu$ m. The smelting continued for 1200–6000 s at 1873 K under the argon atmosphere. After refining, the silicon and slag were physically separated, and the boron contents of the silicon and the slag were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).



**Fig. 1** Schematic drawing of intermediate frequency induction furnace: 1—Rotary vane mechanical vacuum pump; 2—Roots vacuum pump; 3—Feeding device; 4—Intermediate frequency induction melting furnace; 5—Induction coil; 6—Graphite holder; 7—Molten silicon and slag; 8—Graphite crucible; 9—Argon gas

The distribution coefficient of boron between the slag and silicon phase was defined as follows:

$$L_B = \frac{w_1}{w_2} \times 100\% \quad (1)$$

where  $w_1$  and  $w_2$  are the contents of boron in slag and silicon, respectively.

### 3 Results and discussion

Figure 2 shows the longitudinal section of the silicon ingot. The height of the ingot was 0.054 m and the radius of the ingot was 0.06 m. It is clearly seen that most of the slag is distributed at the top of the silicon. The slag can be effectively separated from silicon in the present study.



Fig. 2 Longitudinal section of silicon ingot

#### 3.1 Effect of refining time on $L_B$

The refining time is an important parameter influencing the  $L_B$  value. The effect of refining time on  $L_B$  was investigated over the range of 1200–6000 s, and the CaO to SiO<sub>2</sub> mass ratio and the BaO and CaF<sub>2</sub> contents were fixed at 1.1:1, 5% and 10%, respectively. Figure 3 shows the relationship between refining time and  $L_B$ , indicating that  $L_B$  increased as the refining time increased. The boron content was reduced from  $3.5 \times 10^{-5}$  in the raw MG-Si to  $1.6 \times 10^{-5}$  at 6000 s, and the  $L_B$

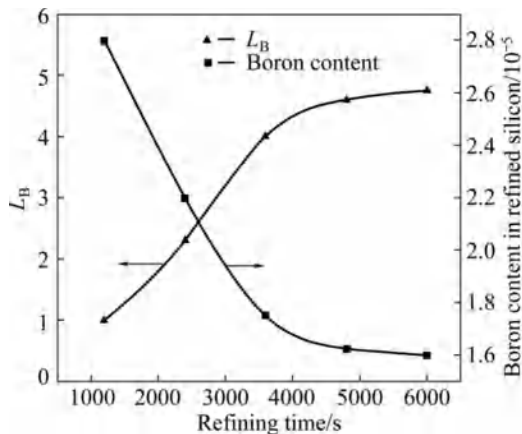


Fig. 3 Effect of refining time on boron removal

increased to 4.75. Most of the boron was eliminated during the first 3600 s, and the slope of the curve became moderate after 4800 s, indicating that further increasing the refining time cannot contribute much to the removal fraction. From this result, 3600 s was selected to be optimal for refining the molten silicon. This may be attributed to the forced melt circulation caused by the electromagnetic force.

#### 3.2 Effect of CaO to SiO<sub>2</sub> mass ratio on boron removal

Figure 4 shows the relationship between CaO to SiO<sub>2</sub> mass ratio and  $L_B$ . The mass ratio of CaO to SiO<sub>2</sub> varied from 0.3:1 to 1.1:1, and the amounts of BaO and CaF<sub>2</sub> were fixed at 5% and 10%, respectively. The mass ratio of silicon to slag was 4:1, and the melt was held at 1873 K for 3600 s. The  $L_B$  decreased first and then increased with the increasing CaO to SiO<sub>2</sub> mass ratio. The minimum  $L_B$  (1.89) was obtained at the CaO to SiO<sub>2</sub> mass ratio of 0.7:1. The maximum  $L_B$  (4) was obtained at the CaO to SiO<sub>2</sub> mass ratio of 1.1:1. These results are similar to those published by TEIXEIRA et al [11].

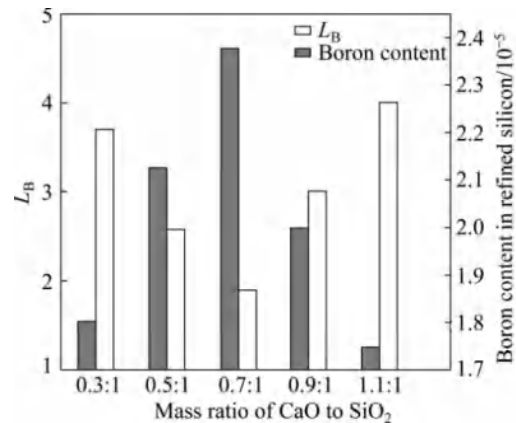


Fig. 4 Effect of CaO to SiO<sub>2</sub> mass ratio on boron removal

When the CaO to SiO<sub>2</sub> mass ratio was less than 0.7:1, the decrease of the CaO to SiO<sub>2</sub> mass ratio resulted in an increase of the amount of SiO<sub>2</sub> and oxygen partial pressure, contributing to an increase of  $L_B$ . When the CaO to SiO<sub>2</sub> mass ratio was above 0.7:1, the increase of the CaO to SiO<sub>2</sub> mass ratio resulted in a decrease of the viscosity as well as the oxygen ion of slag, which was attributed to the decomposition of the silicon–oxygen complex ions. Thus,  $L_B$  increased with increasing CaO to SiO<sub>2</sub> mass ratio when the CaO to SiO<sub>2</sub> mass ratio was above 0.7:1.

Figure 5 compares the results of the present study with those of other researchers. Our curve is similar to the work of ZHANG et al [20] and TEIXEIRA et al [11] with CaO–SiO<sub>2</sub> slag and differs from the work of CAI et al [7]. The  $L_B$  value found in the present study is somewhat lower than that determined by TEIXEIRA

et al [11] and CAI et al [7]. In the work of TEIXEIRA et al [11] with CaO–SiO<sub>2</sub> slag, the refining time was 64800 s and the slag attained the equilibrium and in our research the slag did not reach equilibrium. In the work of CAI et al [7], the mass ratio of slag to silicon was 3:1, contributing to the higher  $L_B$ . The  $L_B$  value determined in the present study was also lower than that determined by ZHANG et al [20], because of the lower BaO and CaF<sub>2</sub> contents. When the BaO and CaF<sub>2</sub> contents were 15% and 20%, respectively, the  $L_B$  value determined in the present study reached 6.94. The  $L_B$  values in the work of TEIXEIRA et al [11] with CaO–SiO<sub>2</sub>–25%CaF<sub>2</sub> slag and CaO–SiO<sub>2</sub>–40%CaF<sub>2</sub> are lower than those of others, which may be attributed to the higher CaF<sub>2</sub> content. When the CaF<sub>2</sub> content is too high, it contributes to the dilution of the slag. According to the study of WU et al [10], the  $L_B$  of CaO–SiO<sub>2</sub> slag is lower than that determined in our study. The addition of 5% BaO and 10% CaF<sub>2</sub> may contribute to the higher  $L_B$  values of our results.

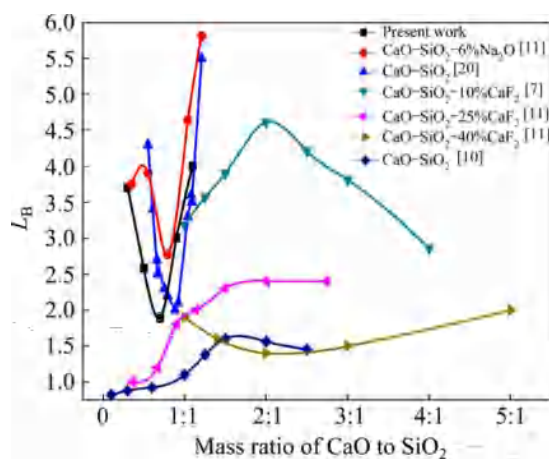


Fig. 5 Comparing results of present study with those of other researchers [7,10–12,20]

### 3.3 Effect of BaO content on $L_B$

The influence of BaO addition to the slag on  $L_B$  was investigated at 1873 K for 3600 s, and the results are shown in Fig. 6. The BaO contents were 0, 5%, 15%, 25% and 35%, and the CaO to SiO<sub>2</sub> mass ratio and CaF<sub>2</sub> content were fixed at 1.1:1 and 10%, respectively. The  $L_B$  initially increased with BaO addition to the slag, reaching a maximum value of 6.18 when the BaO content was 15%. Further BaO addition to the slag resulted in decreasing  $L_B$ .

Addition of small amounts of BaO may decrease the melting point and viscosity of the slag [16,17], resulting in an increase of  $L_B$ . However, a large amount of BaO may also increase the melting point and viscosity of the slag. If the viscosity of the slag increases significantly with a large amount of BaO, the value of  $L_B$  will decrease in a limited refining time.

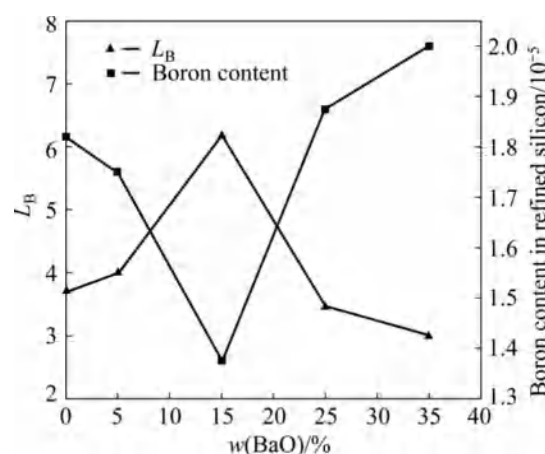


Fig. 6 Effect of BaO content on boron removal

### 3.4 Effect of CaF<sub>2</sub> content on $L_B$

The influence of CaF<sub>2</sub> addition to the slag on  $L_B$  was investigated by varying the content of CaF<sub>2</sub>, and the results are presented in Fig. 7. The CaO to SiO<sub>2</sub> mass ratio and BaO content were fixed at 1.1:1 and 15%, respectively. The contents of CaF<sub>2</sub> were 0, 10%, 20%, 30% and 40%. The  $L_B$  increased and then decreased with increasing CaF<sub>2</sub>, reaching a maximum value of 6.94 when the CaF<sub>2</sub> content was 20%.

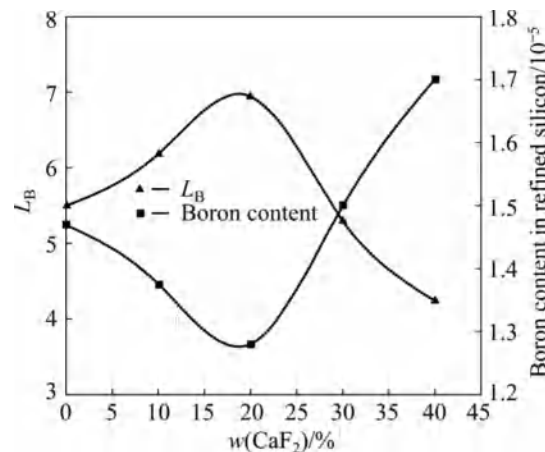


Fig. 7 Effect of CaF<sub>2</sub> content on boron removal

A small addition of CaF<sub>2</sub> may decrease the melting point and viscosity of the slag [18], resulting in an increase of  $L_B$ . However, a larger amount of CaF<sub>2</sub> may also increase the viscosity [21] with increasing the melting point of the slag, resulting in a decrease of the  $L_B$ . In addition, when the CaF<sub>2</sub> content was greater than 20%, the amount of the SiO<sub>2</sub> decreased and CaF<sub>2</sub> significantly diluted the slag, resulting in a decrease of  $L_B$ .

### 3.5 Boron removal using repeated slag treatment

The maximum  $L_B$  was obtained when the CaO, SiO<sub>2</sub>, BaO and CaF<sub>2</sub> contents were 34.1%, 30.9%, 15% and

20%, respectively. Thus, 34.1%CaO–30.9%SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> slag was chosen for repeated slag treatment. The smelting was conducted for 3600 s at 1873 K, and the mass ratio of silicon to slag was 4:1. The results presented in Table 2 show the boron content of the silicon following single and repeated slag treatment. After the initial slag treatment, the boron content of the silicon was reduced from  $3.5 \times 10^{-5}$  to  $1.28 \times 10^{-5}$ , and the boron removal fraction was 63.4%. After the second slag treatment, the boron content of the silicon was reduced to  $3.7 \times 10^{-6}$ , and the total boron removal fraction was 89.4%. Thus, boron can be effectively removed through repeated slag treatment.

**Table 2** Boron content in silicon after slag treatment for once and twice

Sample	Boron content/ $10^{-5}$	Removal fraction/%
Raw material	3.5	0
Slag treatment for once	1.28	63.4
Slag treatment for twice	0.37	89.4

### 3.6 Comparing $L_B$ value of CaO–SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> and CaO–SiO<sub>2</sub>

Table 3 compares the  $L_B$  value of CaO–SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> with that of CaO–SiO<sub>2</sub>. The CaO to SiO<sub>2</sub> mass ratio was fixed at 1.1:1, and the mass ratio of silicon to slag was 4:1, with 3600 s of refining at 1873 K. After CaO–SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> slag refining,  $L_B$  reached 6.94. After CaO–SiO<sub>2</sub> slag refining,  $L_B$  reached only 3.5. Table 3 shows that the addition of 15% BaO and 20% CaF<sub>2</sub> increased the  $L_B$ .

**Table 3** Comparing  $L_B$  values between CaO–SiO<sub>2</sub>–15%BaO–20%CaF<sub>2</sub> and CaO–SiO<sub>2</sub>

CaO–SiO <sub>2</sub>	CaO–SiO <sub>2</sub> –15%BaO–20%CaF <sub>2</sub>
3.5	6.94

## 4 Conclusions

1) The  $L_B$  increased with increasing the refining time. Most of the boron was eliminated during the first 3600 s, and 3600 s was selected to be optimal for refining the molten silicon.

2) The maximum  $L_B$  value of 6.94 was obtained by using slag with CaO to SiO<sub>2</sub> mass ratio of 1.1:1 and 15% BaO together with 20% CaF<sub>2</sub>.

3) After the second slag treatment, the boron content of the silicon was reduced to  $3.7 \times 10^{-6}$ , and the total boron removal fraction was achieved up to 89.4%.

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## CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> 四元渣去除熔硅中的硼杂质

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**摘要:** 为提高硼的去除率, 研究了电磁感应精炼过程中硼杂质在 CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> 四元渣和熔硅之间的分配系数  $L_B$ , 讨论了四元渣系中 CaO/SiO<sub>2</sub> 质量比、BaO 和 CaF<sub>2</sub> 含量、熔炼时间对  $L_B$  的影响规律。结果表明: 随着 CaO–SiO<sub>2</sub> 渣中 BaO 和 CaF<sub>2</sub> 含量的增大,  $L_B$  值增大。当 CaO/SiO<sub>2</sub> 质量比为 1.1:1、BaO 和 CaF<sub>2</sub> 含量分别为 15% 和 20% 时, CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub> 四元渣去除熔硅中硼杂质效果最好,  $L_B$  达到最大值 6.94, 并且  $L_B$  随着熔炼时间的延长而增大。经过两次造渣后, 熔硅中硼含量由  $3.5 \times 10^{-5}$  降到  $3.7 \times 10^{-6}$ , 硼的去除率达到 89.4%。

**关键词:** 冶金级硅; 除硼; CaO–SiO<sub>2</sub>–BaO–CaF<sub>2</sub>

(Edited by Xiang-qun LI)