J. Min. Metall. Sect. B-Metall. 50 (1) B (2014) 83 - 86

Journal of Mining and Metallurgy,
Section B: Metallurgy

Letter to Editor

REMOVING BORON FROM METALLURGICAL GRADE SILICON BY A HIGH BASIC SLAG REFINING TECHNIQUE

J.J. Wu [a,b,c*], K. Liu [b,c], M. Xu [b,c], W.H. Ma [a,b,c*], B. Yang[a,b], Y.N. Dai[a,b,c]

[a] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization/The National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, China
[b] Key Laboratory of Non-Ferrous Metals Vacuum Metallurgy of Yunnan Province, Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, China
[c] Engineering Research Center for Silicon Metallurgy and Silicon Materials of Yunnan Provincial Universities, Kunming University of Science and Technology, China

(Received 02 February 2014; accepted 13 February 2014)

Abstract

A new purification method of removing boron from metallurgical grade silicon (MG-Si) using a high baisicity slag was developed in this paper. The typical impurities Al, Ca, Ti, B, P etc in MG-Si can be removed by the binary calcium sillicate slag and it is especially efficient for removing impurity Boron. It was found that the maximal distribution coefficient of boron between calcium sillicate slag and silicon reaches to 1.57 when the mass ratio of CaO/SiO_2 was 1.5 and the composition was 60%CaO-40%SiO_2. It showed that the oxidizability of calcium sillicate slag was affected and restricted by the basicity and the mass ratio of acid oxide SiO_2 slag according to the thermodynamic relationship. The boron concentration in MG-Si can be reduced from 18×10^{-6} to 4.5×10^{-6} and 1.4×10^{-6}, respectively, when using the ternary slags 40.5%CaO-49.5%SiO_2-10%Li_2O and 32CaO-38%SiO_2-30%Li_2O.

Keywords: *Metallurgical grade silicon; boron; molten slag; basicity; distribution coefficient*

1. Introduction

Silicon is widely used as a photoelectric conversion material due to its relatively low cost and high performance [1] and silicon-base solar cells are a conventional and low-cost semiconductor material applied in photovoltaic (PV) technology with at least 90% of photovoltaic market [2, 3]. Presently, the market demand for solar grade silicon (SoG-Si) has been growing rapidly. In order to meet the high demands on the purity of solar grade silicon (SoG-Si) for a target purity of 99.9999% (6 nines), some inexpensive metallurgical purification techniques have been developed to purify metallurgical grade silicon (MG-Si) to SoG-Si [4-6].

It is well known that boron is an especially obstinate impurity element that is difficult to be removed from MG-Si as a result of its large sgregation coefficient (0.83) in silicon and its low volatility compared to silicon [7]. The molten slag refining is a traditional method using in the purification of steel making [8] and it was also proved that the molten slag refining based on calcium sillicate system is an efficient agent of removing boron from molten metallurgical grade silicon (MG-Si). Impurity boron in MG-Si can be oxidized into boric oxide, which will then enter a basic slag based on calcium sillicate system in the form of lime borate [9-11].

In previous studies, Diet [12] described that impurity boron in silicon can be reduced from 18×10^{-6} to 1×10^{-6} using a calcium silicate slag in an arc furnace. Johnston et al. [13] studied the effects of basicity and oxygen potential of Al_2O_3-CaO-MgO-SiO_2 and Al_2O_3-BaO-SiO_2 slags on removing boron and found that the removal efficiency of boron reached to 80%. Li et al. [14] reported that boron in MG-Si was successfully reduced from 15×10^{-6} to 2×10^{-6} using a ternary slag CaO-SiO_2-Al_2O_3 by an electromagnetic induction slag melting (EISM) method. In this paper, the mechanism of removing boron using molten slag based on CaO-SiO_2 system was studied and then the effects of slag composition and slag basicity on removing boron were primarily investigated by using an high basic slag refining technique in an induction heating method.

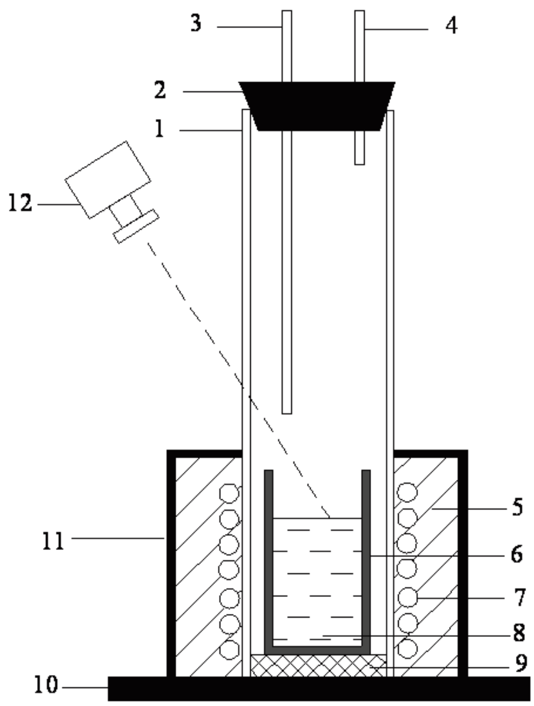
2. Experimental

The metallurgical grade silicon block with a boron concentration of 18×10^{-6} was pulverized into powder

* *Corresponding author: mwhsilicon@163.com*

DOI:10.2298/JMMB140202005W

with a particle size of 50-200µm. At the same time, the reagent grade chemicals of CaO, SiO_2, Li_2O and K_2O were prepared and the different composition of binary and ternary slag systems CaO-SiO_2, CaO-SiO_2-Li_2O and CaO-SiO_2-K_2O were obtained in advance for slag refining. The metallurgical grade silicon powder and the slags were respectively mixed with different ratio of slag to silicon. Then, the mixture was loaded to a graphite crucible, which was put into a quartz tube of the high frequency induction furnace. The quartz tube was blowed argon (Ar) for protection. The crucible was heated up for removing boron at 1600 °C for 2h. The experimental installation was shown in Figure 1. Lastly, the experiment was completed and the refined slag and silicon from cooled sample was drawn out for a chemical analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Elan-5000A USA).



1-quartz tube; 2-rubber stopper; 3-inlet pipe; 4-outlet pipe; 5-thermal barrier; 6-graphite crucible; 7-induction coil; 8-melt(silicon and slag); 9-Al_2O_3 cushion; 10-furnace foundation; 11-furnace shell; 12-infrared radiation thermometer

Figure 1. *Schematic diagram of experimental installation for molten slag refining*

3. Results and discussion

3.1. Distribution ratio of boron between calcium sillicate slag and silicon

The boron in silicon (expressed as [B]) can be oxidized into boric oxide by free oxygen ion and oxygen. The generated boric oxide will enter a basic slag phase based on calcium oxide in the form of negative ion BO_3^{3-} and a calcium borate phase is finally generated via the ionic Eq. (1).

$$[B] + 3/2O^{2-} + 3/4O_2 = (BO_3^{3-}) \quad (1)$$

The deboronization ability of calcium sillicate slag from MG-Si is usually expressed with the distribution coefficient of boron (L_B) defined as Eq. (2) [15].

$$L_B = w(B)/w[B] \quad (2)$$

Where $w_{[B]}$ and $w_{(B)}$ represent the equilibrium concentrations of boron in the refined silicon and the refined slag, respectively. In order to study the distribution ratio of boron between CaO-SiO_2 binary slag and refined silicon, the experiments of removing boron from MG-Si with different composition of CaO/SiO_2 were carried out at 1600 °C. The mass ratio of slag to MG-Si and the refining time were 1:1 and 3h, respectively. The boron concentrations in the refined silicon and the refined slag were then obtained. The distribution coefficient of boron are calculated and shown in Figure 2.

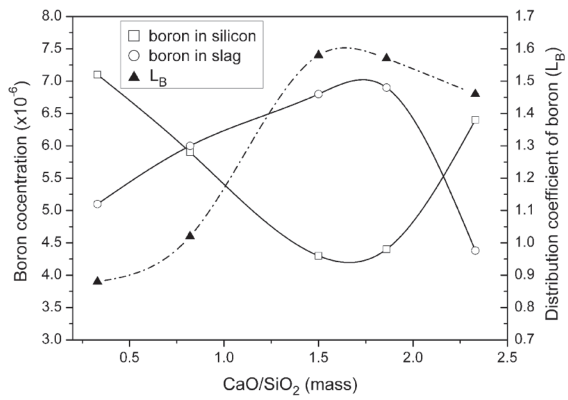


Figure 2. *Distribution coefficient of boron with different CaO/SiO_2 composition*

The concentration of boron in silicon reduces with the increase of the ratio of CaO in calcium sillicate slag and on the contrary it increases in slag. However, the variation trend of boron concentrations in silicon and slag are reversed when the mass ratio of CaO/SiO_2 is more than 1.5. It is found that the concentration of boron in refined silicon reduces to about 4×10^{-6} with 1.5 of CaO/SiO_2 mass ratio and it was also found from the distribution coefficient curve that the maximal value of L_B reaches to 1.57 with 1.5 of CaO/SiO_2 mass ratio. This shows that a satisfied result of removing boron from MG-Si is difficult using a calcium sillicate binary slag and the optimal composition is 60%CaO-40%SiO_2.

It is reported that the efficiency of removing boron can be improved by increasing the basicity of slag [13]. The basicity values of some oxides are listed in Table 1 and it is calculated that the optical basicity of $CaO-SiO_2$ binary slag is 0.71 according to Eq. (3).

$$\Lambda=(x_{CaO}\cdot\Lambda_{CaO}+2x_{SiO_2}\cdot\Lambda_{SiO_2})/(x_{CaO}+2x_{SiO_2}) \quad (3)$$

Where, Λ represents the basicity of molten slag. Λ_{CaO} and Λ_{SiO_2} are the optical basicities of oxides CaO and SiO_2. x_{CaO} and x_{SiO_2} are mole fractions of CaO and SiO_2 in slag, respectively.

Table 1. *Optical basicity parameters of some oxides (Λ) [16]*

Oxides	K_2O	Li_2O	CaO	SiO_2	B_2O_3
Λ	1.4	1	1	0.48	0.42

3.2. Effects of slag basicity on removing boron

In order to study the effect of slag basicity on removing boron, the basic oxides Li_2O and K_2O were added to a calcium sillicate with the compositon of $45\%CaO-55\%SiO_2$. The compositions of ternary refining slag systems are shown in Table 2.

The refining experiments were carried out in the induction furnace at 1600 °C with the amounts of Li_2O and K_2O in ternary slag varying from 2.5-20% and 3-40%, respectively. The mass ratio of ternary slag to MG-Si and the refining time were 1:1 and 2h, respectively. The basicities of ternary slags $CaO-SiO_2-Li_2O$ and $CaO-SiO_2-K_2O$ can be calculated as Eqs. (4) and (5).

$$\Lambda=\sum_{B=1}^{n} x'_B\Lambda_B \quad (4)$$

$$x'_B = n_O x_B / \sum_{B=1}^{n} n_O x_B \quad (5)$$

Where Λ_B represents the optical basicity of oxide B. x_B and x'_B are the mole fraction of oxide B and the mole fraction of oxygen ion in oxide B, respectively. n_O represents the amount of oxygen atom in the molecule of oxide B.

Figure 3 shows the variation trend of boron concentration in the refined silicon with 2.5-20% of Li_2O in the ternary refining slag $CaO-SiO_2-Li_2O$. It is calculated according to Eqs. (4) and (5) that the basicity of this ternary slag varies from 0.65 to 0.73. It is found that the boron concentration in the refined silicon reduces with the increase of Li_2O mass ratio in slag and it reaches to about 4.5×10^{-6} with 10% of Li_2O mass ratio. It shows that the addition of Li_2O increases the basicity of slag, which improves the deboronization ability of calcium sillicate slag. However, it is not helpful any more when it is higher than 10%. The boron concentration in the refined silicon increases again. It is concluded that the oxidizability of slag weakens with more basic oxides CaO and Li_2O and less acid oxide SiO_2 in slag. So the optimal composition of lithia slag for removing boron is $40.5\%CaO-49.5\%SiO_2-10\%Li_2O$, where the basicity of slag is 0.68.

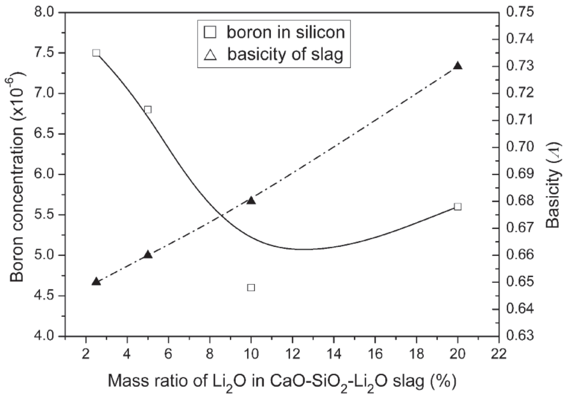


Figure 3. *Effects of Li_2O concentration in the ternary system $CaO-SiO_2-Li_2O$ on removing boron*

The oxidizability of molten slag may be expressed as Eq. (6).

$$3/4(SiO_2)+3/2(CaO)+[B]=3/4Si(l)+(Ca_{3/2}BO_3) \quad (6)$$

The molten silicon and slag are considered as a dilute solution. The equilibrium constant of Eq. (6) might be written as Eq. (7) on condition that the standard state for the Henry's law is chosen.

$$K_p=\frac{w(Ca_{3/2}BO_3)\cdot f_{(Ca_{3/2}BO_3)}\cdot a_{Si(l)}^{3/4}}{a_{(SiO_2)}^{3/4}\cdot a_{(CaO)}^{3/2}\cdot w[B]\cdot f_{[B]}} \quad (7)$$

Where $w(Ca_{3/2}BO_3)$ and $w[B]$ represent the concentration of calcium borate in slag and the concentration of boron in silicon, respectively. Parameters *a* and *f* are

Table 2. *Compositions of the ternary refining slags $CaO-SiO_2-Li_2O$ and $CaO-SiO_2-K_2O$ (mass%)*

Oxides	Compositon of refining slag									
	1	2	3	4	5	6	7	8	9	10
CaO	43.88	42.75	40.5	36	43.65	41.9	38.56	35.01	31.14	27
SiO_2	53.62	52.25	49.5	44	53.35	51.2	47.14	42.79	38.06	33
Li_2O	2.5	5	10	20	0	0	0	0	0	0
K_2O	0	0	0	0	3	6.9	14.3	22.2	30.8	40

the activity and the activity coefficient. For the Henry's law, it is considered as $f_{(Ca_{3/2}BO_3)} = f_{[B]} = 1$ and $a_{Si(l)} = 1$. The distribution coefficient of boron might be written as Eq. (8).

$$\log L_B = 3/4 \log a_{SiO_2} + 3/2 \log a_{CaO} + \log K_p - 1.04 \quad (8)$$

Obviously, it is helpful for removing boron using slag refining with a higher basicity. The oxide K_2O with a basicity value of 1.4 as listed in Table 1 was added to the calcium sillicate slag for removing boron. Figure 4 shows the variation of boron concentration in the refined silicon using different compositon of ternary slag $CaO-SiO_2-K_2O$. The mass ratio of K_2O in slag varies from 3% to 40% and the basicity of slag increases from 0.64 to 0.72. It is found that the efficiency of removing boron improves greatly. The boron concentration in silicon reduces from 3.87×10^{-6} to 1.4×10^{-6}. The efficiency of removing boron reaches to 92.2%. On the contrary however, it reduces again when the ratio of K_2O in slag exceeds 30% although the basicity of slag increases continuously. It is concluded that the oxidizability of slag is weakened with SiO_2 mass ratio of 37% in slag. So it is thought that the optimal composition for a potash slag is 32%CaO-38%SiO_2-30%K_2O for removing boron from MG-Si, where the basicity of slag is 0.7.

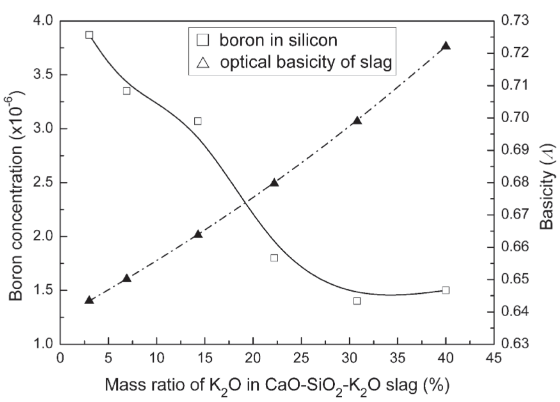


Figure 4. *Effects of K_2O concentration in the ternary system $CaO-SiO_2-Li_2O$ on removing boron*

4. Conclusions

1) The boron concentration in refined silicon is reduced with the increase of ratio for CaO in slag. The maximal distribution coefficient of boron between calcium sillicate slag and silicon is 1.57 when the mass ratio of CaO/SiO_2 is 1.5 and the composition is 60%CaO-40%SiO_2 with a basicity of 0.71.

2) It shows a positive act for the oxidizability of calcium sillicate slag with a higher slag basicity and it will weaken with a low mass ratio of SiO_2 in slag.

3) The additions of Li_2O and K_2O in calcium sillicate slag are helpful for removing boron. The boron concentration in silicon is reduced to 4.5×10^{-6} and 1.4×10^{-6}, respectively, using the slags of 40.5%CaO-49.5%SiO_2-10%Li_2O and 32CaO-38%SiO_2-30%K_2O. The basicities of slags are 0.68 and 0.7, respectively.

Acknowledgements

The authors wish to acknowledge the financial supporst on this research from the National Natural Science Foundation of China (51104080 and 51334002) and the Personnel Training Foundation of Kunming University of Science and Technology in China (14118557).

References

[1] J.T. Wang, X.D. Li, Y.M. He, N. Feng, X.Y. An, F. Teng, C.T. Gao, C.H. Zhao, Z.X. Zhang, E.Q. Xie, Sep. Purif. Technol., 102 (2013) 82-85.
[2] G. Coletti., P.C.P. Bronsveld, G. Hahn, W. Warta, D. Macdonald, B. Ceccaroli, K. Wambach, N.L. Quang, J.M. Fernandez, Adv. Funct. Mater., 21(5) (2011) 879-890.
[3] B.J. Jia, J.J. Wu, W.H. Ma, B. Yang, D.C. Liu, Y.N. Dai, J. Min. Metall. Sect. B-Metall. 49 (3) B (2013) 257-261.
[4] M.D. Johnston, L.T. Khajavi, M. Li, S. Sokhanvaran, M. Barati, JOM, 64 (8) (2012) 935-945.
[5] L.A.V. Teixeira, Y. Tokuda, T. Yoko, K. Morita, ISIJ Int., 49 (6) (2009) 777-782.
[6] W. Lee, W. Yoon, C. Park, J. Cryst. Growth, 312 (1) (2009) 146-148.
[7] K. Morita, T. Miki, Intermetallics, 11 (11-12) (2003) 1111-1117.
[8] M. Morishita, K. Koyama, A. Hatamoto, M. Morinaga, H. Adachi, Adv. Quantum Chem., 29 (1998) 285-296.
[9] M. Tanahashi, Y. Shinpo, T. Fujisawa, C. YAMAUCHI, J. Min. Mater. Process. Inst. Jpn., 118 (7) (2002) 497-505.
[10] M.D. Johnston, M. Barati, Sol. Energy Mater. Sol. Cells, 94 (12) (2010) 2085-2090.
[11] J.J. Wu, W.H. Ma, B.J. Jia, B. Yang, D.C. Liu, Y.N. Dai, J. Non-Cryst. Solids, 358 (23) (2012) 3079-3083.
[12] J. Dietl, Silicon Processing for Photovoltaics, Dordrecht, The Netherlands, 1988.
[13] M.D. Johnston, M. Barati, J. Non-Cryst. Solids, 357 (3) (2011) 970-975.
[14] D.W. Luo, N. Liu, Y.P. Lu, G.L. Zhang, T.J. Li, Trans. Nonferrous Met. Soc. China, 21 (5) (2011) 1178-1184.
[15] L.A.V. Teixeira, K. Morita, ISIJ Inter., 69 (6) (2009) 783-787.
[16] X.G.. Huang, Principle of steel and ferrous metallurgy, Beijing, 2000 (in chinese).