

BORON REMOVAL FROM METALLURGICAL GRADE SILICON USING A FeCl_2 MOLTEN SALT REFINING TECHNIQUE

B.J. Jia^{a,b}, J.J. Wu^{a,b,*}, W.H. Ma^{a,b}, B. Yang^a, D.C. Liu^a, Y.N. Dai^{a,b}

^a Kunming University of Science and Technology, The national Engineering Laboratory for vacuum metallurgy, Kunming, China

^b Kunming University of Science and Technology, Engineering Research Center for Silicon Metallurgy and Silicon Materials of Yunnan Provincial Universities, Kunming, China

(Received 23 August 2012; accepted 04 April 2013)

Abstract

The slag refining for boron removal from metallurgical grade silicon is a promising metallurgical process for producing solar grade silicon. In this paper, FeCl_2 molten salt has been used as a new refining agent to remove boron from MG-Si. The effects of refining time and mass ratio of MG-Si to FeCl_2 molten salt on boron removal have been investigated in detail. The results showed that boron can be efficiently removed in form of BCl_3 and boron concentration in MG-Si was successfully reduced from 22×10^{-6} to 4×10^{-6} at 1823K for 2 h with the mass ratio of FeCl_2 molten salt to MG-Si for 1.0. The rate equation of boron removal using FeCl_2 molten salt was proposed and established in kinetic, which showed a large difference in removal limitation of boron compared with thermodynamics.

Key words: Metallurgical grade silicon; Boron removal; Molten salt; Kinetics

1. Introduction

Solar energy is the most potential energy among all renewable resources and it has been attracting lots of attentions [1-2]. In 2011, the production of solar cells had reached 37.2GW all over the world and spectacularly it contained a share of about 60% for polycrystalline silicon solar cell. In spite of the Siemens process, the metallurgical route upgrading metallurgical grade silicon (MG-Si) to solar grade silicon (SoG-Si) has been developing in the worldwide as a result of low cost and friendly environment [3-5].

Boron is a crucial impurity in polycrystalline silicon solar cells and its concentration in silicon wafer will influence the photoelectric conversion efficiency and the stability of solar cells [6]. The metallic impurities such as Fe, Al, Ca, Ti et al can be easily removed from MG-Si by directional solidification technology due to their small segregation coefficients in silicon. However, it is impossible for boron removal for its large segregation coefficient ($k_0=0.8$) [7-10]. Furthermore, boron can not be removed by volatilization for its low saturated vapor pressure. It is only 10^{-6} Pa at 1773K [11-12]. At present, oxidizing refining is the main technology for boron removal from MG-Si. It includes some methods

such as thermal plasma treatments, gas blowing and slag refining. Several investigative groups [13-14] have developed the thermal plasma treatments for boron removal by a steam added plasma melting or a plasma torch blowing on the surface of MG-Si melt. Erlend et al [15] examined a moist hydrogen gas blowing method for boron removal from MG-Si. In previous studies [16-18], the slag refining technique based on CaO-SiO_2 slag system is used to examine boron removal.

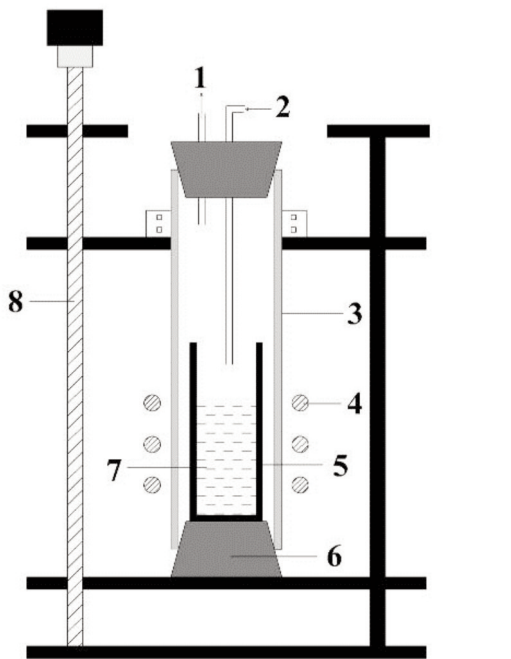
In this paper, boron removal was innovatively studied using a FeCl_2 molten salt technique. It was thought that the gaseous boron chloride species will be formed and volatilized from MG-Si. Then, the efficiency of boron removal was emphasized to examine under different experimental conditions. At last, the mechanism of boron removal from MG-Si using FeCl_2 molten salt was proposed and depicted in detail.

2. Experimental

The reagent grade FeCl_2 powder and MG-Si powder with boron concentration of 22×10^{-6} (mass%) were mixed with the mass ratio of FeCl_2 to Si for 0.5:1, 1:1, 2:1 and 3:1, respectively. The mixture was brought into a high purity graphite crucible with a size

* Corresponding author: dragon_wu213@126.com

of $\phi 50\text{mm} \times 120\text{mm}$. The crucible was then put into a quartz tube of an intermediate frequency inductive furnace. The argon of 99.9% purity (Vol.%) with a flow rate of 10 mL/s was blown into a quartz tube as shielding gas atmosphere. The schematic diagram of experimental apparatus was shown in Fig. 1. The raw materials were heated up to 1823 K with different ratios of FeCl_2 to Si and refining time. After refining, the boron concentration in refined silicon was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, American PerkinElmer Company, ELAN DRC II).



1-gas outlet; 2-gas inlet; 3-quartz tube; 4-induction coil; 5-graphite crucible; 6-rubber plug; 7-melt; 8-lifting gear

Figure 1. Schematic diagram of experimental apparatus

3. Results and discussion

Based on the thermodynamic handbook [19], boron in MG-Si melt will react with FeCl_2 , molten salt and the gaseous boron chloride species BCl , BCl_2 and BCl_3 will be generated. Unavoidably, the gaseous silicon chloride species SiCl , SiCl_2 , SiCl_3 and BCl_4 will also be generated, which causes the lost of Si. It is found that the gaseous species BCl_3 and SiCl_3 will be generated according to the standard Gibbs free energy of formation for species. Therefore, the main forms for boron removal and silicon lost are respectively BCl_3 and SiCl_3 in thermodynamic, when using FeCl_2 molten salt refining technique.

The photos of refined silicon using FeCl_2 molten salt are shown in Fig. 2. It is seen from Fig. 2(a) that the residual molten salt can be separated from silicon melt and covers on the surface of silicon. Fig. 2 (b) shows that the refined silicon is mainly situated in the central of graphite crucible and the molten salt is distributed in the inner wall of the crucible, which further illustrates that the silicon melt and the molten salt can be well separated after refining.

Fig. 3(a) shows the efficiency of boron removal at 1832K for 120min with different mass ratios of FeCl_2 to MG-Si. It is found that the efficiency of boron removal is remarkably improved when increasing the mass ratio of FeCl_2 to MG-Si. Boron concentration in silicon can be reduced from 22×10^{-6} to 4.0×10^{-6} and the removal efficiency reaches 82%. However, the trend becomes weaker when the ratio is greater than 1.0.

Fig. 3(b) shows the varying trend of boron removal at a mass ratio of FeCl_2 to MG-Si for 1.0 with different refining time. It is found that the boron concentration in refined silicon is obviously decreased by prolonging the refining time. However, the trend of boron removal decreases when the refining time is longer than 60min. It was likely to be caused by the decomposition and volatilization of FeCl_2 , which

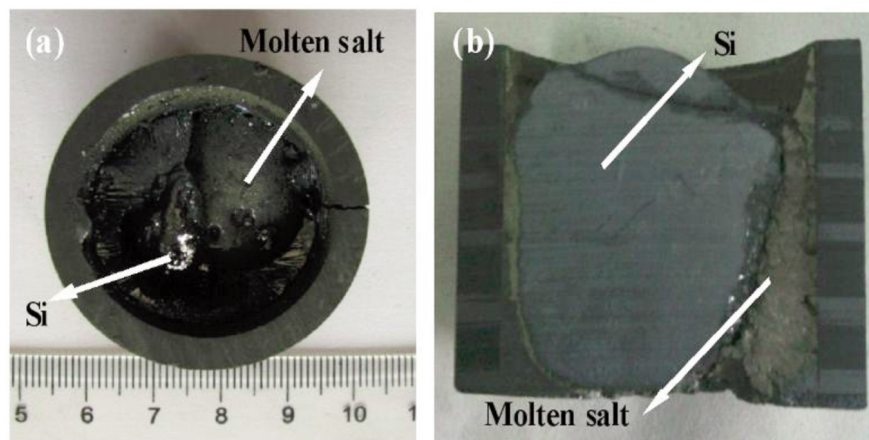


Figure 2. Photos of refined silicon ingot (a) cross section and (b) longitudinal section

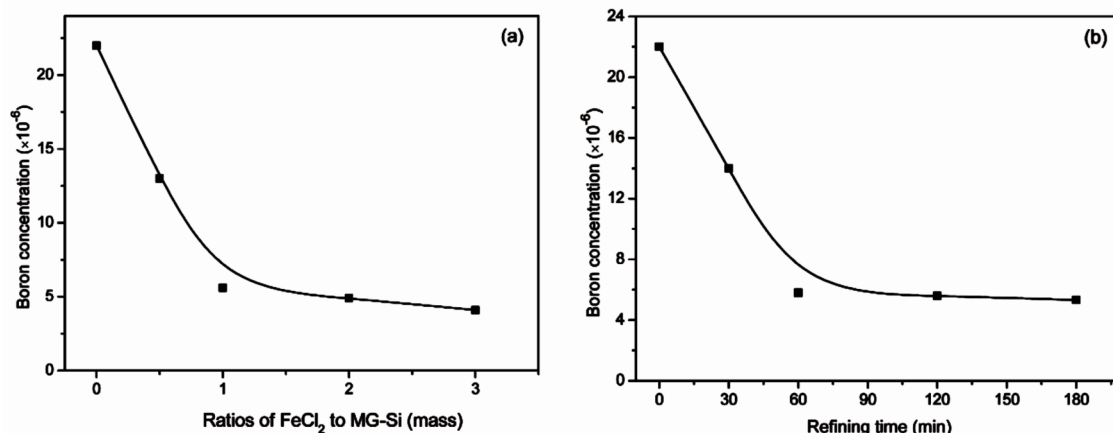


Figure 3. Boron concentration in refined silicon after FeCl₂ molten salt refining at 1823K (a) ratios of FeCl₂ to MG-Si for 2h and (b) different refining time

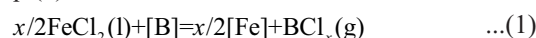
reduces the reaction between boron in silicon and FeCl₂ molten salt.

In order to clarify the effect of Fe left by FeCl₂ molten salt on refined silicon, a SEM-EDS analysis was carried out for refined silicon sample and shown in Fig. 4. It shows that the generated Fe exists in the boundary of silicon, where has no other impurity elements. Diet [20] found that the solubility of Fe in silicon is very low and its biggest solubility in silicon is 2.3×10⁻⁶ at 1673K. Moreover, Fe can be removed from refined silicon by some simple methods such as directional solidification, acid leaching and so on. Therefore, the effect of Fe left by FeCl₂ on silicon may be ignored.

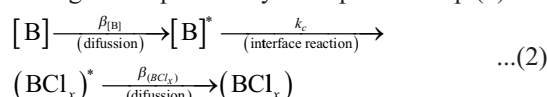
The varying trend of boron removal using FeCl₂ molten salt with different refining time can be explained in kinetic and the mechanism of boron removal from MG-Si can be expressed as Fig. 5.

The original concentrations of boron in MG-Si and FeCl₂ molten salt are assumed to be c_[B] and c_(FeCl₂), respectively. Then, they become c_[B] and c_(FeCl₂).

in the interface of molten salt and silicon melt owing to the diffusion, where the reaction between FeCl₂ molten salt and boron in silicon will occur and shown in Eq. (1).



where [B] represents the dissolved element boron in MG-Si and x represents 1, 2 or 3. In the interface, the concentrations of generated products BCl_x and [Fe] can be expressed as c_(BCl_x) and c_[Fe]. Owing to the concentration difference, BCl_x and [Fe] will transfer from interface to gaseous phase and from interface to silicon melt, respectively. Their concentrations are changed to c_(BCl_x) and c_[Fe]. The varying process of boron concentration from MG-Si phase to gaseous phase may be express as Eq. (2).



where β_[B] and β_(BCl_x) are the mass transfer coefficients of [B] in silicon melt and BCl_x in gaseous phase,

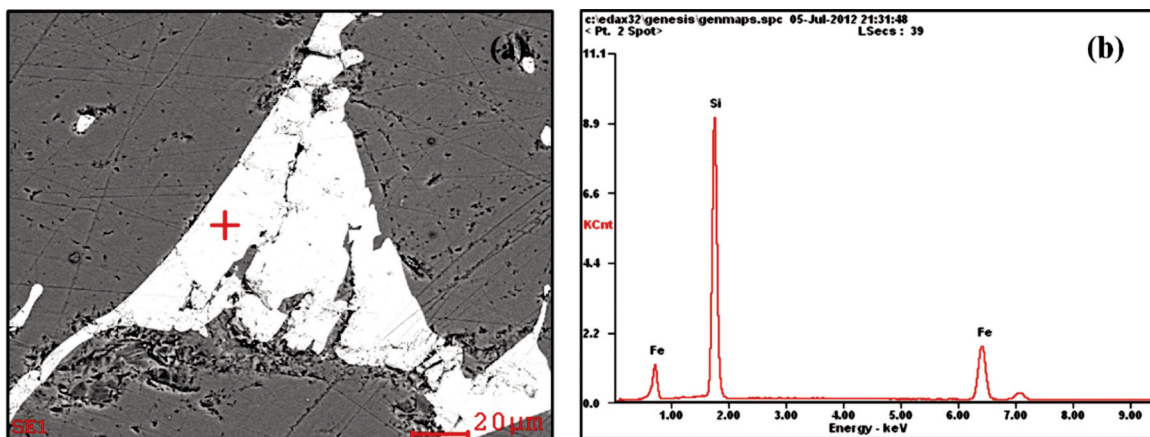


Figure 4. Scanning electron microscope and energy spectrum of refined silicon (a) SEM and (b) EDS

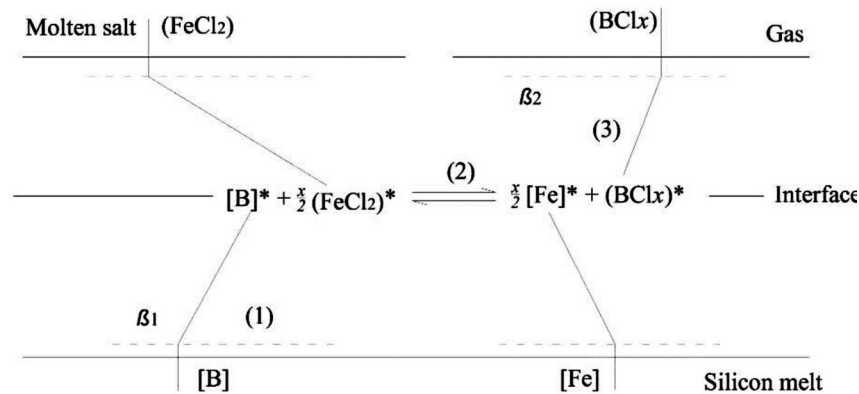


Figure 5. Schematic diagram of boron removal from MG-Si in kinetic using FeCl_2 molten salt

respectively. According to the double-film theory [21], the reactive rate of boron removal can be expressed as Eq. (3).

$$-\frac{dc_{[B]}}{dt} = \frac{c_{[B]} - c_{(\text{BCl}_x)} / K}{1/k_B + 1/(k_{\text{BCl}_x} \cdot K) + 1/k_c} \quad \dots(3)$$

where k_B , k_{BCl_x} and k_c are the rate content for diffusion and interface chemical reaction processes, respectively. $1/k_B$, $1/(k_{\text{BCl}_x} \cdot K)$ and $1/k_c$ are the resistances of transfer and interface chemical reaction of components, respectively. K is the equilibrium constant of Eq. (1). As we known, the rate of interface chemical reaction is much faster than that of diffusion at high temperature and it is concluded that the mass transfer of boron in silicon melt is the restrictive factors for boron removal using FeCl_2 molten salt. Therefore, $1/(k_{\text{BCl}_x} \cdot K)$ and $1/k_c$ may be ignored in Eq. (3), which is expressed as Eq. (4).

$$1/k_B \gg 1/(k_{\text{BCl}_x} \cdot K) + 1/k_c \quad \dots(4)$$

Therefore, the resistances of mass transfer for BCl_x and the interface chemical reaction can be ignored. Eq. (3) can be rewritten as Eq. (5).

$$-\frac{dc_{[B]}}{dt} = k_B (c_{[B]} - c_{(\text{BCl}_x)} / K) \quad \dots(5)$$

The relationships among $c_{(\text{BCl}_x)}^*$, $c_{(\text{BCl}_x)}$, $c[B]^*$ and K may be expressed as Eqs. (6)-(8).

$$c_{(\text{BCl}_x)}^* = c_{(\text{BCl}_x)} \quad \dots(6)$$

$$\frac{c(\text{BCl}_x)^*}{c[B]^*} = K \quad \dots(7)$$

$$\frac{c(\text{BCl}_x)}{K} = c[B]^* \quad \dots(8)$$

At last, Eq. (5) can be expressed as Eq. (9).

$$-\frac{dc[B]}{dt} = k_B (c[B] - c[B]^*) \quad \dots(9)$$

As shown in Eq. (9), it is easy to notice that the value of $(c[B] - c[B]^*)$ is commonly very small when

boron concentration in silicon is reduced to a trace amount by prolonging refining time. At this time, the reactive rate of boron removal is also very small. Therefore, boron removal is very difficult in kinetic when boron concentration in silicon is too low, which usually has large difference with removal limitation of boron calculated in thermodynamic.

5. Conclusions

(1) Boron concentration in silicon was significantly purified from 22×10^{-6} to 4×10^{-6} at 1832K for 2h using FeCl_2 molten salt refining technique and the removal efficiency of boron reaches 82%.

(2) The varying trend for boron removal from MG-Si using FeCl_2 molten salt is unobvious when the mass ratio of MG-Si to FeCl_2 molten salt is larger than 1.0 and the refining time is longer than 60 min.

(3) The rate of boron removal was studied in kinetic and the corresponding kinetic equation is proposed and established. Boron removal is difficult when boron concentration is reduced to a trace amount. The removal limitation of boron in kinetic exists large difference with thermodynamics.

Acknowledgements

The authors wish to acknowledge the financial support on this research from National Natural Science Foundation of China (51104080, u1137601) and the Personnel Training Foundation of Kunming University of Science and Technology in China (14118557).

References

- [1] T. Yoshikawa, K. Morita, Metall. Mater. Trans. B. 36 (2005) 731–736.
- [2] N. Yuge, K. Hanazawa and Y. Kato, Mater. Trans., JIM. 45(3)(2004) 850–857.
- [3] B.N. Mukashev, K.A. Abdullin, M.F. Tamendarov, T.S. Turmagambetov, B.A. Beketov, M.R. Page, D.M.

- Kline, *Sol. Energy Mater. Sol. Cells*. 93(2009) 1785-1791.
- [4] W. Peter, K. Wolfgang, *Sol. Energy Mater. Sol. Cells* 72 (2002) 11-26.
- [5] J.C.S. Pires, J. Otubo, A.F.B. Braga, P.R. Mei, *J. Mater. Process. Technol.* 169 (2005) 21-25.
- [6] J.J. Wu, W.H. Ma, B. Yang, Y.N. Dai, K. Morita, *Trans. Nonferrous Met. Soc. China*. 19(2) (2009) 463-467.
- [7] K. Morita, T. Miki, *Intermetallics*, 11(2003) 1111-1117.
- [8] Y.M. Gao, Y. Jiang, S. Huang, *J. Min. Metall. Sect. B-Metall*, 48 (1) B (2012) 25-36.
- [9] G. Flamant, V. Kurtcuoglu, J. Murray, A. Steinfeld, *Sol. Energy Mater. Sol. Cells*. 90(2006) 2099-2106.
- [10] L. A. V. Teixeira, K. Morita, *ISIJ Intern.* 49(6) (2009) 783-787.
- [11] T. Yoshikawa, K. Arimura, K. Morita, *Metall. Mater. Trans. B*. 36 (2005) 837-842.
- [12] B.X. Pei, H.B. Zhang, M.J. Cao, Y.M. Wang, Y.H. He, S.J. Li, *Special steel Technology*, 12(2006) 5-13. (in Chinese)
- [13] Y. Delannoy, C. Alemany, K.I. Li, P. Proulx, C. Trassy, *Sol. Energy Mater. Sol. Cells* 72 (2002) 69-75.
- [14] N. Nakamura, H. Baba, Y. Sakaguchi, Y. Kato, *Mater. Trans., JIM*. 45(3)(2004)858-864.
- [15] F.N. Erlend, T. Merete, *Metall. Mater. Trans. B*. 43(4)(2012) 814-822.
- [16] L. A. V. Teixeira, Y. Tokuda, T. Yoko, K. Morita, *ISIJ Intern.* 49(6) (2009) 777-782.
- [17] 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.
- [18] M.D. Johnston, M. Barati, *Sol. Energy Mater. Sol. Cells*, 94 (12) (2010) 2085-2090.
- [19] M.W. Chase, *NIST-JANAF thermochemical Tables*, 4th ed. American Chemical Society and the American Institute of Physics for the National Institute of standards and Technology, New York (1998) p. 221-1754.
- [20] J. Diet, *J. Solar Cells*, 10(1983) 145-154.
- [21] R. Zhu, C.L. Wan, G.H. Li, X.H. Wang, *J. Univ. Sci. Technol. B* 23(3) (2001) 208-211. (in Chinese)