Effects of Slag Treatment Conditions on Boron Removal from Metallurgical Silicon by United Gas-slag Refining Technology

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Abstract

Impurities in industrial silicon strongly affect the performance and use value of silicon products, so that raw industrial silicon must be refined to reduce the impurity content and improve its quality. In this work, the effect of the conditions of the refining process on the removal of impurities was studied. The slag agent and industrial silicon powder are uniformly mixed, and a mixed gas of Ar-H₂-O₂ is blown into the melt for refining experiments when the set refining temperature is reached. 3% mass fraction high-purity boron powder is pre-melted into industrial silicon raw materials to prepare Si-3%B alloy raw materials, and then the Si-3%B alloy raw materials are refined and pickled with CaO-SiO₂-CaCl₂. The composition of the slag agent, the slag-agent-to-silicon mass ratio, the refining time, and the refining temperature conditions were explored, and the best efficiency of boron removal was found to be 96.77%, with the boron content in silicon decreased from 22 ppmw to the lowest value of 0.6 ppmw. The boron content in refined silicon shows a clear decrease, demonstrating that slag-making gas blowing refining is effective for the removal of impurities in industrial silicon.

1. Introduction

With the continuous industrialization and economic development, the demand for industrial-grade silicon in metallurgy, chemical industry, electronics, energy development and other fields has grown rapidly. In particular, the ongoing energy crisis and environmental degradation have led to an increase in the demand for installed solar cell capacity. Solar cells currently account for more than 94% of the global photovoltaic market due to their low cost, high solar energy conversion efficiency and stability [1]. For many years, due to the weak technical strength of the organic chemical and polysilicon industries, the market demand is relatively small, and there has been little research on high-quality industrial silicon in China. Traditional production technology only addresses the reduction in the content of the Fe, Al, and Ca impurities in industrial silicon products. As clearly stated in the China Industrial Silicon GB/T2881-2014 standard for the contents of the boron and phosphorus impurities, the boron and phosphorus contents in high-quality industrial silicon are required to be less than 30 ppmw and 50 ppmw, respectively. This has motivated extensive interest in the purification of silicon and the identification of the optimal purification conditions [2], triggering in-depth research on the development of high-quality industrial silicon.

The refining technology used to produce high-quality industrial silicon involves air blowing refining [3], slag refining [4], solvent refining [5], bubble flotation [6], electromagnetic purification [7], vacuum melting [8], directional solidification [9] and many other techniques. Due to the large segregation coefficient of boron in silicon and its low saturation vapor pressure [10], it is difficult to effectively remove it through mature processes such as vacuum refining and directional solidification. By contrast, air blowing refining and slagging refining convert boron impurities into other substances through chemical reactions between boron and oxygen and other compounds, thereby effectively reducing the content of boron impurities. Nishimoto et al. [11] used 55% SiO₂-CaO to conduct refining experiments under 1823 K high-purity argon protection conditions. Their experimental results showed that the boron content was reduced from 360 ppmw to 80 ppmw, and the removal rate reached 77.8%, verifying the feasibility of slagging refining for

boron removal. Wu et al. [12] used 8 L/min compressed oxygen to purify metallurgical silicon by bottom blowing at 1873 K. The boron content was reduced from 35 ppmw to 18 ppmw, and the removal rate of Al and Ca impurities exceeded 90%, but the experiments also revealed problems such as the severe oxidation of the silicon substrate and large silicon loss. Solvent refining [13] and plasma refining [14] are two highly effective methods for the removal of boron impurities in industrial silicon, but their complicated refining process and high energy consumption hinder their application. Blowing refining [15,16] is a simple and inexpensive method for the removal of impurities such as Al, Ca, Ti, and B. The main methods of refining molten silicon outside the ladle furnace are slag refining and air blowing refining [17]. Among these, the slag used to remove impurities has higher solubility for impurities than molten silicon. The solubility of silicon in the slag must be low to minimize losses. In addition, the slag must be inert to molten silicon, and must be able to separate based on density differences. Slagging is usually carried out by treating molten silicon with $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$, CaO-SiO_2 , $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ at high temperature (approximately 1500°C). Boron and phosphorus are the most difficult elements to remove from silicon, so that a slag with strong alkaline and oxidizing properties is preferred [18]. In air blowing refining, industrial oxygen or compressed air is blown into the metallurgical silicon melt through the nozzle system at the bottom of the ladle, the impurities in the metallurgical silicon are converted into corresponding oxides, and the oxide film floating on the surface of the silicon melt is formed and then removed, improving the purity of the metallurgical silicon [19]. In a study performed at the Norwegian University of Science and Technology, Nordstrand et al. [20,21] used a hydrogen generator to blow $\text{H}_2\text{O-H}_2$ mixed gas into a vacuum induction furnace to improve boron removal. They found that the chemical reaction between the gas phase and elemental boron is the rate-limiting step in the process of boron removal from the silicon melt by blowing wet hydrogen. The boron removal rate depends on the partial pressure of hydrogen and water vapor in the gas phase, and the maximum boron removal rate is obtained under the conditions of mixed blowing of hydrogen and water vapor. The increase in the temperature leads to a lower boron removal rate that may be due to the thermodynamics of the H-B-O (HBO) gas [22]. By adding $\text{H}_2\text{-3.2\%H}_2\text{O}$, the boron content can be reduced from 90 ppmw to 1.0 ppmw.

Oxygen blowing refining is a widely popularized refining method. Most factories use oxygen and air mixed bottom blowing to refine silicon outside the furnace. In this work, the slag blowing method combined with pickling technology was used to refine industrial silicon. The slag agent and industrial silicon powder were placed in an agate mortar according to different slag-to-silicon mass ratios when the heating temperature reaches the set refining temperature, the blowing pipe was inserted into the melt, and the mixed $\text{Ar-H}_2\text{O-O}_2$ gas was blown into the furnace for refining and pickling experiments. The composition of the slag agent, the mass ratio of slag agent to silicon, refining time, refining temperature and acid leaching conditions were explored to obtain the highest efficiency for boron removal from industrial silicon.

2. Experimental

2.1 Experimental method

The experiment used industrial silicon with a purity of 99.5% produced by an industrial silicon manufacturer in Yunnan Province, China, with an impurity boron content of 22 ppmw. The reagents used in the fire refining experiment include high-purity boron powder, CaO, SiO₂, CaCl₂, argon, oxygen, and absolute ethanol. The wet acid leaching experiment used HCl and HF, and the reagents used were all of analytical grade. The equipment used in the experiment mainly includes a high-temperature gas converting furnace (16Q-YC), medium-frequency induction furnace, diamond wire cutting machine (SAMICK SK-25), and water steam generator (LDR3). Inductively coupled plasma atomic emission spectroscopy (ICP-AES, ELAN DRC), scanning electron microscopy (SEM, XL30E), and electron microprobe analyzer (EMPA, JXA-8230) instruments were used for the characterization of the samples.

The experimental process is illustrated in Figure 1. The industrial silicon block was ground to the size of 100-200 μm by ball milling and an electronic balance was used to weigh different masses of CaO, SiO₂ and CaCl₂ to obtain different chemical compositions. The slag agent and industrial silicon powder were placed in an agate mortar according to the different slag-to-silicon mass ratios, and the mixture was evenly mixed. The raw materials were placed into a 100 mL corundum crucible. The corundum crucible with the raw materials was placed into a larger magnesia crucible (the magnesia crucible can prevent the leakage of the silicon melt and spray material in the blowing refining process) and the larger crucible was placed in the high-temperature gas blowing furnace. A corundum tube with a length and inner diameter of approximately 80 cm and 1 cm was inserted from the top of the converting furnace to a position 2-3 cm above the surface of the raw corundum crucible. Then, the resistance furnace heating program was started. During the heating process, argon gas was passed from the bottom of the conversion furnace. When the heating temperature reached the set refining temperature, the blowing pipe was inserted into the melt and the Ar-H₂O-O₂ was blown into the furnace. The mixed gas was used in the refining experiments. After refining for a certain period of time, the mixed gas from the blowing pipe was stopped while Ar flow from the bottom of the blowing furnace was maintained until the temperature in the furnace decreased to room temperature.

We have investigated the effect of the mixed Ar-H₂O-O₂ composition on boron removal in our previous studies [23,24]. The optimal ratio of H₂O to O₂ was confirmed to be equal to 2, so that this chemical composition was adopted for all of the experiments in this work. The slag composition, slag-to-silicon mass ratio, refining time, refining temperature and acid leaching were varied in order to obtain the optimal efficiency of boron removal from MG-Si.

Table. 1

Effect of different slagging refining conditions on impurity removal

No.	Slag composition (CaO/SiO ₂ /CaCl ₂)	Mass ratio of slag to silicon	Refining time (h)	Temperature (K)
1	2/4/1	1/1	3	1823
2	2/2/1	1/1	3	1823
3	2/1.33/1	1/1	3	1773
4	2/1.33/1	1/1	3	1803
5	2/1.33/1	1/1	3	1823
6	2/1.33/1	1/1	3	1843
7	2/1/1	1/1	3	1823
8	2/0.8/1	1/1	3	1823
9	2/1.33/1	1/5	3	1823
10	2/1.33/1	1/2	3	1823
11	2/1.33/1	1/1.25	3	1823
12	2/1.33/1	1/0.77	3	1823
13	2/1.33/1	1/1	0.5	1823
14	2/1.33/1	1/1	1	1823
15	2/1.33/1	1/1	2	1823
16	2/1.33/1	1/1	3.5	1823

The refined sample was cut with a diamond wire cutter. The silicon obtained after high-temperature refining was crushed by ball-milling down to the size of 100 μm and then was leached with HCl-HF mixed acid at 343 K for 5 h. The leaching conditions are shown in Table 2. Finally, ICP-AES, SEM-EDS, and EPMA measurements were carried out to analyze high-temperature refined silicon and acid-leached silicon.

Table. 2

Leaching of refined silicon under different experimental conditions

Particle size of refined Si (μm)	Mixed acid (%)			Mass ratio of liquid to solid	Temperature (K)	Time (h)
	HF	HCl	H ₂ O			
100	10	10	80	6/1	343	5

Due to the extremely low concentration of the boron impurity in industrial silicon (only 22 ppmw), it is difficult to detect the occurrence of boron in silicon using physical analysis methods such as SEM and EPMA. To reveal the transformation process of the microscopic morphology of the boron impurity in the refining process, in this study, high-purity boron powder with a mass fraction of 3% was mixed into industrial silicon raw materials. According to the melting conditions shown in Table 3, industrial silicon powder and high-purity boron powder were pre-melted in an intermediate-frequency induction furnace to obtain Si-3%B alloy raw materials, and then the slag agent with a mass ratio of CaO/SiO₂/CaCl₂ of 2/1.33/1 was used to refine the Si-3%B alloy raw materials. The slag-to-silicon mass ratio, the refining time and the refining temperature were 1, 3 h and 1823 K, respectively. Then, the refined silicon sample was pickled according to the conditions in Table 2.

Table. 3

Pre-melting conditions of Si-3%B alloy

MG-Si powder (g)	Boron powder (g)	Premelting atmosphere	Temperature (K)	time (h)
97	3	Ar	1823	3

2.2 Refining mechanism

Slag refining is the addition of a slag-making agent that has a strong affinity to the impurities in silicon and reacts with the impurities to form stable compounds in the silicon melt. In iron and steel smelting, the CaO-SiO₂-CaX (where X is a halogen element) slag system is widely used. Industrial silicon smelting and steel smelting have many similarities. CaO-SiO₂-CaCl₂ can not only oxidize non-metallic impurities to form calcium borate CaO·B₂O₃ in the slag phase, but also generates BOCl and other gas borides for volatilization and removal.

As shown in Figure 2, the Ar-H₂O-O₂ mixed gas is blown into the industrial silicon melt for refining, and Ar gas stirs the melt. This increases the collision probability of the inclusion particles in the silicon liquid, promotes their polymerization and growth, increases the floating speed of the inclusions in the silicon liquid, and makes the inclusions adhere to the surface of the argon bubble. When the bubbles rise, the inclusions are removed from the liquid silicon to achieve the removal of the inclusions. The H₂O and O₂ in the mixed gas oxidize the impurity boron forming boron oxide B_xO_y and boron hydroxide H_zB_xO_y, respectively [23]. The results of thermodynamic calculations show that HBO and SiO are the main volatile substances of boron and silicon, respectively. Secondary volatile species include HBO₂, BH_x (x = 1 to 3) and SiH_y (y = 1 to 3) [25]. Under alkaline conditions, H₂O can decompose into H and OH which is conducive to the formation of gaseous boride HBO through the reaction of boron and OH and the removal

of boron. A previous study showed that the best boron removal effect of 96.77%, and the lowest impurity boron content of 0.71 ppmw are obtained for the H₂O/O₂ volume ratio of 2 [24].

The study conducted by the Norwegian University of Science and Technology concluded that increased water vapor amount will lead to the loss of silicon. In addition to oxidation by oxygen, some of the silicon will also be oxidized by the H₂O vapor to form SiO. The newly formed SiO will be further oxidized to form a passivation layer of SiO₂ that hinders the boron removal reaction. This process is described by Eqs. (1)-(3).

3. Results And Discussion

3.1 Impurity morphology in silicon after refining

(1) MG-Si after slag treatment and acid leaching without doped boron

First, the industrial silicon raw material was mixed with the CaO-SiO₂-CaCl₂ slag agent at a mass ratio of 2/1.33/1 according to the slag to silicon ratio of 1/1. The mixture was refined at 1823 K for 3 h, and then the refined silicon sample was pickled at the process conditions specified in Table 2. Finally, the obtained silicon ingot was sliced, polished, and subjected to SEM-EDS microscopic morphology analysis. The microstructures of the samples are shown in Fig. 3.

Figure 3(a) shows the microstructure of the original silicon sample and Figure 3(b) shows the microstructure of the sample after slagging and refining. It is observed that the sample shown in Fig. 3(b) has less impurities than the original silicon sample presented in Figure 3(a), but many bright white impurity phases enriched in the main Si phase are still observed. Fig. 3(c) shows the microstructure of the sample after pickling. Comparison of Fig. 3(c) to Figs. 3(a) and (b) shows that essentially all of the bright white impurities have been removed, and the main body shows the Si phase, demonstrating that the pickling affects industrial silicon to effectively remove the metal impurities.

(2) Silicon doped with 3%B after slag treatment and acid leaching

The Si-3%B alloy doped with boron was processed by the slag treatment and then by pickling. In the slag treatment process, the mass ratio of the $\text{CaO}/\text{SiO}_2/\text{CaCl}_2$ slag agent, the refining time, the slag-to-silicon mass ratio and the refining temperature were 2/1.33/1, 3 h, 1, and 1823 K, respectively, and the pickling process was carried out according to the conditions specified in Table. 2. Figure 4 shows the microstructure of the polished and refined silicon samples.

Comparison of the samples with and with 3% B doping presented in Figures 4(a) and (b), respectively, shows that a large number of black boron particles appear in the industrial silicon doped with boron. Moreover, the sizes of the boron particles of the two samples are also different. The distribution of boron particles is irregular, and most of boron is enriched in the main silicon matrix, while some boron is enriched with metal impurities. Figure 4(c) shows the sample after slag refining, and the comparison of this figure to Fig. 4(b) shows that the boron impurity removal effect was quite good, with only a few boron particles remaining in the Si matrix and the inclusion phase, and the refined silicon is still enriched with a large amount of the metal impurity phase. Figure 4(d) shows the sample after the subsequent pickling of the refined silicon from the slag. It is observed that the boron impurities are essentially completely removed, and the amount of the impurity phase is also greatly reduced, with the sample consisting mostly of the main silicon phase.

To more clearly observe the occurrence form of the impurity boron in silicon, the boron-doped silicon, directly pickled boron-doped silicon, boron-doped silicon after slagging refining, and borosilicate after slagging and pickling were analyzed by EPMA morphology analysis, by EDS scanning analysis of the impurity area in the images, with the results shown in Fig. 5.

It is observed from Fig. 5(a) that the black area is mainly the Si-B phase, in which a small amount of the Ca metal impurity is dissolved. The dark white inclusions are mainly the Si-Fe-Al phase, which is the enrichment area of the metal impurities in industrial silicon. Fig. 5(b) shows that a large amount of Ca appears in the impurity phase after slagging and refining. This is due to the use of the $\text{CaO}-\text{SiO}_2-\text{CaCl}_2$ slag agent that increases the impurity calcium content in silicon after refining. The calcium acid slag agent has no effect on the removal of the Fe impurities, and an examination of the distribution diagram shows that the amount of boron impurity in silicon after refining is greatly reduced, and boron is mainly enriched with metal impurities in the Si-B-Ca and Si-B-Ti-Fe phases. Comparison of the sample obtained after slagging, refining and pickling presented in Fig. 5(d) to the sample obtained after slagging and refining presented in Fig. 5(b) shows that the boron-containing compounds have completely disappeared. This indicates that the removal of boron is quite thorough, and the amount of metal impurities is further reduced. A small amount of the Si-Al-Cu phase is observed because the impurity Cu in silicon is difficult to remove by pickling with the HCl-HF solution.

3.2 Slag treatment conditions of combined refining

(1) Effect of chemical composition of CaO/SiO₂ on boron removal

In these experiments, the CaO/CaCl₂ mass ratio during the refining process of the slag agent was maintained at 2, the refining time was 3 h, the slag-silicon mass ratio was 1, and the refining temperature was 1823 K. The influence of the CaO/SiO₂ in the slag agent on the removal of impurity boron was examined and the experimental results are shown in Fig. 6.

Fig. 6(a) shows that CaO/SiO₂ has a strong impact on the removal of the boron impurity in industrial silicon. With the increased addition of SiO₂, the boron removal effect is significantly improved, and the boron content in refined silicon reaches the lowest value of 1.37 ppmw for the CaO/SiO₂ mass ratio of 1.5, with the boron removal efficiency boron reaching 93.77%. The boron removal efficiency then decreases with the further increase in the proportion of SiO₂. This is mainly because the increase in the SiO₂ amount will reduce the amount of CaO in the calcium silicate slag agent. The impurity boron removal is affected by the basicity of the slag and the oxygen potential. When the amount of SiO₂ is too high, the O²⁻ and impurity boron are reduced, reducing the reaction rate and the boron removal effect. It is observed from Fig. 6(b) that the distribution coefficient of impurity boron first increases and then decreases. For the CaO/SiO₂ ratio of 1.5, the LB distribution coefficient of boron reaches the maximum value of 6.7. The further increase in the CaO/SiO₂ value results in increasing SiO₂ and reduced activity. As the activity decreases, the boron removal effect also decreases, inevitably leading to a decrease in the LB value. Therefore, the highest boron removal effect is obtained for the CaO-SiO₂-CaCl₂ ternary slag with the CaO/SiO₂/CaCl₂ ratio of 2/1.33/1.

(2) Effect of the slag-to-silicon ratio on boron removal

In these experiments, the CaO/SiO₂ mass ratio in slag refining was maintained at 1.5, the refining time was 3 h, and the refining temperature was 1823 K, and the effect of the slag-to-silicon mass ratio on the removal of boron was studied. The results are shown in Fig. 7.

It is observed from Fig. 7 that as the slag-to-silicon mass ratio increases, the impurity boron concentration gradually decreases. The best boron removal effectiveness of 93.77% was obtained for the slag-to-silicon mass ratio of 1, while a further increase in the amount of slag agent and refine led to the increase in the boron content in silicon to 1.54 ppmw. This shows that when the mass ratio of slag to silicon exceeds a certain limit, the increase in the slag amount is no longer conducive to boron removal. When the slag-to-silicon ratio is too low, the reaction between the slag and silicon is insufficient, leading to decreased boron removal efficiency. According to Fang et al. [26], silicon loss can be explained by two possible mechanisms: silicon may volatilize into the atmosphere at high temperatures, or it may react with SiO₂ during slag refining.

(3) Effect of refining time on boron removal

In these experiments, we varied the refining time in the 0.5-3.5 h range and its effect on the removal of the boron impurity in industrial silicon. Here, the mass ratio of CaO/SiO_2 , the slag-to-silicon mass ratio and the refining temperature were 1.5, 1, and 1823 K, respectively. The results are shown in Fig. 8.

It is observed from Fig. 8 that with the extension of the refining time, the boron content in the silicon was significantly reduced, and the boron removal effect was significantly improved. When the refining time was increased from 0.5 h to 3 h, the boron content in metallurgical silicon was reduced from 22 ppmw in the original sample to 10.74 ppmw and 1.37 ppmw, respectively. When the refining time was extended to 3.5 h, the boron content in the refined silicon was essentially unchanged. The extension of the refining time ensures the full contact of the slagging agent with the impurity boron in silicon, so that the boron is oxidized and removed more thoroughly. When the refining time exceeds a certain range, the contents of boron in the silicon phase and the slag phase reach equilibrium. Considering the cost of refining, the optimal refining time was selected as 3 h.

(4) Effect of refining temperature on boron removal

In these experiments, we varied the refining temperature in the range of 1773-1843 K, and studied the effect of the melt temperature on the removal of the boron impurity in industrial silicon. Here, the composition of $\text{CaO-SiO}_2\text{-CaCl}_2$ slag agent, the slag-to-silicon mass ratio, and refining time were 2/1.33/1, 1/1, and 3 h, respectively. The results are shown in Fig. 9.

It is observed from Fig. 9 that increasing the refining temperature will gradually reduce the content of the boron impurity in silicon. Between 1773 and 1803 K, the boron content in silicon after refining is relatively high. This is because the refining temperature is too low and the refining slag is not completely melted, resulting in the poor fluidity of the slag and limiting the reaction between the slag and silicon. When the temperature reaches 1823 K, the boron content in the refined silicon shows a significant decrease, and the boron content in silicon decreases from 1.4 ppmw to 0.71 ppmw. Between 1823 and 1843 K, the rate of decrease in the boron content in refined silicon with increasing temperature slowed down as the boron content decreased from 0.71 ppmw at 1823 K to 0.6 ppmw at 1843 K. These results show that a higher temperature leads to the greater fluidity of the slag and silicon that enables improved contact between the slag and silicon; then the increased rate of the reaction between the slag and silicon promotes the conversion of impurity boron. The optimal refining temperature was identified in this study as 1823 K.

4. Conclusions

Industrial silicon with a purity of 99.5% and an impurity boron content of 22 ppmw was used as the raw material and then underwent slag refining, air blowing refining and pickling to remove the impurity boron. It was found that the microscopic morphology of boron impurity in the refining process undergoes a

significant transformation. The optimal conditions were identified as the $\text{CaO-SiO}_2\text{-CaCl}_2$ ternary slag ratio of 2/1.33/1, the slag-to-silicon mass ratio of 1/1, the refining time of 3 h, the refining temperature of 1823 K, the $\text{HF-HCl-H}_2\text{O}$ ratio of 1/1/8 and the volume ratio of $\text{H}_2\text{O-O}_2$ of 2. For these conditions, the optimal boron removal of 96.77% is achieved, and the impurity boron content reaches the lowest value of 0.71 ppmw. With regard to temperature variation, it was found that when the temperature is increased from 1803K to 1823 K, the boron content in silicon decreases from 1.4 ppmw to 0.71 ppmw. Between 1823 and 1843 K, the boron content decreased from 0.71 ppmw at 1823 K to 0.6 ppmw at 1843 K. These results show that the slagging refining gas blowing combined with the pickling process has a strong and positive removal effect on impurities in industrial silicon.

Declarations

Author contributions

Ji-jun Wu conceived the study, coordinated the conduct of the study; Qi-liang Wang participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript; Shuang-feng Qian participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript; Hua-zhen Gu participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript; Zhen-fei Xia participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript; Kui-xian Wei participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript; Wen-hui Ma participated in the design of the study, assisted in interpreting the data, and helped to draft the manuscript;

Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Availability of data and material

All data and software application support their published claims and comply with field standards.

Compliance with ethical standards

This study and all procedures performed involving human participants were in accordance with the ethical standards.

Consent to participate

All authors consent to participate to this publication.

Consent for Publication

All authors consent to the publication of the manuscript in SILICON, should the article be accepted by the Editor-in-chief upon completion of the refereeing process.

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References

1. CHEN H, YUAN X Z, KAZUKI M, ZHONG Y J, MA X D, CHEN Z Y, WANG Y (2019) Reaction mechanism and kinetics of boron removal from molten silicon via $\text{CaO-SiO}_2\text{-CaCl}_2$ slag treatment and ammonia injection [J]. *Metallurgical and Materials Transactions B*, 50(10): 2088-2094.
2. LU H F, WEI K X, MA W H, XIE K Q, WU J J, LEI Y (2017) The Effect of secondary refining on the removal of phosphorus from metallurgical-grade silicon by acid leaching [J], *Metallurgical and Materials Transactions B*, 48: 2768-2780.
3. XIA Z F, WU J J, MA W H, LEI Y, WEI K X, DAI Y N (2017) Separation of boron from metallurgical grade silicon by a synthetic CaO-CaCl_2 slag treatment and $\text{Ar-H}_2\text{O-O}_2$ gas blowing refining technique [J]. *Separation and Purification Technology*, 187(31): 25-33.
4. ZHOU Q, WU J J, MA W H, CHEN Z J, LEI Y, WEI K X (2020) Boron removal from industrial silicon by combined slagging and acid leaching treatment technology [J]. *JOM*, 72(7): 2670-2675.
5. CHEN K, CHEN X H, LEI Y, MA W H, HAN J Y, YANG Z H (2018) Mechanism of enhancing B removal from Si with V addition using Al-Si as the refining solvent [J]. *Separation and Purification Technology*, 203(12): 168-177.
6. DONG A, ZHANG L F, DAMOAH L (2011) Beneficial and technological analysis for the recycling of solar grade silicon wastes [J]. *JOM*, 63(1): 23-27.
7. WANG S Q, ZHANG L F, YANG S F (2012) Electromagnetic separation of nonmetallic inclusions from liquid steel by high frequency magnetic field [J]. *Journal of Iron and Steel Research*, 10(S2): 866-878.
8. HOSEINPUR A, TANG K, SAFARIAN J (2020) Kinetic study of vacuum evaporation of elements from ternary melts; case of dilute solution of P in Si-Al melts [J]. *Separation and Purification Technology*, 235: 116284
9. GAN C H, XIONG H P, FANG M, QIU S, XING P F, LUO X T (2016) Natural sedimentation of insoluble particles during directional solidification of upgraded metallurgical-grade silicon [J]. *Journal of Crystal Growth*, 439(1): 74-79.

10. WANG Z, GE Z, LIU J H, QIAN G Y, DU B (2018) The mechanism of boron removal from silicon alloy by electric field using slag treatment [J]. Separation and Purification Technology, 199(30): 134-139.
11. NISHIMOTO H, [KANG Y](#), YOSHIKAWA T, MORITA K (2011) The rate of boron removal from molten silicon by CaO-SiO₂ slag and Cl₂ treatment [J]. Materials Processing and Energy Materials, 31(4): 471-477.
12. WU J J, MA W H, LI Y L, YANG B, LIU D C, DAI Y N (2013) Thermodynamic behavior and morphology of impurities in metallurgical grade silicon in process of O₂ blowing [J]. Transactions of Nonferrous Metals Society of China, 23(1): 260-265.
13. LEI Y, MA W, SUN L (2016) B Removal by Zr addition in electromagnetic solidification refinement of si with Si-Al melt [J]. Metallurgical and Materials Transactions B, 47(1): 27-31.
14. SOUSA M D, VARDELLE A, MARIAUX G, VARDELLE M, BEUDIN V (2016) Use of a thermal plasma process to recycle silicon kerf loss to solar-grade silicon feedstock [J]. Separation and Purification Technology, 161: 187-192.
15. WU J, LI Y, MA W (2013) Impurities removal from metallurgical grade silicon using gas blowing refining techniques [J]. Silicon, 6(1): 79-85.
16. SORTLAND O S, TANGSTAD M (2014) Boron removal from silicon melts by H₂O/H₂ gas blowing: mass transfer in gas and melt [J]. Metallurgical and Materials Transactions E, 1(3): 211-225.
17. LI F, [XING P F](#), [LI D G](#), [ZHUANG Y X](#), [TU G F](#) (2013) Removal of phosphorus from metallurgical grade silicon by Ar-H₂O gas mixtures [J]. Transactions of Nonferrous Metals Society of China, 23(11):3470-3475.
18. CHIGONDO F (2017) From metallurgical-grade to solar-grade silicon: an overview [J]. Silicon, 10(3): 789-798.
19. LUO D W, LIU N, LU Y P, ZHANG G L, LI T J (2011) Removal of boron from metallurgical grade silicon by electromagnetic induction slag melting [J]. Transactions of Nonferrous Metals Society of China, 21(5): 1178-1184.
20. NORDSTRAND E F, TANGSTAD M (2012) Removal of boron from silicon by moist hydrogen gas [J]. Metallurgical and Materials Transactions B, 43(4): 814-822.
21. SORTLAND O S, TANGSTAD M (2014) Boron removal from silicon melts by H₂O/H₂ gas blowing: mass transfer in gas and melt [J]. Metallurgical and Materials Transactions E, 1(3): 211-225.
22. CHEN Z Y, MORITA K (2018) Kinetic modeling of a silicon refining process in a moist hydrogen atmosphere [J]. Metallurgical and Materials Transactions B, 49(3): 1205-1212.
23. WU J J, MA W H, YANG B (2009) Boron removal from metallurgical grade silicon by oxidizing refining [J]. Transactions of Nonferrous Metals Society of China, 19(2): 463-467.
24. WU J J, LI Y L, MA W H, LIU K, WEI K X, XIE K Q, YANG B, DAI Y N (2014) Impurities removal from metallurgical grade silicon using gas blowing refining techniques [J]. Silicon, 6(1): 79-85.
25. CHEN Z Y, MORITA K (2018) Kinetic modeling of a silicon refining process in a moist hydrogen atmosphere [J]. Metallurgical and Materials Transactions B, 49(3): 1-8.

26. WANG Y, MORUTA K (2016) Measurement of the phase diagram of the $\text{SiO}_2\text{-CaCl}_2$ system and liquid area study of the $\text{SiO}_2\text{-CaO-CaCl}_2$ system [J]. Metallurgical and Materials Transactions B, 47(3): 1542-1547.

Figures

Figure 1

Flow chart of MG-Si refining by united refining technology

Figure 2

Schematic diagram of MG-Si by united refining technology

Figure 3

SEM images of samples (a) Raw material of MG-Si; (b) MG-Si after slag treatment; (c) MG-Si after slag treatment and acid leaching

Figure 4

SEM images of silicon samples (a) MG-Si raw material; (b) Si-3%B alloy; (c) Si-3%B alloy after slag treatment; (d) Si-3%B alloy after slag treatment and acid leaching

Figure 5

EPMA and EDS images of samples (a) Si-3%B alloy; (b) Si-3%B alloy after slag treatment; (c) Si-3%B alloy after slag treatment and acid leaching

Figure 6

Effect of CaO/SiO₂ on boron removal (a) Concentration and removal efficiency of boron in refined silicon; (b) Relationship between L_B and CaO/SiO₂ with different slag composition

Figure 7

Concentration and removal efficiency of boron in refined silicon with different mass ratio of slag to silicon

Figure 8

Concentration and removal efficiency of boron in refined silicon with different refining time

Figure 9

Final concentration of boron with different refining temperature