



Removal of impurities from metallurgical grade silicon by addition of ZnO to calcium silicate slag



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ABSTRACT

Slag refining is one of the most effective methods to remove impurities from metallurgical grade silicon. In this paper, ZnO was added to a binary 50% CaO–50% SiO₂ slag system with a mass ratio of 2–30% to study the impurities removal from metallurgical grade silicon. The results showed that boron was reduced from 12.94 ppmw to 2.18 ppmw by a 46% CaO–46% SiO₂–8% ZnO slag system. Compared to the 50% CaO–50% SiO₂ slag system, slag refining with ZnO addition showed a 20% increase in removal efficiency and a 40% increase in the distribution coefficient. After acid leaching, boron was further reduced to 1.52 ppmw with a removal efficiency of 88.25%. By a combined process of slag refining and acid leaching, impurities Al and Fe were reduced from 817 ppmw and 3800 ppmw to 1.2 ppmw and 96 ppmw with removal efficiencies of 99.8% and 97.5%, respectively. The evaporation loss of the generated metallic zinc during slag refining was greater than 99.7%. After acid leaching, the minimum zinc content in silicon was only 4 ppmw.

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1. Introduction

With the persistent increase in global economy demand, solar photovoltaic (PV) power generation has rapidly developed as part of the new energy industry. Solar grade silicon (SoG-Si) is the main raw material used for the fabrication of solar cells. Technologies such as the improved Siemens method, fluidized bed method and the thermal decomposition of silane are traditionally used for the production of solar grade silicon. However, high cost and environmental load have seriously hampered the development of polysilicon industry. In recent years, a metallurgical route with low cost, low energy consumption and more environmentally friendly has become the primary process for the production of solar grade polysilicon. The challenge of this metallurgical route is the effective removal of boron, phosphorus, and other impurities in metallurgical grade silicon (MG-Si).

Solar grade silicon requires a final boron concentration of less than 0.3 ppmw in silicon chip because boron will reduce the minority carrier lifetime, and thus affect the conversion efficiency of solar cell [1]. Since boron has a large segregation coefficient and low saturated vapor pressure, it is unable to be removed effectively by the conventional directional solidification and the vacuum refining techniques [2,3]. Solvent refining [4–6] and plasma technology [7–9] are two effective methods for the removal of boron and other impurities, but the complicated process and the expensive cost limit their industrial application. Gas refining [10,11] is a simple and inexpensive method to remove aluminum, calcium, titanium and boron. However, the gas refining technology for boron removal is still rarely used.

Slag refining is an effective method to remove impurities from MG-Si. The active oxygen supplied by slag can oxidize boron and the generated boron oxide (B₂O₃) is then absorbed by the slag. In this way, impurity boron can be removed from MG-Si by the separation of metal silicon and molten slag. Binary CaO–SiO₂ slag [12] is a basic slag system for boron removal. Teixeira et al. [13] studied the variation of distribution coefficient of boron in a basicity range of 0.55–1.21. Morita and Miki [14] studied the activity of (BO₃)³⁻ ions in the slag, and determined the relationship of boron capacity and slag basicity. Cai et al. [15–17] studied boron removal using a ternary CaO–SiO₂–CaF₂ slag system and found

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the distribution coefficient can reach 4.61. Luo et al. [18] studied the addition of Al_2O_3 to the binary CaO-SiO_2 slag system, and observed a boron decrease from 15 ppmw to 2 ppmw in MG-Si. Wu et al. [19–21] found the form of boron removal was the basic $\text{K}_2\text{O-4B}_2\text{O}_3$ when the basic oxide reagent K_2O was added to the binary CaO-SiO_2 slag system. It was also reported that the addition of Li_2O and K_2O could significantly improve the basicity of slag and increase the absorption capacity of slag for borates. Boron was reduced from 22 ppmw to 1.3 ppmw. Safarian et al. [22,23] studied the boron removal mechanism of the $\text{Na}_2\text{O-CaO-SiO}_2$ slag system and found that boron was removed in the form of the volatile $\text{Na}_2\text{-B}_2\text{O}_4$. In addition, the slags for boron removal were composed of $\text{CaO-SiO}_2\text{-MgO}$, $\text{CaO-SiO}_2\text{-CaCl}_2$, $\text{CaO-SiO}_2\text{-BaO}$ and other type slags [24–27]. Diet [28] used CaSiO_3 slag to refine MG-Si and found that the concentrations of impurities Al and B were reduced to 40 ppmw and 1 ppmw, respectively.

In this paper, we studied slag refining for impurities removal from MG-Si by adding different amounts of ZnO to the binary CaO-SiO_2 slag system. The addition of ZnO acts to reduce the melting point of CaO-SiO_2 slag and enhance the fluidity of slag. Zinc vapor generated by the reaction can agitate melt and improve the touch between molten slag and the impurities. Both ZnO and SiO_2 can react with boron and allow removal of boron in two ways. Slag agent ZnO is better able to react with impurities of Al and Fe compared to SiO_2 and allows increased removal of Al and Fe.

2. Experimental

We used MG-Si containing 12.94 ppmw boron from Yunnan province as the raw material as shown in Table 1. Mass fractions of 2%, 5%, 8%, 10%, 20%, 25%, or 30% of ZnO were individually added to 50% CaO-50% SiO_2 binary slag samples. The slag agents CaO, SiO_2 , and ZnO were of analytical grade. The experiments used 30 g silicon and 30 g slag agents. The refining temperature was kept at 1823 K, the refining time was 1 h, and the experimental conditions were as shown in Table 2.

The slag refining experiments were carried out in a medium frequency induction furnace as shown in Fig. 1. A high-purity graphite crucible of 140 mm height, 36 mm outside diameter, and 28 mm inside diameter was used as the reactor for slag refining. The crucible was located in the center of the induction coil on the bricks. During all experiments, a high-purity (99.9%) argon gas was blown into the quartz tube. The experimental temperature was raised slowly by adjusting the induced current and an infrared thermometer was used to measure the temperature. After a refining

time of 1 h, the induced current was reduced slowly to cool the graphite crucible to room temperature. STX-603 type diamond cutting was used to cut the crucible and after polishing, the morphology of sample was analyzed. The refined silicon and refined slag were separately detached from the graphite crucible and both materials were ground into 100 mesh powder size in an agate mortar for phase and chemical analysis.

The silicon refined by the binary 50% CaO-50% SiO_2 slag system, the ternary 46% $\text{CaO-46% SiO}_2\text{-8% ZnO}$, and 40% $\text{CaO-40% SiO}_2\text{-20% ZnO}$ slag systems were subjected to acid leaching at room temperature under magnetic stirring for 2 h. The acid liquid was 5% HCl-5% HF-90% deionized water and the ratio of liquid to solid was 5:1. Scanning electron microscopy and energy dispersive spectrometer (SEM and EDS, FEI QUANTA200) were used to observe the morphology of refined silicon. X-ray diffraction (XRD, D/max-TTR III) was used to study the phase of refined silicon and refined slag. In addition, the chemical compositions of refined silicon and refined slag were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 8000).

3. Results and discussion

3.1. Morphology analyses

The refined silicon by the ternary 46% $\text{CaO-46% SiO}_2\text{-8% ZnO}$ slag system was longitudinally and transversely sliced off as shown in Fig. 2. In the image shown in Fig. 2(a) the metallic luster area is the refined silicon and the gray area is refined slag. The slag had good contact with the graphite crucible and it was distributed around the molten silicon. Fig. 2(b) shows the refined silicon and the refined slag had a good separation after cooling.

Fig. 3 shows the morphologies of MG-Si and refined silicon by the ternary $\text{CaO-SiO}_2\text{-ZnO}$ slag system. The impurity-rich phases, the white points in the SEM photos, are much more abundant in Fig. 3(a) than those in Fig. 3(b). This indicates that the ternary 40% $\text{CaO-40% SiO}_2\text{-20% ZnO}$ slag refining results in increased removal of impurities from MG-Si.

As shown in Fig. 4 and Table 3, the different impurity-rich phases Si-Fe-Al, Si-Fe-Al-Ti and Si-Fe-Al-Ca were observed in MG-Si. However, as shown in Fig. 4(b) and (f), only phase Si-Fe-Ti-Ca was detected after slag refining by 40% $\text{CaO-40% SiO}_2\text{-20% ZnO}$ slag refining.

3.2. Boron removal by ternary $\text{CaO-SiO}_2\text{-ZnO}$ slag system

The distribution coefficient of boron (L_B) as shown in Eq. (1) [29] can be used to measure the effect of boron removal by slag refining.

$$L_B = \frac{w(B)}{w[B]} \quad (1)$$

Table 1
Main impurity elements in the raw materials.

Impurity	B	P	Zn	Fe	Al	Ca
Concentration (ppmw)	12.94	49.81	0.33	3800	817	170

Table 2
Experimental conditions using ternary $\text{CaO-SiO}_2\text{-ZnO}$ slag reagent.

Experiments	Slag Composition (wt.%)			Slag (g)	Silicon (g)	Holding time(min)	Temperature (K)
	CaO	SiO_2	ZnO				
1	50	50		30	30	60	1823
2	49	49	2	30	30	60	1823
3	47.5	47.5	5	30	30	60	1823
4	46	46	8	30	30	60	1823
5	45	45	10	30	30	60	1823
6	40	40	20	30	30	60	1823
7	37.5	37.5	25	30	30	60	1823
8	35	35	30	30	30	60	1823

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