Boron and Phosphorus Removal in Si Purification with Ca-Si Alloy under Air Atmosphere

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Abstract. To further discuss the reduction of phosphorus (P) in the purification of metallurgical grade silicon (MG-Si), MG-Si alloyed with Ca-Si alloy first and then acid leaching was employed to removal $CaSi_2$ phase in which P was enriched under air atmosphere at 1723 K in this paper. The higher removal fraction of P can be obtained by adding more Ca-Si alloy to Si. The P removal fraction is 95.45% when the mass ratio of Si to Ca-Si alloy is 0.5. However, B cannot be removed from Si by alloying with Ca-Si alloy due to the concentration of B in the Si phase is higher than that in $CaSi_2$ phase.

1. Introduction

Solar energy which is converted into direct current electricity via the photovoltaic effect is considered to be the main renewable energy source in the future due to its relatively infinite reserves. Silicon (Si) will remain the dominant material for solar cells in the foreseeable future [1]. The purity of Si used in manufacturing solar cells which is called solar grade Si (SoG-Si) is higher than 6N, thus the total metal impurities content is < 1ppmw, P < 0.1ppmw, and B < 0.3ppmw [2].

It is wasteful that crystalline silicon made by the chemical method (mainly the improved Siemens method) must dope boron (B) or phosphorus (P) to make solar cells. It is considered as a cost-effective method to purity metallurgical grade Si (MG-Si) to SoG-Si by metallurgical technology due to its simple equipment, low investment, low energy consumption and no pollution. The main methods of removing B from Si by metallurgical method are plasma treatment [3] and slag refining [4], while vacuum technology [5] and electron beam [6] for the removal of P. Alloy refining combined with directional solidification can also be used to remove B and P from Si. Hu et al. [7] claimed that P can be further reduced by adding Ca when using Sn to purify Si. The removal efficiency of P in Si increased from 73.4% to 86.5% when Ca addition accounted for 4 mass percent in the Sn-Si system and it was found that the mass ratio of P in the Si phase containing P after purification was up to 17.8%. Johnston and Barati [8] achieved a P removal fraction of 98.8% by adding 4% calcium as getter metal to Si containing 326 ppmw of P combined with acid leaching. He et al. [9] studied the role of calcium oxide in the process of removing metal impurities from MG-Si by acid leaching, they stated that acid insoluble Si-Fe-based precipitates transferred into acid soluble Si-Ca-based alloys, thus promoting the effect of acid leaching. Meteleva-Fischer et al. [10] believed Si alloying with Ca resulted in the agglomeration of inclusions and better segregation of impurity

phases. They pointed out that the $FeSi_2Ti$ phase became enriched with P in the Ca-alloyed samples, however, no P content was detected in $CaSi_2$ phase in their work.

Slag treatment using CaO-based slag coupled with acid leaching is also applied in removing metal impurities and P elimination from Si. In our previous study [11], we found that part of P was likely reduced to Ca-Si-P compounds uniformly distributed into the $CaSi_2$ phase among Si grains after a short period of slag refining using CaO-SiO_2-CaF_2 system under air atmosphere, and the scattered distributed $CaSi_2$ phase contributed to the removal of Fe, Al and Ca impurities from MG-Si. And, it is found that the removal effect had a positive correlation with the content of Ca in Si.

However, research on the effect on the removal of B from Si by slag treatment using CaO-based slag or by alloying with Ca has not been conducted so far. In the present paper, the result of slag refining using CaO-based slag is simulated, a certain amount of Ca-Si alloy is molten with MG-Si to be refined in medium frequency induction, which results in a certain amount of Ca in Si. And the distribution of B and P in Si and $CaSi_2$, the removal efficiency of B and P will be discussed.

2. Experiments

2.1. Alloy refining

The alloy refining experiments was conducted in a laboratory scale medium frequency induction furnace. Si-Ca alloy used in this study was provided by Shaanxi Shenghua metallurgical Co. Ltd., and its element analysis was shown in Table 1. The composition of MG-Si to be refined in the present paper was shown in Table 2. Samples of MG-Si and Ca-Si alloy were placed in a high-purity dense graphite crucible (99.99%, 45 mm outer diameter, 30 mm inner diameter, 120 mm height, and 105 mm depth). Thereafter, the crucibles with the samples were placed in medium frequency induction furnace. After melting and holding at 1723 K $\pm$ 20 K for 10 min, the samples were cooled to 1273 K at 10 K/min for solidification refining. After cooling to room temperature, the samples were cut into pieces, and some parts were polished to examine the morphology and microarea composition by SEM-EDS.

Table 1. Contents of main elements in Ca-Si alloy.

Elements	Ca	Al	Si	C	S	P	B
Content (wt%)	30.22	1.24	60.74	0.52	0.035	0.021	0.0079

Table 2. Content of main impurities in MG-Si analyzed by ICP-AES.

Elements	Fe	Al	Ca	B	P
Content (ppmw)	3960	2156	904	20.24	89.92

2.2. Acid leaching

Samples after alloy refining were crushed into powder to be leached with aqua regia (HCl:HNO_3 = 3:1 by volume, diluted by deionized water by volume ratio of 3:2) and HF (diluted by deionized water by volume ratio of 1:1) successively at room temperature for 1 hour, respectively. Finally, the concentrations of impurities in the leached Si powder was analyzed by inductively couple plasma-atomic emission spectroscopy (ICP-AES, Thermo Fisher iCAP 6300).

3. Results and discussions

According to the content of Ca and Si in $CaSi_2$ listed in Table 1, the raw material Ca-Si alloy can be considered as a mixture of $CaSi_2$ and Si. In our previous study [11], it's found that $CaSi_2$ phase was produced among the silicon grains after slag treatment by CaO-SiO_2-CaF_2 system. After solvent refining, $CaSi_2$ will be produced by a eutectic reaction at 1301 K during the cooling of Ca-Si melt

according to the Ca-Si phase diagram. The content of B and P in Si changed after alloy refining and the following acid leaching, as listed in Table 3 and shown in Figure 1. This is due to segregation of B and P impurities between $CaSi_2$ and Si phases. It is difficult for B or P in liquid Si to volatilize under air atmosphere, so the B or P concentration in $CaSi_2$ can be calculated based on the conservation of mass.

The distribution ratio of B or P in $CaSi_2$ and Si is calculated according to the following equation,

$$L_{B\ or\ P} = \frac{C_{B\ or\ P\ in\ CaSi_2}}{C_{B\ or\ P\ in\ final\ Si}} \tag{1}$$

Table 3. Experiment results of Si after alloy refining and acid treatment.

Mass ratio of Si to Ca-Si alloy		0.5	1	2	4	8	16
Content in mixture (ppmw)	B	59.41	49.62	39.83	31.99	26.77	23.70
	P	169.97	149.96	129.95	113.94	103.26	96.98
Yiled during acid leaching (%)		44.80	58.90	74.00	85.00	90.90	93.00
Content after acid leaching (ppmw)	Si B	45.66	39.19	30.49	26.31	22.10	19.92
	Si P	4.09	6.88	11.14	22.35	42.77	65.42
	$CaSi_2$ B	70.58	64.57	66.41	64.22	73.45	73.93
	$CaSi_2$ P	304.60	355.00	468.10	632.94	707.55	516.37
L_B		1.55	1.65	2.18	2.44	3.32	3.71
L_P		74.39	51.58	42.03	28.32	16.54	7.89

3.1. Removal of phosphorus

P content in raw Si, Ca-Si alloy, mixture of Si and Ca-Si alloy, solvent refined Si, $CaSi_2$ and yield of Si during acid leaching as a function of mass ratio of Si to Ca-Si alloy in starting material are shown in Figure 1.

Generally, the content of P in commercial Ca-Si alloy is higher than that in MG-Si. It is obvious that the P content in the mixture is between Si and Ca-Si alloy after smelting Si and Ca-Si alloy with different mass ratios. And with the increase of Si ratio, the P content in the mixture is more and more close to that in Si. However, after acid leaching, the content of P in purified Si and that in the mixture after smelting are different with the change of the mass ratio of Si to Ca-Si alloy in the initial raw material: Even though the P content in mixture is higher than that in MG-Si, but P content in the purified silicon is lower than that in MG-Si after acid leaching instead. This indicates that the addition of Ca-Si alloy to MG-Si is beneficial to the removal of P from Si. This is because the $CaSi_2$ has aggregation effect to P, which results in P from MG-Si into $CaSi_2$ phase. Therefore, Ca-Si alloy can be employed to remove P from Si, and the higher removal fraction of P can be obtained by adding more Ca-Si alloy to Si.

After alloy refining experiment, P content in $CaSi_2$ is shown in Figure 1. The content of P in $CaSi_2$ is much higher than that of P in refined Si after acid leaching. The distribution ratio of P between $CaSi_2$ and Si, and the Si yield during the acid leaching, with the mass ratio of Si to Ca-Si alloy in the initial material are shown in Figure 2. As can be seen from Figure 2, L_P increases with the increase of Ca-Si alloy content. L_P between $CaSi_2$ and Si reaches 74.39 and the P removal fraction is 95.45% when the mass ratio of Si to Ca-Si alloy is 0.5, which means effect of P removal is obvious. However, it can also be seen from Figure 2 that the Si yield during acid leaching decreases rapidly while the P removal fraction is high. Therefore, it is important to find an optimal mass ratio to reduce the P content in Si with Si yield to be considered in industrial production.
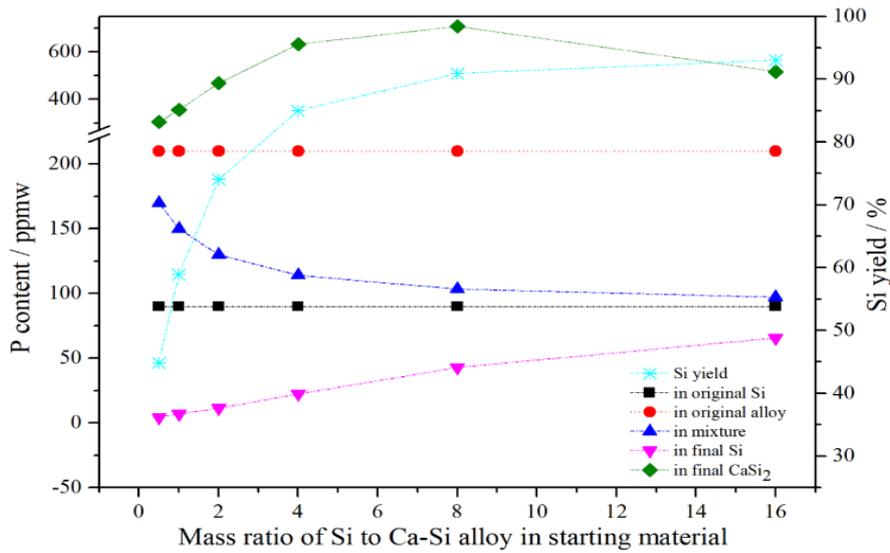
Figure 1. Content of P and Si yield during acid leaching as a function of mass ratio of Si to Ca-Si alloy in starting material.
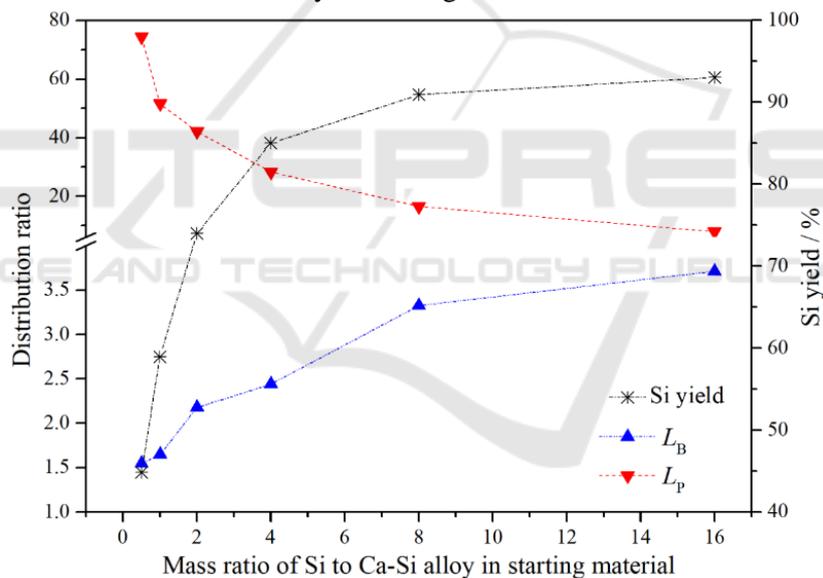
Figure 2. L_P, L_B and Si yield as a function of mass ratio of Si to Ca-Si alloy in starting material.

3.2. Removal of boron

B content in raw Si, Ca-Si alloy, mixture of Si and Ca-Si alloy, solvent refined Si, CaSi$_2$ and Si yield during acid leaching as a function of mass ratio of Si to Ca-Si alloy in starting material are shown in Figure 3.

Apparently, the B content in the mixture reduces with the increase of mass ratio of Si to Ca-Si alloy because the B content in commercial Ca-Si alloy is also higher than that in MG-Si. The content of B in refined Si decreased slightly after acid leaching which indicated that acid leaching had a positive effect on removal of B from Si after alloying with Ca, and the change trend of B content in Si was the same before and after acid leaching. The B content in CaSi$_2$ is slightly lower than that in the Ca-Si alloy, which may be due to the diffusion of B from the Ca-Si alloy into the MG-Si. The

distribution ratio of B between $CaSi_2$ and Si, and Si yield during the acid leaching changed with the mass ratio of Si to Ca-Si alloy in the starting material shown in Figure 3. L_B increases with the increase of the mass ratio of Si to Ca-Si alloy in raw material, from 1.55 at the ratio of 0.5, to 3.71 at 16. Despite the large L_B, the B content in refined Si couldn't be reduced from the view of B concentration in refined Si compared to raw MG-Si. This could be illustrated by an EPMA diagram of a Si sample containing a $CaSi_2$ phase. It is can be observed that the content of B in Si phase is higher than that in $CaSi_2$ phase from the EPMA-WDS analysis of a Si sample containing $CaSi_2$ phase shown in Figure 4. Therefore, B cannot be removed from Si alloyed with Ca or Ca-Si alloy.
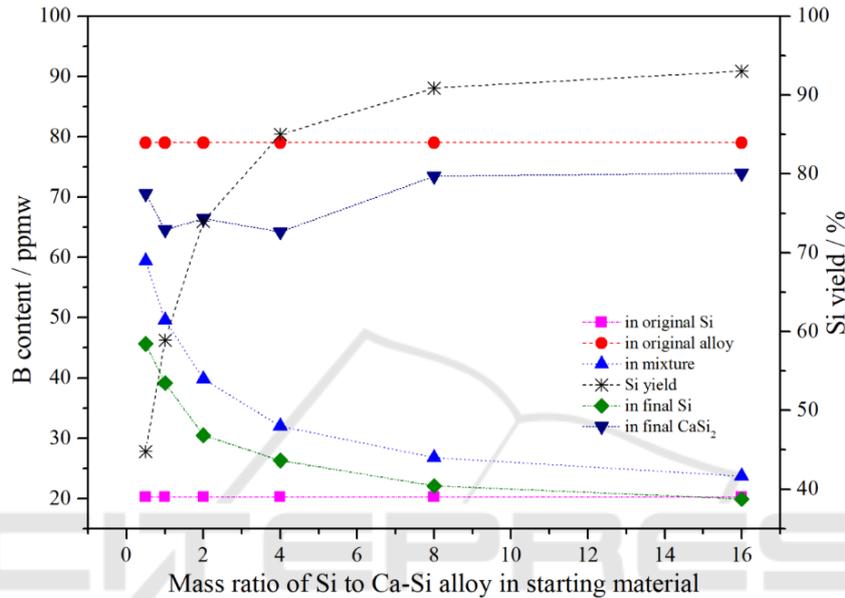
Figure 3. Content of B and Si yield as a function of mass ratio of Si to Ca-Si alloy in starting material.
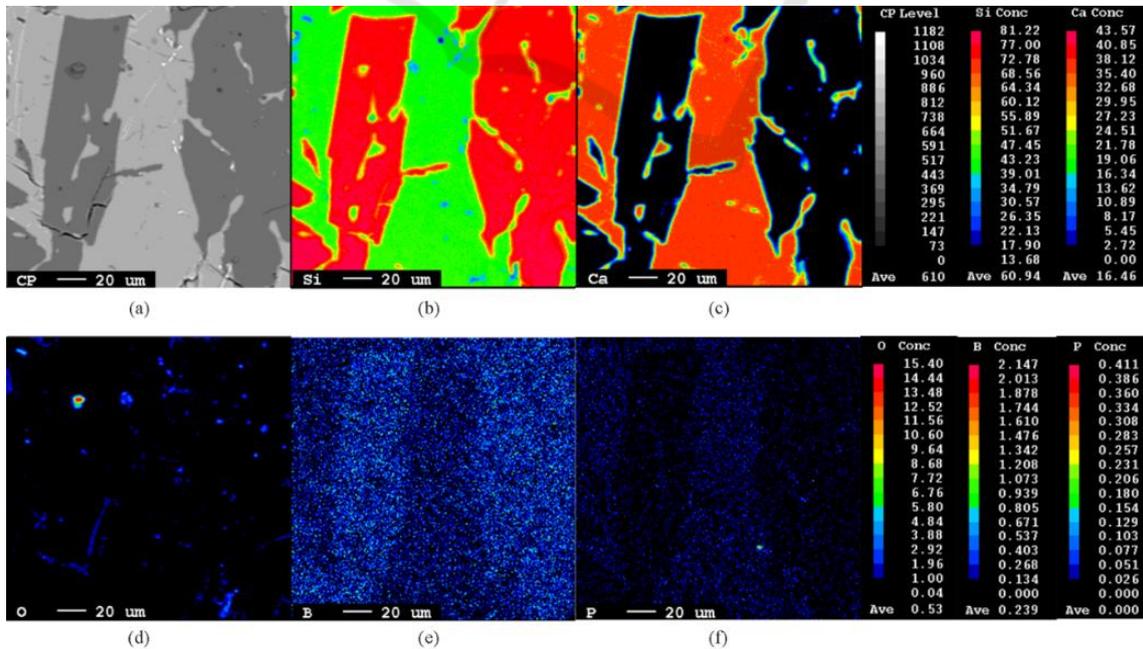
Figure 4. EPMA-WDS elements mapping of Si containing $CaSi_2$.

4. Conclusions

Ca-Si alloy was employed to refined MG-Si in the intermediate frequency furnace under air atmosphere at 1723 K. The removal of B and P was discussed, and the main conclusions were as follows:

1. Ca-Si alloy can be employed to remove P from Si, and the higher removal fraction of P can be obtained by adding more Ca-Si alloy to Si. L_P between $CaSi_2$ and Si reaches 74.39 and the P removal fraction is 95.45% when the mass ratio of Si to Ca-Si alloy is 0.5.

2. Si yield during acid leaching decreases rapidly while the P removal fraction is high.

3. B cannot be removed from Si by alloying with Ca-Si alloy due to the concentration of B in the Si phase is higher than $CaSi_2$ phase.

Acknowledgment

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