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Boron Removal From MG-Si By Slag Treatment With Copper Addition

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Abstract: The effect of slag treatment with Copper addition in silicon purification by metallurgical methods was examined in this paper. The microstructures and contents of Si-Cu alloy after slag refining were investigated by XRD and ICP, respectively. The majority phases in the Si-Cu alloy were Cu_3Si and Si. The partition ratio of boron (L_B) between slag and silicon was studied with and without Cu addition. Experimental results show that slag treatment with Cu addition can improve the L_B in CaO-SiO_2-CaF_2 slag system, where a maximum boron removal ratio of 85% could be achieved.

Introduction

So far, high purity polycrystalline silicon is the fundamental material of solar cell and is mostly produced by Siemens methods. However, the metallurgical method to purify silicon has also been intensively researched since it is considered as a more economy route. Impurities in MG-Si are usually divided into two kinds from the point of metallurgical methods: metal elements Al, Fe, Ca, Ti and Ni which could be easily separate from the MG-Si by directional solidification and nonmetal elements P and B with high segregation coefficient (0.35 and 0.8, respectively).

Higher B content leads to high electrical resistivity of solar cell, so its content must be less than 0.3ppmw. Therefore, slag refining, acid leaching, solvent refining and plasma are introduced to eliminate B in MG-Si. Slag refining is considered most cost efficient among these methods. In order to choose appropriate slag, the condition below should be satisfied: 1) The slag can provide enough oxide to reaction with B 2)The density between slag and silicon should be differed therefore slag can be easily separate from the silicon. 3)The slag should have a good fluidity which ensure the refining reaction completely finished .4)The slag should not introduce impurities which could not be eliminated from the subsequent procedure. 5)The slag must be cheap.

The solvent refining is based on the retrograde solubilities of impurity elements in silicon. The Si-Al system [1, 2], Si-Cu system [3], Si-Ca system [4] and the Si-Na system [5] have been intensively investigated. The removal effect on impurity elements from MG-Si by binary alloy solvent refining systems is clear[6]. Combination of solvent refining and slag refining[7] is an innovating methods which can enhance the slag refining effect by increase the L_B by Sn addition. Hence, slag refining with Cu addition shows theoretical potential and it should be investigated to get a better understanding of both slag refining and solvent refining.

The main objective of this work is to develop a promising technique which boron can be efficient removed by slag refining with Cu addition. The microstructure is also examined. According to the condition above, CaO-SiO_2 slag system was chosen for the based slag system.

Addition of CaF_2 into the system can change its slag network to get higher separation coefficient in molten silicon.

Experimental

Raw material. MG-Si(99%) used in this research was provided by Liancheng Co., Ltd., and the content of boron was 8.3ppmw. Slag system used in this study was 40.5 mol pct CaO-35.5 mol pct SiO2-24 mol pct CaF_2. Pulverized slag of reagent-grade CaO_3, SiO_2 and CaF_2 was mixed by a planetary ball mill for 3h, the ball mill was set at alternating rotary direction each 10 minutes. Then the mixture was dried in a drying oven for 24h to eliminate the possible moisture introduced during the producing process. Table 1 gives the details of chemical agents.

Table 1

Chemical	Purity	Production Unit
Cu	99.99%	Sinopharm Chemical Reagent Co.,Ltd
B	95-97%	Sinopharm Chemical Reagent Co.,Ltd
CaO	99.99%	Xilong Chemical Co.,Ltd,
SiO_2	99.99%	Xilong Chemical Co.,Ltd,
CaF_2	99.99%	Xilong Chemical Co.,Ltd,

Experimental procedures. This experimental was compared MG-Si slag refining with Si-Cu Alloy slag refining. Procedures of MG-Si slag refining was showed in Fig.1 and Si-Cu Alloy slag refining was showed in Fig.2. In order to get some slag refining treated Si without acid leaching, 25g MG-Si with 0.1g boron mixed in and 25g CaO-SiO_2-CaF_2 slag were melted in induction furnace. Heat program was from room temperature to 1473K in 120min, then after 60min reached 1723K. Heat preservation lasted for 10h and cool down in the induction furnace. The slag refining treated Si-Cu alloy without acid leaching was also studied in above method. The difference compared with former was that 7.6g MG-Si, 17.4 copper and 0.1g boron were melted.

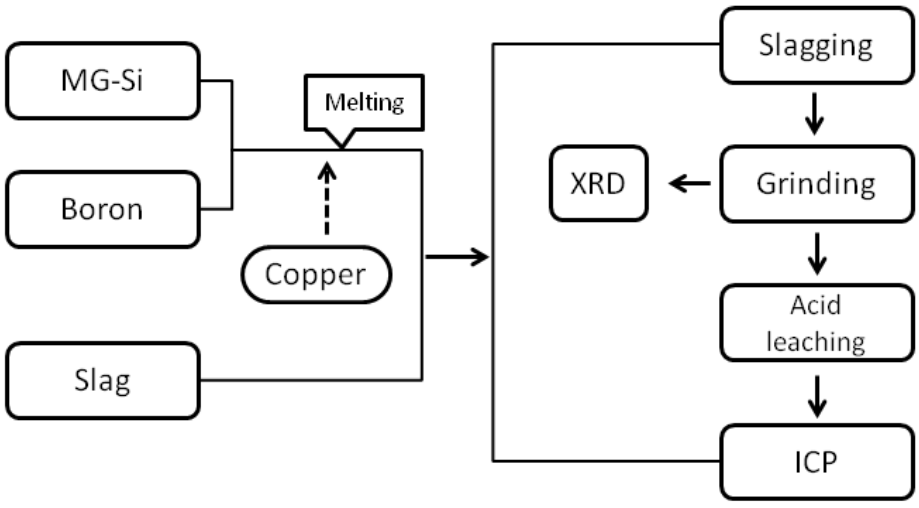

Fig.1 The experimental procedures of slag refining with copper addition

Result and Discussions

The microstructure analysis

Researchers investigated phase of slag with XRD. The results were showed blow.As Cu-Si phase diagram presented and expected, Cu_3Si was found from the analysis which meets the expectation because in the system Si is excessive. Due to a very big different density of Si and Cu_3Si, separation is easy in the way of heavy media method.

The effect of boron removal of slag refining with Cu addition

5 samples that contain one MG-Si whose boron content was 500ppwm untreated in any methods(No.1), one slag refining treated Si without acid leaching (No.2),and one slag refining treated Si-Cu alloy without acid leaching (No.3) were studied. Their boron contents were investigated by ICP and shows in Fig. 2.

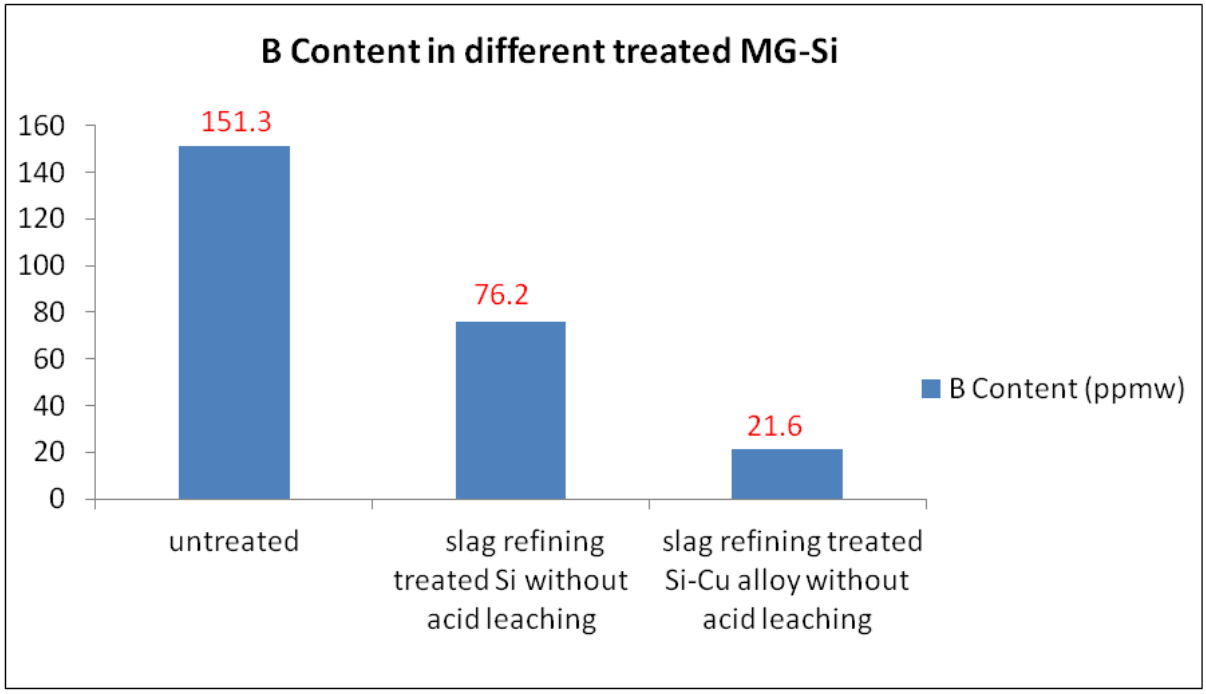

Fig. 2 The B content in different treated MG-Si

Compared slag refining treated Si without acid leaching and slag refining treated Si-Cu alloy without acid leaching, the boron content of latter was so distinctly lower than former. With the result above, boron removal ratio of the one without acid leaching is 50%, while the one with acid leaching is nearly 85%.

The Role of Cu addition

Due to the strong affinity between B and oxygen, B could be oxidized in slag refining. The mechanism is shown in Eq. (1)

$$B_{(l)} + \frac{3}{4}O_{2(g)} = BO_{1.5(l)} \quad (1)$$

Meanwhile, the Si oxidation reaction happened at the slag/silicon interface as Eq.(2). Therefore, the whole reaction could be considered as Eq.(3). Hereby, the partition ratio(L_B), which is critical to judge the efficiency of different slag systems, can be derived from Eq.(3) as follow:

$$Si_{(l)} + O_{2(g)} = SiO_{2(l)} \tag{2}$$

$$B_{(l)} + \frac{3}{4} SiO_{2(l)} = O_{2(g)} + \frac{3}{4} BO_{1.5(l)} \tag{3}$$

$$K = \frac{a_{BO_{1.5}} \left(a_{Si}\right)^{3/4}}{a_B \left(a_{SiO_2}\right)^{3/4}} = \frac{\gamma_{BO_{1.5}} X_{BO_{1.5}}}{\gamma_B X_B} \cdot \left(\frac{a_{Si}}{a_{SiO_2}}\right)^{3/4} \tag{4}$$

$$L_{\mathbf{B}} = \frac{X_{BO_{1.5}}}{X_B} = \frac{K_3 \gamma_B}{\gamma_{BO_{1.5}}} \cdot \left(\frac{a_{Si}}{a_{SiO_2}}\right)^{3/4} \tag{5}$$

Where K is the equilibrium constant of Eq.(3), a_i, γ_i and X_i stand for the activity, activity coefficient and molar ratio of component i, respectively.

The value of L_B represents the ability of boron removal in slag systems. According to Eq.(5), it is effected by the activity of SiO_2, activity coefficient of B and $BO_{1.5}$. Since the activity coefficient of $BO_{1.5}$ for given slag systems is constant at fixed slag basicity, the determining factor is activity coefficient of B in silicon-based alloy melt. The activity coefficients of B in Si and Cu are shown as below:

$$\log \gamma^0_{B(Si)} = -\frac{11100}{T} + 5.82 \tag{6}$$

$$\log \gamma^0_{B(Cu)} = \frac{4450}{T} - 3.03 \tag{7}$$

It is clear that the activity coefficient of B in Cu at 1723 is higher than that in Si. Meanwhile, the activity of Si is low in the Si-Cu melt compared to that of pure silicon melt. Therefore, the partition ratio of boron in CaO-SiO2 slag system with Cu addition will be significantly higher than that without Cu. The experimental result is agree with theoretical expect.

Conclusion

1) In the system of Si-Cu alloy with CaO-SiO_2-CaF_2 slag refining, Si phase and Cu_3Si phase were found, which meets the expectation.

2)Boron removal ratio of the one without acid leaching is 50% and the one with acid leaching is nearly 85%,which present good boron removal effect of slag treatment with copper addition.

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