Materials Science in Semiconductor Processing 57 (2017) 59–62

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Short communication

Effect of zinc oxide addition in slag system and heating manner on boron removal from metallurgical grade silicon

Jijun Wu[a,b,*], Zhenfei Xia[a], Wenhui Ma[a,b,*], Fanmao Wang[b], Yeqiang Zhou[b], Kuixian Wei[a,b]

[a] *State Key Laboratory of Complex Nonferrous Metal Resources Cleaning Utilization in Yunnan Province, Kunming University of Science and Technology, Kunming 650093, People's Republic of China*

[b] *The National Engineering Laboratory for Vacuum Metallurgy and Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, People's Republic of China*

ARTICLE INFO

Keywords:
Metallurgical grade silicon
Slag reagent
Boron removal
Removal efficiency
Vacuum distillation

ABSTRACT

Different amount of ZnO was added to calcium silicate reagent to improve boron removal from metallurgical grade silicon (MG-Si). The thermodynamic analysis showed that the reagent $CaO-SiO_2-ZnO$ had a stronger ability to boron removal than the reagent $CaO-SiO_2$. Two kinds of heating manners of electromagnetic induction and resistance were used to refine MG-Si. Compared with the resistance heating, the induction heating showed a much higher efficiency of boron removal. The mechanism of boron removal from MG-Si by ternary $CaO-SiO_2-ZnO$ slag reagent was put forward and the role of ZnO in slag to boron removal was described. The by-product Zn in refined silicon can be thoroughly removed by a vacuum distillation treatment, which showed an absolute advantage to the residual zinc removal in silicon by comparison with the acid leaching treatment. The residual zinc in silicon was reduced to lower than 0.05 ppmw after a vacuum treatment at 1723 K.

1. Introduction

The demand for solar grade silicon (SoG-Si) has been rapidly growing annually. The metallurgical route for the yield of low-cost SoG-Si materials is a promising method. Boron removal from metallurgical grade silicon (MG-Si) to SoG-Si by this route is still the technical difficulty [1]. Slag refining, traditionally used as the purification of steel making [2], is also very efficient technique for boron removal from MG-Si. The refining flux for boron removal is based on the calcium silicate slag system. Some attempts had also been made to improve the boron removal efficiency and some additives were used to calcium silicate slag. They include binary, ternary and polynary slag reagents such as $CaO-SiO_2$ [3], $CaO-SiO_2-CaF_2$ [4], $Al_2O_3-CaO-MgO-SiO_2$ [5], $CaO-CaCl_2-SiO_2$ [6], $Na_2O-CaO-SiO_2$ [7], $CaO-SiO_2-K_2O$ [8] and so on. Morita [6] et al. found that the boron removal efficiency reached to 86% while adding $CaCl_2$ to $CaO-SiO_2$ binary slag. As described by Tan [9] et al., boron can be reduced from 25 ppmw to 4.4 ppmw with Na_2O addition. In the experimental results by Wu et al. [10], the boron in MG-Si can be reduced from 22 ppmw to 1.8 ppmw at 1823 K with a composition of 40% CaO-40% SiO_2–20% K_2CO_3 and the removal efficiency of boron reached to 91.8%.

In our recent study [11], a ZnO addition to 50% CaO-50% SiO_2 slag showed a 20% increase in boron removal efficiency and a 40% increase in distribution coefficient due to a stronger oxidizing ability to boron for ZnO than SiO_2. The saturated vapor pressure of Zinc is very large at high temperature, and it can easily volatilize during the high temperature experiment. In this study, the effects of an electromagnetic heating manner and a resistance heating manner on boron removal using $CaO-SiO_2-ZnO$ slag reagent were investigated. Subsequently, a vacuum distillation treatment to remove residual zinc in refined silicon was studied compared with the results of acid leaching treatment.

2. Experimental

The MG-Si powder of 30 g with a boron concentration of 12.94 ppmw and the ternary $CaO-SiO_2-ZnO$ slag reagent of 30 g were mixed and used as raw materials. The refining experiments were carried out in a medium frequency induction furnace (20 kHz) and in a resistance furnace (~1650 °C), respectively. The schematics of apparatuses are shown in Fig. 1. Consequently, a high-purity graphite crucible and a corundum crucible were accordingly used as the reactors of raw materials in the apparatuses. The refining temperature was kept at 1823 K for 60 min or 120 min. The initial slag compositions and the experimental conditions are listed in Table 1. During the experiment, an argon gas with 99.9% purity was blown into the quartz tube to avoid the oxidation of silicon in crucible.

* Corresponding authors at: State Key Laboratory of Complex Nonferrous Metal Resources Cleaning Utilization in Yunnan Province/The National Engineering Laboratory for Vacuum Metallurgy and Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, People's Republic of China.

E-mail addresses: dragon_wu213@126.com (J. Wu), mwhsilicon@126.com (W. Ma).

http://dx.doi.org/10.1016/j.mssp.2016.10.001
Received 29 July 2016; Received in revised form 30 September 2016; Accepted 3 October 2016
Available online 13 October 2016
1369-8001/

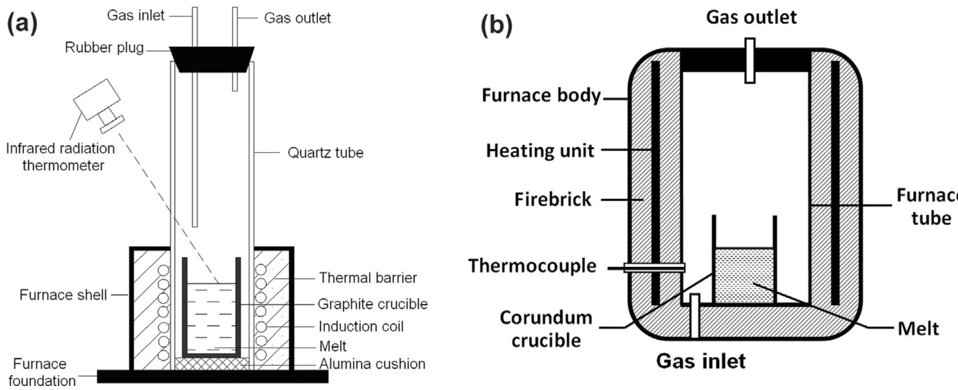

Fig. 1. Schematic diagrams of experimental apparatuses (a) medium frequency induction furnace and (b) resistance furnace.

Table 1
Experiment conditions of refining MG-Si by ZnO-CaO-SiO_2 slag reagent.

No	Slag compositions/%			Refining time/min	Temperature/K	Heating manner
	CaO	SiO_2	ZnO			
1	47.5	47.5	5	60 (I) and 120 (*R*)	1823	I and R
2	46	46	8	60 (I) and 120 (*R*)	1823	I and R
3	45	45	10	60 (I) and 120 (*R*)	1823	I and R
4	40	40	20	60 (I) and 120 (*R*)	1823	I and R
5	37.5	37.5	25	60	1823	I
6	35	35	30	60 (I) and 120 (*R*)	1823	I and R
7	30	30	40	120	1823	R
8	25	25	50	120	1823	R

I=Induction heating and R=Resistance heating.

After the refining experiments, a STX-603 type diamond wire cutting machine was used to cut open the crucible loaded with samples. The refined silicon was ground to a powder of 100 meshes. The refined silicon was subjected to acid leaching at room temperature for 120 min under a magnetic stirring. The acid solution was made up of 5%HCl-5% HF-90%H_2O. The ratio of acid to refined silicon was 5:1. At the same time, the refined silicon was distilled in a vacuum furnace for zinc removal at 1723 K for 60 min under 20–50 Pa. The concentration of both boron and zinc in refined silicon were analyzed by an inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 8000).

3. Results and discussion

The photographs of refined silicon samples using CaO-SiO_2-ZnO slag reagent are shown in Fig. 2. The samples both in the induction furnace and the resistance furnace show that the refined silicon and the refined slag are thoroughly separated after experiments. The refined silicon is surrounded by the slag, which aggregate on the inner wall of graphite or corundum crucible on account of the larger viscosity and surface tension than those of molten silicon [12–14].

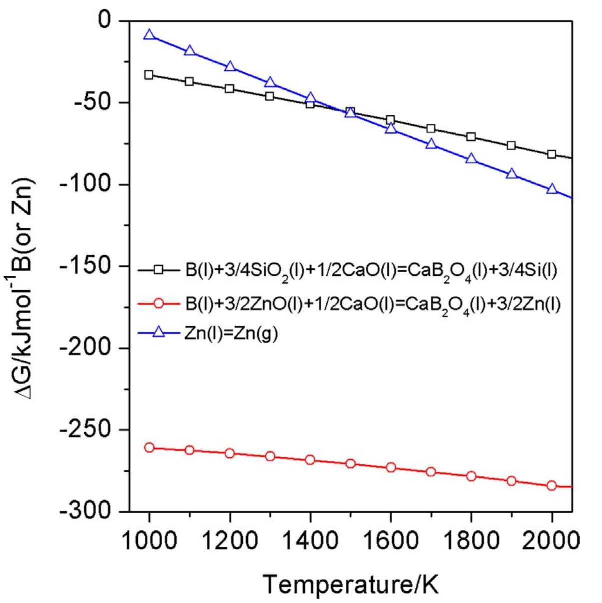

Fig. 3. Standard Gibbs free energy of reactions between dissolved boron in silicon and ZnO-CaO-SiO_2 slag reagent.

The chemical reaction between the dissolved boron in silicon and the slag of CaO-SiO_2 and the standard Gibbs free energy (ΔG^{θ}) calculated by HSC software are represented [5,15,16].

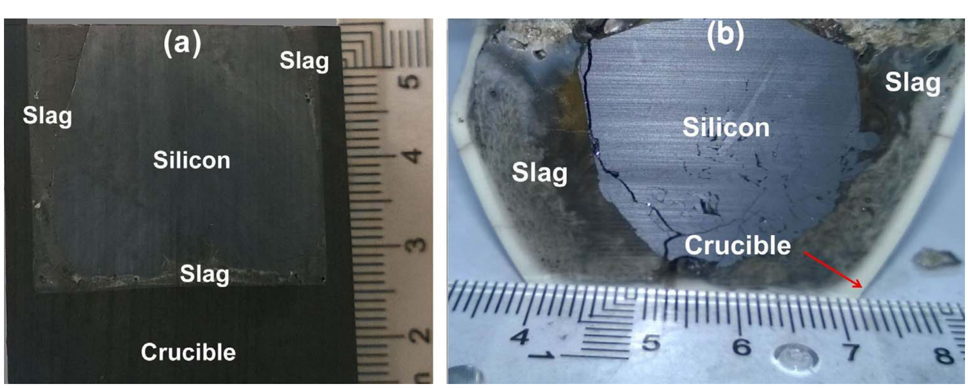

Fig. 2. Photographs of longitudinal sections of refined samples using ZnO-CaO-SiO_2 slag reagent (a) in induction furnace and (b) in resistance furnace.