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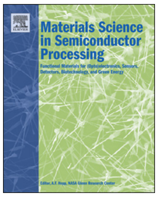

Study of boron removal from molten silicon by slag refining under atmosphere

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ABSTRACT

Solar energy is expected to be in great demand within the next few years. In relation to this, a global shortage in the solar-grade silicon (SoG-Si) used in the production of solar cells has motivated numerous studies on metallurgical-grade Si (MG-Si) refining. However, improvements in this material are limited by the difficulties involved in reducing boron (B) and phosphorus content. The present study investigated the removal of B using (CaF_2)-Al_2O_3-CaO-SiO_2 and Na_2SiO_3-CaO-SiO_2 slag in an ambient air atmosphere in order to refine MG-Si. The mass transfer coefficients of B in molten Si ($k_{d[B]}=1.19\times10^{-4}$ cm s^{-1}) and $BO_{1.5}$ in molten slag ($k_{d(B^{3+})}=1.01\times10^{-5}$ cm s^{-1}) were deduced through kinetic analysis. The mass transfer process of boron oxide limited slag refining; however, secondary slag treatment effectively improved the efficiency of B removal. L_B was determined by the combined effect of the oxygen partial pressure and the molten slag structure.

1. Introduction

The rapid growth of the photovoltaics (PV) industry has resulted in a severe shortage of solar-grade Si (SoG-Si). Metallurgical-grade Si (MG-Si) must be refined prior to the removal of certain impurities because it is the raw material used in the production of SoG-Si [1–4]. Boron (B) impurity higher than 0.3 ppmw could severely decrease the photoelectric conversion efficiency. Slag treatment is one approach in removing B from molten Si [5–9]. B impurities can be removed under reasonable conditions and parameters.

Several recent studies have attempted slag refining in a vacuum, generating some ideal results. For example, Morita et al. conducted many systematic studies and presented the relevant thermodynamic analysis [10–15]. Many works have been conducted to confirm the effects of certain parameters, such as slag basicity and oxygen potential [16], on distribution coefficients (i.e., B concentration ratio of the slag (wt% B) and Si phase [wt% B], L_B). However, most of these refining processes were conducted in a vacuum or in argon atmosphere, and the samples were limited to laboratory scales. Industrial slag refining in ambient air atmospheric conditions can lower equipment costs and greatly shorten the production cycle. Slag refining in the air should be investigated, in order to confirm the changes caused by variations in the atmosphere and in the melting amount.

The present study examined the possibility of removing B impurities to refine MG-Si using the (CaF_2)–Al_2O_3–CaO–SiO_2 (FACS) and Na_2SiO_3–CaO–SiO_2 (NSCS) slag systems under 2073 K atmosphere. B impurities must be removed quickly to ensure the mass production of solar cells. The factors affecting L_B, which include the limiting conditions and experimental parameters of slag refining, slag optical basicity and secondary slagging, have been investigated in prior research. The mass transfer coefficients of B in molten Si ($k_{d[B]}$) and of $BO_{1.5}$ in molten slag ($k_{d(B^{3+})}$) were

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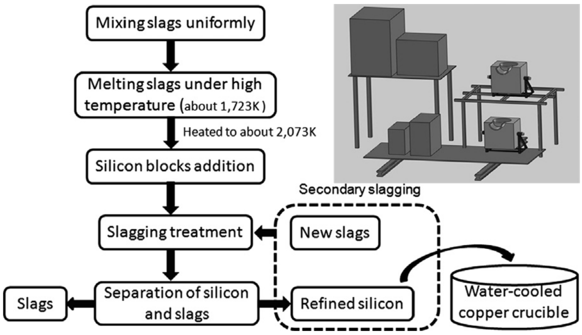

Fig. 1. Process of slag treatment and the schematic diagram of experimental devices.

deduced through kinetic analysis. The effects of the parameters on the oxidization rate of B were also discussed.

2. Experimental

All the experiments were conducted in an ambient air atmosphere. The experimental device is an induction furnace (IF) with a maximum power of 160 kW. Samples of the (CaF_2)–Al_2O_3–CaO-SiO_2 and Na_2SiO_3–CaO–SiO_2 slag systems were selected. Fig. 1 shows the process of slag treatment and the schematic diagram of experimental devices. All oxides of the pulverized slag were of reagent grade, and Si was of industrial-grade. The slag samples were mixed in a cylindrical graphite crucible (Φ210 mm × 300 mm) and melted through the induction heating of the graphite crucible. About 10 min after being completely melted, cleaned Si blocks were uniformly poured into the molten slag and melted together by both the heat of the slag and induction. B impurities were oxidized and diffused into the slag. After undergoing slag refining, which lasted from 0.5 h to 4 h, the resulting molten slag and Si were separately poured into the water-cooled copper crucible, a step that was difficult to conduct in a vacuum. Secondary slag treatment was conducted by directly pouring the molten Si after the first slagging treatment into the other graphite crucible with pre-melted slag and then refining for 0.5 h to 4 h.

The test samples were cut from the center of each ingot. The impurity content in the Si and slag phases were analyzed using inductively coupled plasma mass spectroscopy (ICP-MS, Perkin Elmer, DRC II, America, Accuracy: ppb) and inductively coupled atomic emission spectroscopy (ICP-AES, Perkin Elmer, Optima 2000DV, America), respectively. The parameters and experimental conditions are listed in Table 1.

Table 1
Experimental conditions in the slag refining process.

Parameters			Conditions	
Initial boron content in silicon			13.5, 25 ppmw	
Optical basicity			0.52–0.71	
Temperatures			2073 K	
The ratio between Si and slags			0.4–1	
Melting time			0.5 h–4 h	
Air pressure			0.1 MPa	
Humidity			40–60%	
IF frequency			1 KHz–20 KHz	
Λ	CaF_2 (wt%)	Al_2O_3 (wt%)	CaO (wt%)	SiO_2 (wt%)
(CaF_2–Al_2O_3–CaO–SiO_2 system, initial B content: 13.5 ppmw)				
0.551	5	10	20	65
0.577	5	15	25	55
0.597	5	15	30	50
0.632	5	10	40	45
Λ		Na_2SiO_3 (wt%)	CaO (wt%)	SiO_2 (wt%)
(Na_2SiO_3–CaO–SiO_2 system, initial B content: 25 ppmw)				
0.523		65	5	30
0.530		70	5	25
0.559		60	10	30
0.572		65	10	25
0.577		50	15	35
0.692		46.7	30	23.3
0.696		46.2	30.7	23.1

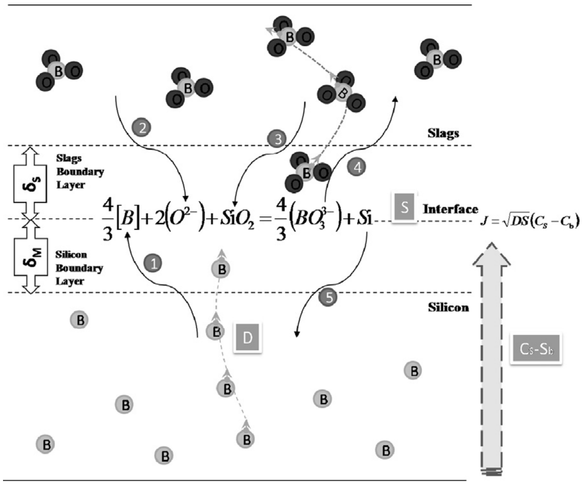

Fig. 2. Schematic of the B removal process.

3. Results and discussion

3.1. Restrictions of the removal process

B removal from MG-Si by slag refining is a metallurgical extraction process. Fig. 2 presents a schematic of the whole process, including the chemical interaction and mass transfer processes [17]. First, all the reactants are transferred to and are diffused through the Si boundary layer, after which the reaction occurs at the interface. The products then diffuse through the boundary layer and into the corresponding bulk phase. Steps 2, 3, and 5 in Fig. 2 are not the limiting conditions because they are components of the bulk phases. The three possible limiting conditions are the mass transfer of the B impurities, the reaction process (Step 1) and the mass transfer of boron oxide (Step 4). Metallurgical chemical reaction rates are generally fast at high temperatures. Thus, the reaction can be considered a rapid equilibrium process. The oxidization reaction can be affected by the objective conditions such as slag structure and refining temperature.

Prior to the reaction, B impurities must diffuse through the concentration boundary layer. This process is caused