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Boron removal from molten silicon using $CaO-SiO_2-BaO-CaF_2$ slag

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Abstract: The distribution coefficient (L_B) of boron between $CaO-SiO_2-BaO-CaF_2$ slag and silicon was investigated using electromagnetic induction melting for the purpose of improving the boron removal fraction. The dependence of the boron distribution coefficient between slag and silicon on the fundamental parameters of CaO to SiO_2 mass ratio and refining time and the additions of BaO and CaF_2 to the slag was discussed. The results show that L_B can be increased by adding BaO and CaF_2 to $CaO-SiO_2$ slag. The maximum value of L_B (6.94) is obtained when the CaO to SiO_2 mass ratio is 1.1:1 and the contents of BaO and CaF_2 are fixed at 15% and 20%, respectively. Increasing the refining time increases the L_B. After the slag treatment is performed twice, the boron content of the silicon is successfully reduced from 3.5×10^{-5} to 3.7×10^{-6}, and the removal fraction of boron reaches 89.4%.

Key words: metallurgical silicon; boron removal; $CaO-SiO_2-BaO-CaF_2$

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1 Introduction

Because of environmental pollution and the depletion of fossil fuels, solar energy is an option to provide renewable energy to adapt to the demands of sustainable development. Silicon has been used as a starting material in the photovoltaic industry. In recent years, metallurgical grade silicon (MG-Si) [1] has been used as a feedstock alternative to substitute electronic grade silicon to solve the problem of silicon feedstock shortage. The purity of metallurgical grade silicon is 2N. Therefore, to satisfy the purity requirements of solar grade silicon (SOG-Si), it is necessary to remove a variety of impurities, such as phosphorus and boron impurities.

Theses metallic impurities can be removed by directional solidification because of their low segregation coefficient. Phosphorus can be removed using vacuum refining because of its high vapor pressure. However, boron is difficult to remove using either directional solidification [2,3] or vacuum treatment [4,5] because of its high segregation coefficient [6] and low vapor pressure. Slag treatment is an effective method to remove boron from metallurgical silicon. Boron reacts with slag to form boron oxides that transfer to the slag phase, whereas, refined silicon can easily be separated from the slag phase.

In recent years, various $CaO-SiO_2$-based slag systems have been investigated to evaluate the removal of boron from metallurgical silicon [7−10]. TEIXEIRA et al [11,12] conducted systematic research to understand the thermodynamics of the $CaO-SiO_2$ slag system. JOHNSTON et al [13,14] discussed the effects of slag basicity, oxygen potential and the mass ratio of slag to silicon on the boron removal process. LUO et al [15] studied the kinetics of boron removal using an electromagnetic induction melting process.

Apparently, the boron removal fraction is strongly dependent on slag chemistry. BaO is one of the most basic fluxes, which is preferred to remove acidic impurities such as boron. Besides, the slag basicity of BaO is stronger than that of CaO, and BaO can decrease the melting point and viscosity of the slag [16,17].

CaF_2 can further reduce the viscosity and liquefaction temperature of the slag [18,19], promoting the mass transfer process. Therefore, BaO and CaF_2 were chosen in the present study to improve the boron removal fraction.

The extraction of boron from silicon using

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$CaO-SiO_2-BaO-CaF_2$ slag has not been systematically studied. SUZUKI et al [8] only investigated the effect of the CaO to SiO_2 mass ratio on extraction using $CaO-SiO_2-BaO-CaF_2$ slag. Therefore, in the present study, comprehensive data on the fundamental parameters including CaO to SiO_2 mass ratio, refining time, additions of BaO and CaF_2 to the slag and repeated slag treatment have been investigated. The values of the boron distribution coefficient between slag and silicon (L_B) of $CaO-SiO_2-15\%BaO-20\%CaF_2$ and $CaO-SiO_2$ were compared.

2 Experimental

$CaO-SiO_2-BaO-CaF_2$ slag was used to remove the boron. Although liquid slag is an ionic melt composed of cations and anions, the F^- ions in the slag are assumed to exist with Ca^{2+}, and this component is expressed as CaF_2. All of the oxides and CaF_2 were reagent grade. The metallurgical grade silicon that was used as the raw material in this study was supplied by Xinlong Co., Ltd. The boron content of this MG-Si was 3.5×10^{-5}. The effects of varying the CaO to SiO_2 mass ratio, refining time, as well as the BaO and CaF_2 proportions were studied to obtain high values of L_B. The CaO to SiO_2 mass ratio was varied from 0.3:1 to 1.1:1 with the BaO and CaF_2 contents fixed at 5% and 10%, respectively. The refining time varied from 1200 to 6000 s. BaO content varied from 0 to 35%, and CaF_2 content varied from 0 to 40%. The L_B values of $CaO-SiO_2-15\%BaO-20\%CaF_2$ slag and $CaO-SiO_2$ slag were also compared.

Table 1 Experimental parameters used in this study

Parameter	Value
Initial boron content in silicon	3.5×10^{-5}
Temperature/K	1873
Mass ratio of silicon to slag	4:1
Melting time/s	1200−6000
Filled argon pressure/kPa	10

The experimental parameters are shown in Table 1. The experimental process consisted of the following steps. The metallurgical silicon was ground to a particle size of 0.1−0.2 mm. The metallurgical grade silicon was then washed with acetone in an ultra-sonic cleaner to remove possible solid residue from the surface. After drying, 0.3 kg of metallurgical silicon and 0.075 kg of slag (silicon to slag mass ratio of 4:1) were placed in a pure graphite cylindrical crucible (inner diameter: 0.06 m; outer diameter: 0.07 m; height: 0.16 m) that was surrounded by a graphite holder (inner diameter: 0.07 m; outer diameter: 0.09 m; depth: 0.16 m). The slag layer was placed in the middle of the graphite crucible. Then, the crucible was loaded into an intermediate frequency (2000 Hz) induction melting furnace. The schematic diagram of the apparatus is provided in Fig. 1. The basic equipment consisted of a rotary vane mechanical vacuum pump, a diffusion vacuum pump, a feeding device, an induction coil heating system and an argon gas inlet. Firstly, the rotary vane mechanical vacuum pump and the diffusion vacuum pump evacuated the furnace. When the absolute pressure was below 30 Pa, electric power was applied to melting the metallurgical silicon and slag, and argon gas was added to the furnace to maintain a pressure of approximately 1.0×10^4 Pa. An infrared thermometer was used to measure the temperature. Two colors of pyrometer were used in the present experiments and the wavelength is 1.0 μm. The smelting continued for 1200−6000 s at 1873 K under the argon atmosphere. After refining, the silicon and slag were physically separated, and the boron contents of the silicon and the slag were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

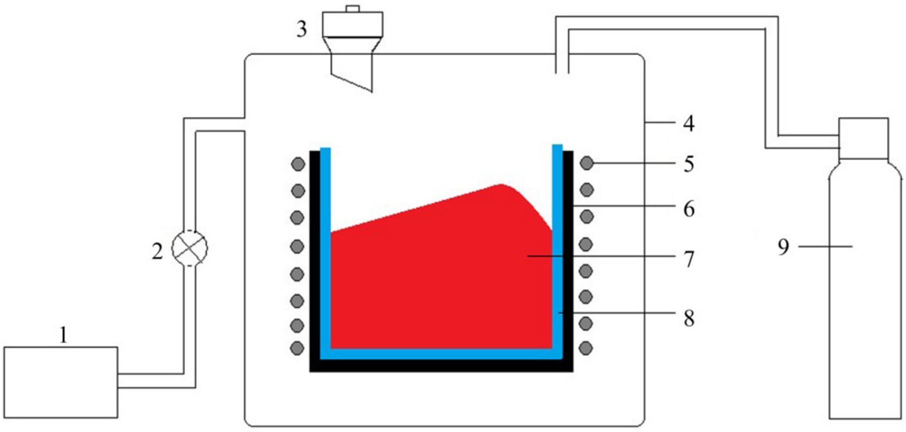

Fig. 1 Schematic drawing of intermediate frequency induction furnace: 1—Rotary vane mechanical vacuum pump; 2—Roots vacuum pump; 3—Feeding device; 4—Intermediate frequency induction melting furnace; 5—Induction coil; 6—Graphite holder; 7—Molten silicon and slag; 8—Graphite crucible; 9—Argon gas