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Influence of the oxygen partial pressure and the boron content on the behavior of boron in calcium silicate melts

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ABSTRACT

The dissolution behavior of boron in a molten slag was evaluated at 1823 K to establish the boron refining mechanism. From the thermodynamic consideration, two refining mechanisms are confirmed, and a modified equation is suggested. In addition, the structural characteristics of boron in molten slag in different oxygen partial pressure were evaluated to confirm the boride and borate behaviors. The changes in ionic state of boron caused by the oxygen partial pressure were confirmed via Raman spectroscopy. In addition, the network forming characteristics of borate and the network modifying characteristics of boride were observed. From the above results, to improve the boron refinement and the slag fluidity, thereby preventing the silicon loss, refinement of the boron through a slag having much lower equilibrium oxygen partial pressure is suggested.

1. Introduction

Recently, the slag refining technology of metallurgical grade silicon has been developed as the alternative production process for solar grade silicon. [1–7] The removal of boron by slag treatment is an attractive process because of the relatively lower cost and higher refining efficiency. [1,2] But the removal of boron from metallurgical grade silicon still remains a challenge. [3,4] In the slag treatment process, the removal efficiency of boron increases with the addition of fluxing agents, such as CaF_2 and Li_2O. [2,4,5] Additionally, the slag basicity (CaO/SiO_2 ratio) and oxygen partial pressure strongly affect the removal efficiency of boron from Si melts. [6,7] Recently, the V-shaped curve was observed in the relationship between the distribution ratio of boron (L_B) between slag and Si melt, and the basicity of slag, namely, CaO/SiO_2 ratio. Teixeira et al. proposed that this tendency was due to the changes of the activity coefficient of borate ions, which was influenced by the ionic state of boron in slag. [3,4] However, the variation of the slag composition, i.e., CaO/SiO_2 (Vee ratio, basicity), simultaneously results in the change in the oxygen partial pressure, p_{O_2}, at the slag-metal interface due to the variation of the activity of SiO_2 in the slag based on the following equations:

$$Si(l) + O_2(g) = SiO_2(l) \tag{1}$$

$$\Delta G^0 = -969024 + 211.05T(J/mol). [8]$$

Recent experimental results for a fixed slag composition indicated a V-shaped dependence of L_B ($=(\%B)_{slag}/[\%B]_{Cu}$) on the p_{O_2}. [9] The L_B linearly increased with increasing p_{O_2}, with the slope of 3/4 in logarithmic scale above $p_{O_2}^{cr}$, which is the oxygen partial pressure of the refining mechanism transition. In this region, the oxidation reaction is dominant. [3,4,9] However, the L_B decreased by increasing the p_{O_2}, with the slope of $-1/6$ in logarithmic scale below $p_{O_2}^{cr}$, wherein the reduction mechanism is dominant. [9] The results indicated that the 'borate' ion is relatively stable for oxygen partial pressure values above $p_{O_2}^{cr}$, whereas the 'boride' ion is stable in molten slag for values below $p_{O_2}^{cr}$.

The borate ions in silicate were reported to melt at high oxygen partial pressure in the form of tetrahedral borate (BO_4), which is charge compensated by cations and trigonal borate (BO_3), regardless of the boron content in (boro-)silicate melts. [3,10–12] Because borate in silicate melts is stabilized in the form of incorporation with silicate, the structural behavior of borate is strongly affected by the major components, such as CaO and SiO_2. [3,13,14] Despite the well-known structural characteristics of a 'borate ion' in slag, the structural characteristics of a 'boride ion' in slag at low oxygen potentials has not been studied to date; the possibility of boride, namely, reducing refining mechanism was recently observed by our group. [9]

Consequently, the aim of the present study is to clarify the refining mechanism and the structural behavior of boron species (boride, borate) in silicate melts in the viewpoint of slag refining of molten silicon. The gas-slag and slag-metal equilibrium experiments were performed at fixed slag composition to confirm the effect of oxygen partial pressure on the distribution behavior and structural behavior of boron in the

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$CaO—SiO_2$ slags. Quenched slag was investigated using a Raman spectroscopy for the structural implication of the boron species.

2. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. High temperature equilibrium experiments were performed using a super-kanthal resistance furnace and a mullite reaction tube. A B-type thermocouple and a proportional integral differential controller were used to control the temperature at 1823 K (±2 K).

Using an alumina lance, the CO/Ar mixture was injected into the reaction tube to control the oxygen partial pressure through the C/CO equilibrium (Eq. (2))

$$C(s) + \frac{1}{2}O_2(g) = CO(g) \tag{2}$$

$\Delta G^0 = -114828 + 86.1T$ (J/mol). [8]

The gases were passed through columns of soda lime and $CaSO_4$ to remove excess moisture and CO_2. In addition, residual oxygen in Ar gas was removed by passing through a Mg turning furnace of 873 K using Mg/MgO equilibrium (Eq. (3))

$$Mg(s) + \frac{1}{2}O_2(g) = MgO(S) \tag{3}$$

$\Delta G^0 = -603246 + 107.98T$ (J/mol). [8]

The regent grade chemicals were used to prepare the slag. CaO was obtained by calcinating $CaCO_3$ at 1273 K for 24 h. For the slag-metal equilibrium experiments, 4 g of slag was equilibrated with 4 g of Cu-B melt in a carbon crucible during 18 h at 1823 K to investigate the boron distribution behavior according to the oxygen partial pressure. The compositions are provided in Table 1. After equilibration was reached, the samples were immediately removed from the reaction tube and quenched by Ar gas stream.

For the gas-slag equilibrium experiments, 10 g of slag was equilibrated in a carbon crucible during 18 h at 1823 K. The compositions are listed in Table 2. After 18 h, the samples were immediately removed from the reaction tube and subsequently quenched by Ar gas.

Table 1
Slag composition and experimental results of 4 g of $CaO—SiO_2$ slag equilibrated with 4 g of Cu_3B_2 at 1823 K.

CO (SCCM)	Ar (SCCM)	log p_{O_2} (atm)	Slag components (wt%)			Boron in slag (wt%) (±2%)	Boron in metal (wt%) (±2%)	Distribution ratio (L_B)
			CaO	SiO_2	C/S			
6	294	−18.93	55	45	1.22	2.380	0.035	68.97
18	282	−17.98				1.946	0.036	54.15
45	255	−17.18				1.987	0.048	41.06
75	225	−16.74				2.472	0.056	43.86
120	180	−16.33				2.266	0.056	40.15
180	120	−15.98				1.457	0.030	49.04
240	60	−15.73				1.589	0.027	60.16
300	0	−15.54				1.713	0.028	58.36

The boron content in metal and slags was analyzed using ICP-AES (PerkinElmer-optima 4300DV) within the error range (%RSD < 2). Raman spectroscopy (Horiba Jobin Yvon/LabRam HR) was used for structural analysis of quenched glass samples. A laser emitting light at a wavelength of 514.532 nm (Ar-ion laser, power = 2 mW @ sample) was used.

3. Results and discussion

3.1. The dependence of the boron distribution behavior between the slag and the metal on the oxygen partial pressure.

The distribution ratio of boron between Cu—B alloy and $CaO—SiO_2$ (C/S = 1.2) slag, log L_B, as a function of the oxygen partial pressure, log (p_{O_2}), is shown in Fig. 2 (a). The slope of the line is approximately 0.22 at $p_{O_2} > 10^{-16.3}$ atm (linear fitting, Adj. R-Square: 0.87). Although the slope of the line is lower than the expected value 0.75 within the experimental scatter, it is believed that the oxidation mechanism (Eq. (4)) is available at $p_{O_2} > 10^{-16.3}$ atm. However, despite the linear

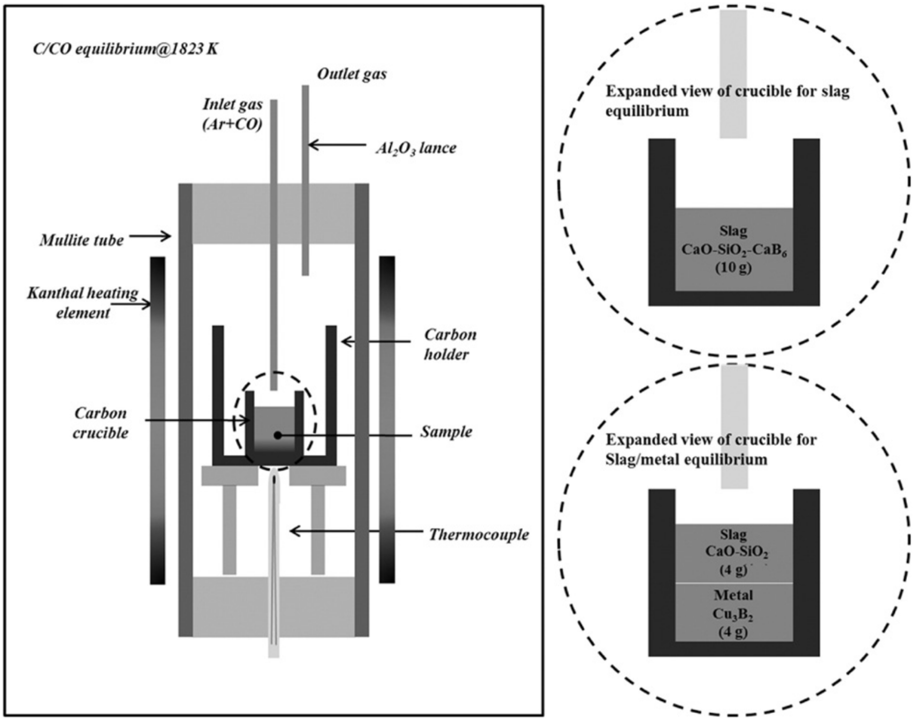

Fig. 1. Schematic diagram of the experimental apparatus.