論文題目

Physical chemistry on evaporation removal of boron in molten silicon using reactive fluxes
（反応性フラックスを用いたシリコン中ホウ素の揮発除去に関する物理化学）

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The availability of abundant and low-cost solar grade silicon (SOG-Si) feedstock is essential for the widespread use of solar cells. Although there has been great progress in reducing energy consumption in the modified Siemens and fluidized bed reactor processes, the potential for cost reduction in these processes is limited by the low productivity of Si and chemical energy required to convert metallurgical grade silicon (MG-Si) to gaseous compounds, followed by distillation, reduction, and deposition into solid Si. An alternative cost-effective, energy-efficient process to produce solar grade silicon (SOG-Si) is the metallurgical process, which is considered to be sustainable and offers benefits in productivity and process cost. In the metallurgical process, the physiochemical properties of SOG-Si are greatly influenced by impurity elements such as Fe, A1, Ca, P and B which exist in the MG-Si. In general, the metallic impurity such as Fe, Al, Ca can be separated by the directional solidification method, other metallurgical methods such as directional solidification, gas blowing, alloy refining, oxidation with plasma melting and vacuum melting have been investigated. However, each process has its own limitation and does not allow all impurities to be removed. Because the segregation coefficients of B and P are close to 1, they are not easily removed. Hence, for solving the strong demand of B and P removal with low cost process, slag treatment as a method for B and P removal has received attention because of its low cost and mass productivity.

B removal by slag treatment has been studied mainly for $CaO-SiO_2$ slag. The partition ratio (L_B), which is defined as (mass% B in slag) / (mass% B in Si), is not high enough for B removal by a single slag treatment. In order to improve B removal efficiency in slag refining, other oxide compounds were tried to utilize. $CaO-SiO_2-NaO_{0.5}$, $CaO-SiO_2-LiF$ was used as slag agents to remove B by M.Tanahashi et al., D. Zhao et al., respectively. $CaO-SiO_2-TiO_2$ and $Al_2O_3-MgO-SiO_2$ were used to remove B by Helene Bjerke, but the improvements of B removal effects have their own limitation. Nishimoto et al. introduced chlorination in which Cl_2 gas was supplied into the $CaO-SiO_2$ slag. It was found that if only Cl_2 gas blowing into the molten Si, the B was not decreased, but if Cl_2 gas with $CaO-SiO_2$ slag together was supplied, the B was decreased, which presumably due to B oxy-chloride gas formation. Although such removal by gaseous evaporation during slag treatment is considered to be a possible refining technique, the reaction mechanism has not been clarified yet. In addition, considerable Si loss occurs during the reaction with Cl_2 gas.

The availability of abundant and low-cost solar grade silicon (SOG-Si) feedstock is essential for the widespread use of solar cells. The potential for cost reduction in chemical processes is limited by the low productivity of Si. An alternative cost-effective, energy-efficient process to produce solar grade silicon (SOG-Si) is the metallurgical process, which is considered to be sustainable and offers benefits in productivity and process cost.

B removal by slag treatment has been studied mainly for $CaO-SiO_2$ slag. The partition ratio (L_B), is not high enough for B removal by a single slag treatment. In order to improve B removal efficiency in slag refining, evaporation of B in hydrogen and chlorine atmosphere with various slags were investigated by Helene Bjerke *et al.* and Nishimoto *et al.*, respectively. It was found that if only Cl_2 gas blown into the molten Si, the B did not decrease, but if Cl_2 gas together with $CaO-SiO_2$ slag were supplied, B content decreased which presumably is due to B oxy-chloride gas formation. Although such removal by gaseous evaporation during slag treatment is considered to be a possible refining technique, the reaction mechanism has not been clarified yet. In addition, considerable Si loss occurs during the reaction with Cl_2 gas.

Thus, the innovation of this study is that instead Cl_2 gas, high purity $CaCl_2$ was selected as another candidate material for the Si refining with $CaO-SiO_2$ slag by considering the following advantages: (a) B is expected to be removed by slag and oxy-chloride gas formation; (b) $CaCl_2$ can reduce the melting point and viscosity of slag; (c) Compared with Cl_2 gas, $CaCl_2$ is more safe and environmental friendly.

In this study, physical chemistry on MG-Si refining using $CaO-SiO_2-CaCl_2$ slag was investigated with the objective of developing a new B removal process for meeting the requirement of SOG-Si production (B<0.3 ppmw).

This dissertation contains 7 chapters, and the first chapter is introduction.

In chapter 2, in order to determine the possibility of B evaporation from $CaO-SiO_2-CaCl_2$ slag system, thermodynamics of the reaction was investigated and the estimated relationships between the partial pressures of $BOCl$, BCl_x, $SiCl_x$, and $CaCl_2$ and the mole fraction of CaO in the $CaO-CaCl_2$ slag were also studied. Both of standard Gibbs free energy and partial pressure of reactions between B, Si with chloride demonstrate the BOCl gas should be generated at 1723K theoretically.

In chapter 3, to identify the property of $CaO-SiO_2-CaCl_2$ slag, the density and mole volume of $CaO-SiO_2-CaCl_2$ slag at 1723K were investigated by an improved Archimedian method. The solidus, liquidus and binary phase diagram of SiO_2-CaCl_2 were investigated by TG-DTA method. Furthermore, the liquidus and phases of $CaO-SiO_2-CaCl_2$ ternary slag were also investigated at 1723K.

In chapter 4, for the sake of quantifying the transfer rate of B from molten Si to the $CaO-SiO_2-CaCl_2$ slag, reaction mechanism of B removal from molten Si to molten slag and that of evaporation from slag to gas phase was clarified. Hence, assuming a diffusion model of B transfer from Si to molten slag and its evaporation as a gas phase, the diffusion coefficient of B in the slag was investigated based on the tube-molten pool method at 1723K. Furthermore, the mass transfer coefficients of B in the slag were also measured and calculated according to Fick's law. The rate-limiting step in the removal of B from Si by slag refining is the transfer of B at both the boundary layer adjacent to Si and at the surface of the slag. However, the former of these has the greater influence.

In chapter 5, after confirming the possibility of evaporating B oxychloride species through the reaction of

$BO_{1.5}$ with $CaCl_2$, B removal processes from MG-Si using CaO-$CaCl_2$, SiO_2-$CaCl_2$ and CaO-SiO_2-$CaCl_2$ slag systems were carried out at 1723K in the resistance furnace at laboratory scale. Having confirmed that a CaO-SiO_2-$CaCl_2$ slag system offers the best potential to achieve good B-removal, it was explored further to ascertain whether this performance held true at various scales in an industrial environment. Therefore, various scales of Si/slag refining were carried out with the times of 1, 1.5 and 2 hours at 1723K using induction furnace and vacuum furnace. The $30mol\%CaO$-$23mol\%SiO_2$-$47mol\%CaCl_2$ shows the best potential to achieve B-removal (90 %) efficiency.

Chapter 6 summarizes the important findings in this research.

Eventually, based on the findings throughout this research, physical chemistry on SOG-Si refining using CaO-SiO_2-$CaCl_2$ was clarified, and the low-cost overall process, comprising of slag and solidification refining, acid leaching, vacuum melting and directional solidification steps, for producing SOG-Si from MG-Si was proposed, which can be applied to practical application.