

論文の内容の要旨

論文題目

PHYSICAL CHEMISTRY ON SOLAR GRADE SILICON REFINING USING Si-Sn SOLVENT

(Si-Sn 溶媒を用いた太陽電池用シリコン精製の物理化学)

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Photovoltaic industry has been in rapid development in this decade under the global policies supporting the renewable energies and reduction of CO₂ emission. While production of solar grade silicon (SOG-Si) has been dominated recently by the modified Siemens process and a fluidized bed reactor process, obtaining a stable SOG-Si feedstock at lower cost is of essential importance for the widespread use of solar cells. Metallurgical routes offer benefits both in mass productivity and low cost. As one of those, the solvent refining process offers the possibility of cost reduction due to its high purification efficiency and low processing temperature. In this study, Si-Sn alloy was selected as a candidate solvent focusing on the moderate liquidus slope, and the physical chemistry on SOG-Si refining using Si-Sn solvent was investigated with the aim of developing a new Si refining process for SOG-Si production.

In chapter 2, solid solubility of Sn in Si is indispensable to evaluate the incorporation of Sn after solidification refining of Si using Si-Sn solvent. The solid solubility of Sn in Si was measured by temperature gradient zone melting (TGZM) method, and was determined to be 0.001~0.0015 in molar fraction at the temperature range of 1379 to 1634 K. The excess partial molar Gibbs energy of Sn in solid Si at infinite dilution was determined to be 57,700 (\pm 1400) J/mol. As the solid solubility of Sn was higher than the target Sn content in SOG-Si, the subsequent process for removal of Sn was indispensable.

On the other hand, the diffusion coefficient of Si in the Si-Sn melt was also determined to acquire the fundamental property for the Si growth from the Si-Sn solvent. The coefficient of Si in the Si-Sn melt was determined to be $1.2\sim 1.9\times 10^{-3}$ mm²/s at the temperature range of 1379 to

1634 K, which was increased slightly with the increase in temperature.

In chapter 3, in order to identify the higher growth rate of Si, the growth conditions for bulk Si crystal growth by directional solidification of the Si-Sn solvent as well as the purification efficiency of refined Si grown from Sn-50mol%Si melt (1605-1555 K), Sn-70mol%Si melt (1633-1603 K) and Sn-95.8mol% melt (1666-1636 K) were investigated.

The morphology of grown Si was found to be changed due to the constitutional supercooling. The plate-like Si crystals were floated upwards due to the significant difference in the density between solidified Si and Si-Sn liquid when the constitutional supercooling occurs. The growth rate of Si was increased with the increase in initial Si content of the melt.

The purification efficiency of refined Si showed that more than 98% of metallic impurities were removed and 60% and 70% for B and P, respectively.

In chapter 4, in order to understand the thermodynamic property of B in the Si-Sn melt for design the removal of B from the Si-Sn melt, the solubilities of B in molten Sn from 1673 to 1873 K and in the Si-Sn melt at 1673 K were measured by equilibrating solid B with molten Sn or Si-Sn melt. The isothermal section for the Si-Sn-B system at 1673K was measured by the equilibration of the liquid phase with B solid solution or silicon boride. The activity coefficient of B in the Si-Sn melt at 1673K was evaluated, which was found to be three orders of magnitude larger in the Sn-rich side than that in the Si-rich side. Accordingly, it was suggested that B removal can be achieved easily from the Si-Sn melt with the larger Sn content.

In chapter 5, B removal from Si-Sn alloy was investigated by using a CaO-SiO₂-24mol%CaF₂ slag. The partition ratio of B was measured by equilibrating Si-Sn melt with slag, and the effects of slag and alloy composition on partition ratio of B were investigated. The required amount of slag for the B removal from Si-Sn melt was then estimated for designing the B removal from Si-Sn melt.

The partition ratio of B was increased with the increase in the ratio of CaO/SiO₂ at the fixed alloy composition of Si-30.5mol%Sn. And it was found that the partition ratio of B was remarkably increased from 2 to 200 with the increase in the Sn content from 5% to 82mol% at the fixed slag composition of 40.5%CaO-35.5%SiO₂-24mol%CaF₂. It has twofold effects by increasing Sn content on the partition ratio of B, both activity coefficient of B and oxygen partial pressure are increased.

As higher partition ratio of B was obtained, the required amount of slag in once slag treatment was decreased from 66.2 to 10.3, 5.8 and 4.3 by adding 30 mol%, 40 mol% and 50 mol % Sn, respectively.

In chapter 6, to accelerate the mass transfer of Si, the separation of Si from Si-Sn melt by

induction heating was investigated. Silicon after solidification refining can be efficiently separated from Si-Sn melt under the fixed alternating magnetic field.

The continuous process in laboratory scale for purification of MG-Si by using Si-Sn solvent was conducted combining with slag treatment and solidification refining. The upgraded Si was obtained and the effective removal of impurities was confirmed, in particular, B was reduced to 0.3 ppmw.

Eventually, based on the findings throughout this research, physical chemistry on SOG-Si refining using Si-Sn solvent 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.

Keywords: Physical chemistry; SOG-Si refining; Si-Sn solvent; Solid solubility; Directional solidification; B partition ratio; Slag refining; Si separation.