

## 論文の内容の要旨

論文題目 Physical Chemistry on B Removal from Si  
Using Si-Sn-Cu Solvent with Zr Addition  
(Zr添加Si-Sn-Cu溶媒を用いたSiからのB除去に関する物理化学)

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Under the policies of supporting renewable energy and reducing CO<sub>2</sub> emissions to solve the energy crisis and global warming, the photovoltaic industry has developed rapidly in the past decades. Currently, the improved Siemens and fluidized bed methods serve as mainstream techniques to produce solar grade silicon (SOG-Si). Nevertheless, these methods are energy-intensive with high cost. The metallurgical refining route enables the purification of metallurgical grade Si (MG-Si) to SOG-Si as a sustainable process, and it has advantages of mass productivity and relatively low cost. Solvent refining, can be applied at a considerably low temperature that is more conducive to B removal. Moreover, if B can be removed by adding small amount of additives which have strong affinity for B to enhance the formation and precipitation of boride, thus it would become more effective and practical. The objective of this study is to clarify the mechanism of (i) separation of bulk Si by flotation based on the significant density difference, and (ii) enhancing B-removal fraction by using additives (Zr, Ti *etc*) in the solidification process of Si with the Si-Sn(-Cu) solvent.

In Chapter 2, to confirm whether the upwards or downwards motion generated better Si enrichment results, the growth control and enrichment of Si crystals from the Si-50.0 at.% Sn melt were conducted in the 1605-1505 K temperature range, under different moving directions, and at different rates ranging from 0.01-0.10mm/min.

The upwards process was more favorable than the downwards one: the amount of precipitated Si increased and floated upwards easily due to the buoyancy caused by the significant difference in density between solidified Si and the Si-Sn melt during the upwards process.

The Si enrichment percentage increased with the decrease of the moving rates. The largest Si enrichment percentage reached 98.6% at the 0.01 mm/min upwards moving rate. After HCl leaching, the residual Sn (molar fraction) in the enriched Si area could be easily reduced to the 0.00132–0.00163 range, which was almost the same as but slightly higher than the range of the solid solubility of Sn in Si. The obtained bulk Si is polycrystalline Si, and the priority growth direction is from crucible wall based on the EBSD results. And a model was established to simulate the Si growth process using COMSOL Multiphysics 5.2, which explained the defects (grain boundaries and dislocations) formation and residual Sn content in the enriched Si part dependence on the width of S/L interface, caused by the moving rate. The most critical first step for using Si based alloy solvent refining to produce SOG-Si was analysed in this Chapter.

In Chapter 3, after determining the advantage of the upwards motion in the separation of bulk Si during the directional solidification process, the effect of Zr/Ti addition on B removal fraction was compared. The B-removal mechanism is discussed from the aspects of theoretical analysis and experimental design. The effects of different variables, such as the moving direction, moving rate, Zr/Ti addition content, and initial Sn content in Si-Sn alloys, on the B-removal fraction were observed.

Although the removal fraction of B has been improved, it is not as significant as expected (highest B-removal fraction was 73.6% with 1057ppma/6857 ppmw Zr addition, B: 120 → 31.2 ppmw). To further explain this phenomenon, the distribution behavior of B and Zr in the directional solidification refining process was studied by SEM-EDS. B- and Zr-enriched areas were found only in the mushy zone, but not combined to form B-Zr intermediate compounds.

Furthermore, the solubility product ( $K_{sp}$ ) of Zr and B in Si-Sn melt was also measured using equilibrium technology. The constants were determined as  $\geq 9.62 \times 10^{-10}$  (1605 K, Si-50 at.% Sn) and  $\geq 3.32 \times 10^{-10}$  (1575 K, Si-65 at.% Sn), which were 100 times higher than those in the Si-Al melt measured by Yoshikawa et al. A high refining temperature was responsible for the lower removal fraction of B when the Si-Sn alloy was employed as the refining solvent.

Finally, a series of comparative experiments were carried out by adding Ti additive. The results showed that the effect of B removal by adding Ti was very weak, even worse than that by adding Zr. It can be explained by that  $ZrB_2$  is more stable at low temperature and the solubility product constant of  $ZrB_2$  is smaller than  $TiB_2$ , based on the activity coefficients of Zr and Ti in Si-Sn melt. I concluded

that the refining process should be carried out at a low temperature, which is more conducive to boride formation.

In Chapter 4, based on (i) the low liquidus temperature of Si-Cu systems, (ii) low solubility of Cu in solid Si, and (iii) strong affinity of Zr to B for the enhanced boride formation, a novel attempt to remove B from Si using Zr as a trapping agent via a Si-Cu solvent was developed. Therefore, this chapter aimed to clarify the formation mechanisms of  $ZrB_2$  in a Si-Cu melt by using chemical equilibrium technology and to measure important thermodynamic data (such as solubility products).

Firstly, the SEM-EDS result showed that B-bearing polygonal  $ZrB_x$  precipitations found at the bottom of test samples, and further were confirmed as  $ZrB_2$  by electron probe microanalysis. Thermodynamic analysis revealed that the solubility products of  $ZrB_2$  in a Si-Cu melt were  $2.50 \times 10^{-12}$  (1258 K, Si-57.0 at.% Cu) and  $4.11 \times 10^{-12}$  (1345 K, Si-50.0 at.% Cu).

Finally, the compositions of Si-Cu alloys that can form stable  $ZrB_2$  particles were estimated by calculating the solubility products of  $ZrB_2$ , and the equilibrium contents between B and Zr at different corresponding liquidus temperatures ranging from 1133 to 1450 K. B in a Si-Cu melt at 1133 K can be reduced to a content less than 10 ppma when adding an amount of Zr greater than 1000 ppma, which is lower than the content estimated by Lei in a Si-Al melt at the same temperature. All of the results above indicate that a Si-Cu system forms  $ZrB_2$  more easily than a Si-Al system.

In Chapter 5, after confirming that B in a Si-Cu melt can be reduced by precipitating  $ZrB_2$  via Zr addition, the solidification refining of Si using Si-Cu solvent with Zr addition was studied. A series of experiments of directional solidification refining were carried out.

The B-removal fraction, bulk Si enrichment percentage, and residual Cu content in refined Si were investigated. The results showed that (i) the B-removal fraction was improved significantly as expected, the highest of which is 93.4% (80 → 5.3 ppmw with 211ppma/915 ppmw Zr addition); (ii) Large area of bulk Si was obtained by upwards, and highest Si enrichment percentage is 99.2%; (iii) the residual Cu content can be reduced to a relative low level, the molar fraction of which ranging from 0.00099 to 0.00191; and (iv)  $k_B$  was concluded become smaller in Si-Cu system (0.29 at 1345 K) than that in pure Si system (0.80 at 1687 K) and continuous

decreasing with increasing in Zr addition content (0.21 when 915 ppmw Zr was added).

It is concluded that the reason for the high removal fraction of B in the Si-Cu system is not only the small solubility products of Zr and B mentioned in Chapter IV, but also the smaller segregation coefficient of B in the Si-Cu system rather than in the pure Si system and continuous decreasing with increasing in Zr addition content.

Finally, in Chapter 6, to further enhancing B removal fraction and make full use of the advantages of aforementioned Si-Sn and Si-Cu system, I tried to use Si-based ternary alloy (Si-Sn-Cu) method. The separation of Si and B removal fraction were investigated using Si-25at.% Sn-25at.% Cu alloy.

Based on the FactSage results, the primary Si began to precipitate at about 1210°C, so I set three holding temperatures (1230, 1200, 1170°C, respectively) in the process of directional solidification to confirm which is closer to its real liquidus temperature. The upwards moving rate was 0.01mm/min and the moving distance was 10 cm, and initial B and Zr content were set as 100 ppmw and 211ppma/1140 ppmw, respectively.

The results showed that the liquidus temperature was determined at about 1170 °C, the Si enrichment percentage can reach 99.2%, and the B removal fraction was 95.3% (100 → 4.7 ppmw). Although the B removal fraction has been further improved, but the absolute content of B still needs to be further reduced by subsequent process to meet the requirements of SOG-Si ( $\leq 0.3$ ppmw).

In Appendix, another new concept of using high entropy alloy (ZrTiHfCuNi) as additive for B removal from Si was put forward. The results showed that B was adsorbed near HEA and not exist in Si. This provides a perspective for B removal by using pure Si system with B-friendly high entropy alloy as additive. However, further study is needed to explain the specific mechanism.

**Keywords:** Physical chemistry; Solar grade silicon refining; Si-Sn-Cu solvent; B removal fraction; Zr/Ti additive; Solubility product; Boride; Solid solubility; Directional solidification; Bulk Si separation; High entropy alloy.