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Purification of metallurgical-grade silicon using Si–Sn alloy in presence of Hf, Zr, or Ti

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ABSTRACT

Hf, Zr, or Ti was employed as additive to enhance removal of the main impurities from metallurgical-grade Si (MG–Si) during the Si–Sn alloy refining process. The microstructure of Si-Sn alloy without/with Zr, Hf, or Ti was observed and analyzed by electron probe microanalysis (EPMA) to investigate the distribution of impurities. Compositions of intermetallic phases precipitated in Sn or among the grain boundaries of Si were quantitatively analyzed using EPMA. The mechanisms of their formation and the removal of impurities are discussed. The results of Si refining showed that the addition of Hf or Zr slightly enhanced the removal of Al. The high refining temperature in the Si-Sn alloy refining process was responsible for the low extraction of B. Most of Zr, Hf, or Ti was removed simultaneously with other impurities during the Si–Sn alloy refining process.

1. Introduction

Si is still the main material for manufacturing solar cells to convert solar energy to electrical energy. Si is thus an important material in the fields of sustainable and clean energy. As the impurities in Si decrease the photovoltaic conversation efficiency significantly, metallurgical--grade Si (MG–Si, purity: > 99%) must be upgraded to solar–grade Si (SoG–Si, purity: > 99.9999%) to maintain high photovoltaic conversation efficiency.

SoG-Si is mainly manufactured by the Siemens process, which is a chemical manufacturing approach. This process is costly and may cause environmental problems because of its complex chemical processes. Therefore, a more economic and environmentally friendly technology is necessary and many approaches have been proposed and developed. Alloy refining (or solvent refining) is proposed because MG-Si can be refined below its melting temperature and no waste gases or slags will be discharged into the environment. The segregation coefficients of impurities in MG-Si decrease with decrease in refining temperature, indicating that low refining temperatures are preferred for Si purification. Many alloy refining approaches have been proposed such as Si–Sn [1–3], Al–Si [4–8], Si–Ga [9], Si–Fe [10,11], Si–Na [12,13], Si–Cu [14,15], Al–Si–Sn [16], and Al–Si–Zn [17]. Although alloy refining is efficient for the removal of impurities, the residual concentrations of impurities in the refined Si are still larger than that required for SoG-Si, particularly for B (boron), which is more difficult to remove than others.

Small amounts of transition metals such as Zr, Hf, and Ti are employed as additives to enhance B removal because of their strong affinity for B. The segregation coefficients of these elements between the solid/liquid phases are extremely small (4.9×10^{-6} [18], 1.6×10^{-8} [19], and 2.0×10^{-6} [19] for Hf, Zr, and Ti, respectively, at the melting point of Si, 1687 K). This indicates that these elements can be removed with the impurities and that their addition will not contaminate the refined Si. For example, extraction ratios of Zr, Hf, and Ti were reported as 99.998% (from 32000 ppmw to 0.6 ppmw; ppmw indicates per million by weight), 99.9994% (from 62000 ppmw to 0.4 ppmw), and 99.997% (from 17000 ppmw to 0.5 ppmw), respectively, in our previous study when Al–Si alloy was the refining solvent [20]. Si–Sn alloy is also one of the promising solvents for Si refining because the yield of refined Si was significantly larger than that using other solvents to refine Si (i.e., the loss of Si in the solvent after Si refining is significantly small) according to the Si–Sn binary phase diagram [21]. Some impurities were not removed efficiently using Si–Sn solvent and a more efficient approach is required to enhance impurity removal [1–3].

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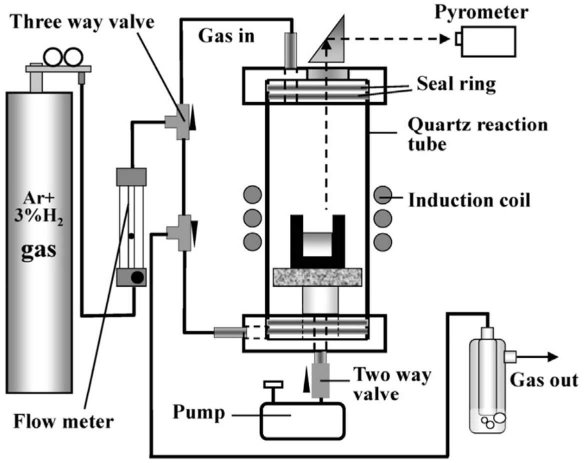

Fig. 1. Schematic of the induction furnace employed for Si solidification refining.

As the additives (Zr, Hf, and Ti) enhanced the removal of some impurities when Al–Si alloy was employed as the refining solvent, we expect they could enhance the removal of impurities in the Si–Sn solvent refining process. However, few studies have been reported, to the best of our knowledge. In this study, the microstructure of Si–Sn alloy—without/with addition of Zr, Hf, or Ti—after Si refining was observed and analyzed by electron probe microanalysis (EPMA) to investigate the distribution of impurities in different precipitated phases. The effects of Zr, Hf, or Ti on the removal of the impurities are also discussed.

2. Experimental

An induction furnace was employed to carry out Si solidification refining and its schematic is shown in Fig. 1. Thirty-five grams of MG–Si (99.38%) and Sn shots (99.999%) with different amounts of Hf (99.95%), Zr (99.95%), or Ti (99.99%) granules were charged in a high-purity dense graphite crucible (99.98%, 25 mm inner diameter, 35 mm outer diameter, 65 mm depth, and 80 mm height). The composition of the Sn-Si alloy was Sn–60 at%Si (Sn–26 wt% Si), whose melting point was 1628 K (59 K lower than the melting point of pure Si, 1687 K). This composition was chosen considering the yield of Si after purification. Higher concentration of Sn may be better for Si purification, but the yield of Si might be too low to be acceptable for an economical technology. The concentration of each additive (Zr, Hf, or Ti) in the Si–Si alloy was set to 0.2 at% and 1 at% to investigate the influence of the amount of additives on removal of impurities.

The sample was charged in the graphite crucible and placed in an induction furnace. The bottom of the graphite crucible was located 35 mm lower than the bottom of the induction coils to ensure that the precipitated Si crystals were separated from Sn by electromagnetic force. The purpose of separation of Si and Sn was to reduce the loss of Sn in the following acid leaching process, thus making this approach more economical. A vacuum pump was employed to evacuate the air in the chamber of the furnace to avoid oxidation of the Si–Sn alloy. After evacuation, the chamber was refilled with a mixture of Ar + 3% H_2 before heating. The evacuation and refilling process were repeated at least thrice to ensure that the air in the chamber was evacuated completely.

The sample was first heated to 1743 K at 105 K/min to ensure it melted completely. The molten melt was held at 1743 K for 30 min to homogenize the composition and then cooled to 1143 K at 4 K/min for solidification refining. The temperature of the melt was monitored using a pyrometer through a triple prism, as shown in Fig. 1. The precipitated Si crystals were agglomerated at the bottom of the melt with electromagnetic force in the solidification process, as shown in Fig. 2. The solidified sample was cut into two pieces along the cross-section. One piece was polished for EPMA analysis. The agglomerated Si crystals in the other piece were cut from the Sn alloy and crushed to powder (< 75 μm). The pulverized Si was first leached with HCl + HF (1:1 by volume; guaranteed reagent HCl: 36–38% and guaranteed reagent HF: 40%) and then aqua regia (HCl:HNO_3 = 3:1 by volume; guaranteed reagent HNO_3: 65–68%) at 348 ± 1 K for 3 h, respectively. The weight ratio of solid to liquid for each leaching process was 1:10. Finally, inductively coupled plasma optical emission spectroscopy (ICP–OES) was employed to determine the concentrations of impurities in the leached Si particles.

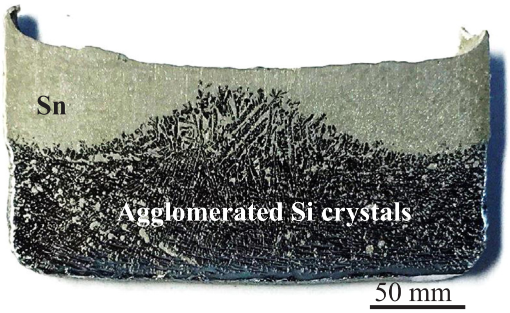

Fig. 2. Cross-section of Sn–60 at% Si alloy after the solidification refining process with electromagnetic separation.

3. Results and discussion

3.1. Microstructure of the Si–Sn alloy without additives

Fig. 2 shows Si–Sn alloy after solidification with electromagnetic force. The Si–Sn alloy was separated into two different regions. The lower region contained agglomerated Si crystals (black color) and the upper region was Sn, indicating that Si was separated from Sn by the electromagnetic force. The mechanism of separation has been reported [4]. Some small Sn phases were observed in the region of agglomerated Si crystals, as shown in Fig. 2.

Fig. 3 shows enlargement of the agglomerated Si crystal region in the Si–Sn alloy without additives. The most observed phases were Si and Sn, which were separated from each other. The enlarged image shows that the main impurity phase—except for Sn—was the Fe–bearing phase because Fe is the main impurity in metallurgical–grade Si (3494 ppmw), as shown in Table 1. Many small granules were observed in Sn. The compositions of Si, Sn, the granule phase, and the Fe-bearing phase were determined quantitatively by EPMA and the results are shown in Table 2. The Fe–bearing impurity phase was Si–Fe and the average calculated formula was $FeSi_{2.47}$. $FeSi_{2.47}$ was assigned to α $FeSi_{2.4}$ [22]. The α-$FeSi_{2.4}$ compound is stable in temperature range 1201–1480 K while another (β-$FeSi_2$) compound is stable below 1201 K in the Fe–Si binary system [22]. α-$FeSi_{2.4}$ rather than β-$FeSi_2$ was observed because the sample was cooled from 1743 K to 1143 K, which was close to the temperature region (1201–1480 K) of stable α-$FeSi_{2.4}$. The Sn phase contained small amounts of Si, Al, and Ca, according to Table 2. After solidification refining (finished at 1143 K), the average concentration of Si in the Sn phase was 1.21 at%, which was close to the liquidus of the Si–Sn system (1.12 at% at 1150 K) [21]. Al was the main impurity after Fe in metallurgical-grade Si, as shown in Table 1. Its enrichment in the Sn phase indicated it could be removed with Sn in the following leaching process. The concentration of Ca in metallurgical-grade Si is 165 ppmw. However, the average concentration of Ca in the Sn phase was 2.37 at% (0.8 wt%), which was larger than expected. The large concentration of Ca determined was influenced by the Sn matrix (the peak of Ca was 107.51 mm and that of Sn was 115.12 mm). The granule phase in the Sn phase was pure Sn, which had smaller