Refining of Si by the Solidification of Si–Al Melt with Electromagnetic Force

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Aiming at the development of Si solidification refining process with Si–Al melt, investigations on separation method of Si grains solidified from Si–Al melt and the laboratory scale refining test were carried out. By the use of electromagnetic force under the fixed alternating magnetic field, solidified Si grains were successfully agglomerated in the Si–Al alloy and the high Si density part was obtained, although the use of gravity force was not effective. Furthermore, the refining test with induction heating revealed the high purification ability of this refining.

KEY WORDS: refining; solidification; electromagnetic force; Si; Si–Al melt.

1. Introduction

The production amount of solar cell, especially that of polycrystalline Si(poly-Si) type, increases significantly in response to a growing demand for clean energy worldwide. As the amount of expensive off-grade Si for semiconductor (SEG-Si), a primary resource of poly-Si solar cells, is limited, solar grade Si (SOG-Si) would be short of supply with increasing demand for solar cell in the near future. In order to overcome the problem, a new metallurgical refining process of SOG-Si using metallurgical grade Si (MG-Si) as a starting material has been developed in Japan. However, further development of low cost refining process is required for spreading Si solar cells.

Most impurity elements in Si possess the retrograde solidus curves, namely rapid decrease in solubilities with temperature decrease much above the eutectic temperature in each binary system, and are considered to be more thermodynamically unstable at lower temperature. Although directional solidification refining processes, Czochralski (CZ) method and the floating zone (FZ) method, etc., are known to be effective for the removal of impurity elements from Si due to the extremely small segregation ratios of metallic impurities between solid/liquid Si, more effective purification is expected at lower temperature with the tendency of solidus curves of Si. Accordingly, the authors have been aiming at the development of innovative low cost Si refining processes at lower temperature, which consist of alloying of Si with Al, solidifying Si from that melt and collecting the refined Si, and clarified the purification ability thermodynamically by measuring or evaluating the segregation ratios of major impurities between solid Si and Si–Al melt.

As is described later, it is quite difficult to obtain the bulk Si solidified from Si–Al melt. Therefore, removal of inter-grains composed of Si–Al eutectics between Si grains by acid cleaning is necessary for collecting the solidified Si from Si–Al melt, and separation of Si grains in the melt during cooling the alloy would be of significant importance for the effective acid cleaning process. On separation of solid Si in the Si–Al alloy with electromagnetic force, segregation of Si in the hyper-eutectic Al–Si alloy for the high wear-resistance by applying Pinch force from difference in the conductivities of Al–Si melt and solid Si under the DC electric field with the steady magnetic field was archived by Park et al. In the present study, separation of Si grains in the Si–Al melt was investigated by use of the fixed alternating magnetic field, where improvement of Si segregation is mainly caused by the induced fluid flow. Also, the laboratory scale refining test was conducted by solidification under the fixed alternating magnetic field by induction heating.

2. Experimental Procedures

2.1. Separation of Si Grains from Si–Al Melt by Gravitation Force

In order to evaluate the separation of solidified Si grains from Si–Al melt by the difference in density between solid Si (≈2300 kg/m³) and Si–Al melt (≈2400 kg/m³), solid Si dispersed Si–Al alloys were settled under the external heating.

A SiC electric resistance furnace connected to a PID controller with a Pt/6%Rh–Pt/30%Rh thermocouple was used. Four grams of Si–55.3at%Al alloy was settled for 12h in a purified Ar atmosphere at 1173 K, where the liquidus composition in the Si–Al system is Si–64.6at%Al, for the investigation of the morphologies of solidified Si grains in the Si–Al melt. From lever rule, molar ratio of solid Si to Si–Al melt is 0.168. Here, two types of Si–Al alloy were prepared for investigating the influence of Si grain sizes on
the morphologies. First one was prepared by melting the weighed Si–Al mixture in a dense graphite crucible with an induction furnace and quenching in water, for the morphologies of the needle-like solidified Si grains. Second one was prepared by pelletizing the Si–Al powder mixture (diameters of both powder are less than 32 μm) at 100 MPa for the morphologies of the minute Si particles.

2.2. Solidification of Si–Al Alloy under the Fixed Alternating Magnetic Field
(For separation of Si grains from Si–Al melt with electromagnetic force and for refining test of solidification refining with Si–Al melt)

Figure 1 shows the experimental apparatus mainly composed of an induction furnace (12 kV A, 50 kHz). A quartz tube (50 mm OD, 44 mm ID, 500 mm length) was used as a reaction tube, and the perpendicular position of the sample was changed with a stepping motor unit controlled by PC. During the experiments, surface temperature of the sample was monitored by a dual wavelength infrared pyrometer through the gas inlet tube and the prism.

A 4 g sample, Si–55.3 at%Al alloy (liquidus temperature 1 273 K) or Si–64.6 at%Al alloy (liquidus temperature 1 173 K), was inserted into a purified dense graphite crucible (5N2, I.D. 12 mm, O.D. 15 mm, height 50 mm), whose bottom was initially set 3 cm below the lower end of the induction coil in the reaction tube. After melting and holding at 1 323 K or 1 223 K for 10 min in an Ar–10%H2 gas atmosphere, the sample was cooled and solidified by lowering the sample at the rate of 0.25–1.0 mm/min. For the refining test, the high Si density part of the solidified sample, which accounted for 40–50% of the entire sample, was cut out and crashed into the particles less than 840 μm, and Si was collected by dissolving the intergrains of Si composed of Al–Si eutectics with H2SO4 added dilute aqua regia. Fe, Ti, Al and B contents of refined Si were determined by ICP emission spectroscopy and P content was determined by molybdenum blue absorption spectrometry.

Si–Al alloys were prepared with pure Al and non-doped single crystalline Si for separation of solidified Si grains, or synthesized MG-Si, which was made by melting single crystalline Si with high-grade Fe, Ti, Al, B and P powders in a dense graphite crucible at 1 723 K in an Ar atmosphere for 1 h and quenching in water, for the refining test.

3. Results and Discussion
3.1. Separation of Si Grains From Si–Al Melt
3.1.1. Separation with Gravity Force

Prior to separation of Si grains from Si–Al melt, critical rate of Si faceted growth from the Si–Al alloy was discussed for evaluating the probability of bulk Si growth of Si from Si–Al melt in the refining process. Under the assumption of diffusion control growth for Si faceted growth, Si growth rate, \( V \) (m/s), can be calculated from Eq. (1) by steady-state diffusion equation on Si.

\[
V = D_{Si} \frac{\partial X_{Si} \text{ in Si–Al melt}}{\partial x} \quad \text{............(1)}
\]

Here, \( D_{Si} \text{ in Si–Al melt} \) (m²/s) and \( X_{Si} \text{ in Si–Al melt} \) denotes the diffusion coefficient of Si and Si content at the solid/liquid interface in the Si–Al melt, respectively, and it is supposed that difference in molar volumes of solid Si and any composition of the Si–Al melt can be ignored. When Si–Al alloy is placed in a temperature gradient, \( \partial T/\partial x \) (K/m), Si growth rate is rewritten as Eq. (2).

\[
V = D_{Si} \text{ in Si–Al melt} \frac{\partial X_{Si} \text{ in Si–Al melt}}{\partial T} \frac{\partial T}{\partial x} \quad \text{............(2)}
\]

As shown in Fig. 2, \( \partial X_{Si} \text{ in Si–Al melt}/\partial T \) is the largest in the slope of liquidus curve without solidification of Si in the melt apart from solidification interface under the hypothetical constant temperature gradient. From Eq. (2), critical growth rate, \( V_c \) (m/s), at 1 173 K is expressed as Eq. (3) with \( \partial X_{Si} \text{ in Si–Al melt}/\partial T=0.0011 \) from the Si–Al phase diagram\(^7\) and \( D_{Si} \text{ in Si–Al melt} = 1.8 \times 10^{-8} \text{ m}^2/\text{s} \)\(^8\).

\[
V_c = 2.0 \times 10^{-11} \frac{\partial T}{\partial x} \quad \text{............(3)}
\]

If a temperature gradient is as much as 5 000 K/m, critical
growth rate becomes $1.0 \times 10^{-8}$ m/s. Here, Si growth was investigated experimentally by directional solidification of Si–55.3at%Al alloy from 1323 K at the cooling rate of 0.0167 K/s in a temperature gradient of 500 K/m or 5000 K/m, and cross sections of samples are shown in Fig. 3. Si faceted growth could not be obtained in both samples, and these results are in accordance with the calculated result of the growth rate if the experimental growth rate is taken as $\partial x / \partial T'$, where $T'$ (K/s) is the cooling rate. Compared with Si growth rate at the order of $10^{-5}$ (m/s) at directional solidification of Si in the metallurgical refining process for Si [1], critical growth rate of Si from Si–Al melt is much smaller, and bulk Si growth is unrealistic for an actual refining process with Si–Al melt. Therefore, in the Si solidification refining process with Si–Al melt, removal of intergrains composed of Al–Si eutectics between Si grains by acid cleaning is necessary for collecting the solidified Si.

In order to investigate the behavior of solidified Si grains from Si–Al melt by flotation, Si–55.3at%Al alloys were settled at 1173 K. In both pre-melted and pelletized samples after settling, Si grains and particles distributed uniformly in the sample as shown in Fig. 4, and were found to stay without flotation during the experiment. Therefore, it is clarified that the separation of the solidified Si from Si–Al melt by flotation is difficult probably due to the high viscosity of the melt in which particles dispersed. Henceforth, the effect of magnetic force was investigated.

3.1.2. Separation with Electromagnetic Force

Figure 5 shows the cross section of Si–55.3at%Al alloy solidified in the induction furnace, where cooling rate was 20 K/min around the liquidus temperature. Needle-like solidified Si grains were successfully agglomerated at the bottom of the sample, and the high Si density part was obtained nevertheless the density of solid Si is smaller than that of Si–Al melt. Agglomeration of Si with electromagnetic effect is explained as follows. In our sample setup shown in Fig. 6, Lorentz force from the interaction between the induced swirl current and the magnetic field is generated toward the center of the melt, and the upward and downward fluid flow are induced. On the other hand, temperature gradient is driven to the perpendicular direction from the difference in the swirl current intensity. Therefore Si is expected to start solidifying at lower positions of the sample at lower temperature, and needle-like Si grains are carried.
to the bottom by the downward fluid flow induced from the inward Pinch force, subsequently pile up by adhesions each other. Measured with a pyrometer, in the present work, Si–Al melt was heated more intensively than a graphite crucible so the effect of electromagnetic force would be effective on the Si–Al melt. Temperature gradient in the melt was confirmed and measured 10 K/cm by pyrometer when using a SiO₂ crucible instead of a dense graphite crucible, although the use of a graphite crucible is expected to decrease the temperature gradient due to the higher thermal conductivity of graphite than SiO₂. Accordingly, solidification of Si–Al alloy under the fixed alternating magnetic field can bring extensive segregation of Si by induced temperature gradient and fluid flow surpassing the gravity force, furthermore was found to be a suitable technique for the effective solidification refining of Si with Si–Al melt.

3.2 Refining Test of Solidification Refining of Si with Si–Al Melt under the Fixed Alternating Magnetic Field

Synthesized MG-Si of which compositions are summarized in Table 1 were alloyed with pure Al to prepare Si–55.3at%Al alloy for SR-01–04 and Si–64.6at%Al alloy for SR-05 and 06. Temperature profiles during cooling are shown in Fig. 7. Cooling rates around liquidus temperatures were ranged from 10 to 20 K/min. Determined impurity contents of refined Si together with removal fractions are summarized in Table 2, where removal fraction is defined from the ratio of the impurity content of refined Si to that of synthesized MG-Si. The Si yield after the purification would be 72% for SR-01–04 and 64% for SR-05–06 from the initial compositions of the melt and the eutectic composition, assuming that all of Si grains solidified down to the eutectic temperature were collected. Large removal fractions of Fe and Ti were obtained although those were not so large as expected from extremely small segregation ratios5) between solid Si and Si–Al melt summarized in Table 3. Removal fractions of B were larger than those evaluated from directional solidification calculation with the segregation ratio5) (solidified from 1 273 K; removal fraction 97.4%, from 1 173 K; 98.5%), and this is caused by decrease in B content of Si–Al melt due to TiB₂ formation with soluble Ti which was clarified in the previous work,9) whereas removal fractions of P show fairly good agreements with evaluated values (solidified from 1 273 K; removal fraction 94.7%, from 1 173 K; 97.0%). Al contents of refined Si were larger than solid solubilities of Al in Si (260 ppmw: 1 273 K, 160 ppmw: 1 173 K),10) and this tendency implies the non-equilibrium solidification occurred. As a whole, solidification refining of Si with Si–Al melt under the fixed alternating magnetic field is clarified to be effective.

4. Conclusions

(1) For the separation of Si grains solidified from Si–Al melt during the solidification refining, the use of electromagnetic force was found to be effective from obtaining the high Si density part in the solidified Si–Al alloy, although the gravity force was not effective.

(2) Laboratory scale refining test of the solidification refining of Si with Si–Al melt was demonstrated using electromagnetic field, and the high purification ability of this refining was confirmed.

| Table 1. Impurity contents of synthesized MG-Si (ppmw). |
|-------------|-------------|-------------|-------------|-------------|-------------|
| Sample No.  | Fe          | Ti          | Al          | B           | P           |
| PrSi-1      | 4500        | 691         | 1280        | 56          | 36          |
| PrSi-2      | 2160        | 248         | 1560        | 36          | 19          |

| Fig. 7. Time-cooling curves of Si–Al melts during solidification with induction heating. |

| Table 2. Impurity contents (ppmw) and removal fractions in the parenthesis of refined Si. |
|-------------|-------------|-------------|-------------|-------------|-------------|
| Sample No.  | Source      | Fe          | Ti          | B           | P           |
| SR-1        | PrSi-1      | 13 (99.7%)  | 5.2 (99.2%) | 0.81(98.6%) | 0.93(97.4%) | 599(53.1%) |
| SR-2        | PrSi-1      | 13 (99.7%)  | 2.7 (99.6%) | 0.88(98.4%) | 1.2(96.7%)  | 534(58.1%) |
| SR-3        | PrSi-2      | 20 (99.1%)  | 2.8 (98.9%) | 0.71(98.1%) | 0.72(96.3%) | 575(63.1%) |
| SR-4        | PrSi-2      | 27 (98.8%)  | 4.5 (98.2%) | 1.09(94.8%) | 1.1(95.1%)  | 602(61.3%) |
| SR-5        | PrSi-1      | 47 (99.0%)  | 7.7 (98.9%) | 0.98(98.3%) | 0.42(98.8%) | 538(57.8%) |
| SR-6        | PrSi-1      | 36 (99.2%)  | 5.6 (99.2%) | 0.99(98.2%) | 0.66(98.2%) | 453(64.5%) |

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