Effect of Si Content on the Morphology Evolution of the Si Primary Dendrites in Al-Si Alloy Solvent Refining Process

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Abstract

Solvent refining with Al-Si alloy is a promising purification method for production of solar-grade silicon (SoG-Si) feedstock owing to the advantages of low production cost and high impurity removal efficiency. In this process, larger refined Si primary dendrites are easily collected after acid leaching, which is favorable to recovery, thereby to reduce the production cost. Hence, the growth behavior of the precipitated Si crystal must be investigated systematically. In present work, the morphology evolution of solidified Al-Si alloys with a wide range of Si content (30~70 wt.%) was analyzed. The typical plate-like Si primary dendrites grown following the twin plane re-entrance edge (TPRE) mechanism formed in all alloy compositions. As increasing the Si content from 30 wt.% to 50 wt.%, the Si primary dendrites underwent a coarsening process attributed to the preferred growth along <211> and <111> directions, leading to an increase in the experimental recovery rate. However, the preferred growth along <211> direction was inhibited when the Si content is higher than 55 wt.%. Moreover, the broken effect originating from grain collision and thermal stress on the Si primary dendrites was enhanced as further increasing the Si content, resulting in a decrease in the experimental recovery rate. Therefore, the optimum composition is determined as Al-50~55 wt.% Si for solvent refining solution, based on the cost reduction consideration.

1. Introduction

Solar cell production based on Si wafers has increased significantly over decades, as there is a growing demand for clean energy. Material resources for this application are mainly high-purity solar-grade silicon (SoG-Si), either for single crystal wafers or for multi-crystalline wafers. Currently, the SoG-Si feedstock is mainly produced via the traditional Siemens process or its modified alternatives [1], which is fairly energy intensive and environment-unfriendly [2]. As an alternative, the metallurgical refining processes, which employ metallurgical grade Si (MG-Si) as the starting materials, have been developed. There include, but no mean complete, slag treatment [3], plasma treatment [4], acid leaching [5], directional solidification [6], solvent refining [7], and so on. Among these, solvent refining is a promising technique for the SoG-Si feedstock production. It demonstrates the potential to removal almost all impurities in MG-Si, including B and P elements, relying on the decrease of segregation coefficients of impurities due to the lowered liquidus temperature [8].

Aluminum, in fact, has been validated as one of appropriate alloying elements, and being developed the advanced processing techniques [9, 10]. The refining process could be divided as follows: alloying MG-Si with Al, solidifying the Si phase, and separating the primary Si. There in general are two requirements that should be satisfied for this process. One is the purity of refined Si crystal, which is associated to the photoelectric conversion efficiency in the final cells; the other is the recovery of primary Si dendrites, which is related to the production costs of feedstocks.

Some interesting researches have been shown that most of the metallic impurities could be removed effectively, owing to the declined segregation coefficients by one or several orders of magnitude in Al-Si alloy. The residual metallic impurity concentrations for the purified silicon that was employed die casting scraps as starting materials were below 1 ppmw, except for Al, meeting sufficiently the specification of SoG-Si [11]. Moreover, removal of boron and phosphorous impurities that are generally considered as hardly removal impurities since their high segregation coefficients could be also exerted, either by adding trace amounts of Hf [12] or Ti [13] to Al-Si alloy or by lowering the cooling rate of Al-Si melt [14].

On the other hand, several collecting techniques have been carried on to recover primary silicon dendrites, such as super gravity separation [15, 16], electrolysis separation [17], heavy medium separation [18] and solidification under an electromagnetic field [9]. Using these techniques, the purified Si crystals could be recovered from Al-Si alloy, probably followed by acid leaching for the last two techniques. However, it is unavoidable that fine silicon particles will be lost during the collecting process in all solutions. Larger primary dendrites therefore should be grown during refining solidification process. To increase the dendrite thickness the realizable way is either to lower the cooling rate [19, 20] or to increase the Si content in the Al-Si alloy. Based on the mass conversation law, the later solution is more effective. J.L. Gumaste, et.al [21] investigated the effect of Si content on the recovery rate of primary Si. The results showed that the optimum alloy composition is Al-35 wt.% Si, for which the recovery rate of primary Si was 58.8%. Although this value is as high as 99.42% of the theoretical one, the recovery rate should be further improved, once considering the production cost. However, there is little work focusing on this issue, especially on illustrating systematically the relationship between Al-Si alloy composition and the recovery rate of primary Si until now.

The present study is aimed at investigating the effect of Si content on the morphology evolution and recovery rate of the Si primary dendrites during solvent refining process. A series of samples with various Al-Si alloy compositions (Si content from 30 wt.% to 70 wt.%) was prepared. The morphology and recovery rate of Si dendrites was analyzed, and then the optimum alloy composition was determined. Based on the obtained results, the growth model of Si dendrites as increasing Si content was proposed.

2. Experimental Details

The starting materials were MG-Si lumps and commercial Al powder (2N, 200–400 mesh), which were blended together to form Al-*x*wt.% Si (where *x* is 30, 40, 50, 55, 60, 70) mixtures. Approximately 30 g mixtures for each composition were put in a corundum crucible and then heated to 1450°C and held for 2 h in a SiC electric resistance furnace (GSL-1600X of MTI, Hefei) under an flowing Ar-4%H_2 atmosphere to form alloy melts. Then, the alloy melts were cooled down to 600°C with a constant cooling rate of 3°C/min and held for 2 h. Afterwards the power of furnace was turned off, and the samples were treated by furnace cooling.

The obtained ingots were cut along vertical direction to form two parts using a diamond wire cutting machine (STX-603, MTI). One part was polished and slightly leached with HCl solution (6mol/L) to analyze the microstructure using the Metallographic Microscope (ZMM-500, Zhoushan, China) and scanning electron microscope (SSX-550, SHIMADZU). The macrostructure of ingots were scanned by Canon scanner (FAX-L1418SG, Canon), and the length and width of primary Si dendrites were statistically analyzed by IPP (Image-Pro plus) software. In this paper, the primary Si grain was defined as larger than 0.5 mm in size. As illustrated in Fig. 1, the defined primary Si was marked by red, while the grains with no more than 0.5 mm in size was not counted (as grains marked by blue circle in Fig. 1).

The other part of the ingot was acid leached to separate and collect the primary Si crystals. The acid leaching process was as follows: first, the sample was immersed in hydrochloric acid solution (6 mol/L) for 6 h to dissolve the metal Al; then, the Si crystals were leached in aqua regia solution for 6 h to remove other metals and compound phases, and third was in dilute hydrofluoric acid solution (0.5 mol/L) for 1.5 h to react with SiO_2 phase. These three leaching processes were performed at 298 K. After leaching, the collected Si particles were sieved by 35 mesh standard sieve (0.5 mm) to separate the primary Si and eutectic Si. Based on the Al-Si phase diagram and the mass of collected primary Si, the theoretical and experimental recovery rates, *η*, could be calculated following equations (1) and (2).

$$\eta_{theoretical} = \frac{f_x}{x\%} \times 100\% \quad (1)$$

$$\eta_{experimental} = \frac{m_x}{M_x \times f_x} \times 100\% \quad (2)$$

where f_x is the fraction of precipitated Si phase calculated by the lever law from the Al-Si phase diagram, m_x is the weight of collected primary Si after sieving, M_x is the total weight of Si raw materials, $x\%$ is the Si content in Al-Si alloy.

3. Results

The morphology evolution of primary Si dendrites for Al-Si alloy with Si content from 30 wt.% to 70 wt.% is depicted in Fig. 2. Since the investigated alloy composition is addressed at hypereutectic alloy, the shape of primary Si appears plate-like structure, which is a characteristic morphology for the precipitated grains in hypereutectic Al-Si alloy with high Si content [22]. It is clear from Fig. 2(a) that, for the Al-30wt.% Si alloy, the primary Si dendrites distribute homogeneously in the whole eutectic matrix, some of them are more than 10 mm in length. Although the primary silicon appears to be a thin needle shape, most of the silicon dendrites are realistic plate-like morphology after acid leaching (inserted in Fig. 2(a)). As increasing the Si content in Al-Si alloy, the primary Si dendrites seem to be larger, appearing thicker plate-like morphology, which are easily distinguished by naked eyes through the inserted figures in Fig. 2(a) and 2(e). Moreover, more silicon grains exist with increasing the Si content in Al-Si alloy. Therefore, it could be concluded that the primary Si dendrites become larger and denser in the alloy with high Si content after solidification.

In order to analyze the morphology evolution of primary Si dendrites for Al-Si alloys with various silicon contents, the length and width of silicon dendrites have been calculated by means of the IPP software (mentioned in Sect. 2). Herein, the primary Si was defined as grains larger than 0.5 mm in size. All grains on the whole vertical section surface for each sample were marked and countered to improve the calculation accuracy, thereafter the average values were obtained. The effect of Si content on the length and width of primary Si dendrites is depicted in Fig. 3. It can be seen that the average width of primary Si dendrites increases gradually from 0.54 mm to1.23 mm with increasing Si content from 30 wt.% to 70 wt.% in Al-Si alloys. This result indicates that the thickness of Si dendrites become larger in the Al-Si alloy with high Si content, which is beneficial for improving the recovery rate of the refined Si [20]. Moreover, the average length of primary Si dendrites demonstrates similar tendency in the content range from 30 wt.% to 55 wt.%. This result is consistent with the conventional understanding that the Si size increases with increasing initial Si content in a hypereutectic Al-Si alloy [23]. However, further increasing the Si content (> 55 wt.%), the average length of primary Si dendrites decreases inversely. Consequently, higher Si content in Al-Si alloy has a detrimental effect on the growth of primary Si dendrites along the length direction. Undoubtedly, it could be deduced that higher initial Si content (> 55 wt.%) in the Al-Si alloy, will influence the growth pattern of the primary Si dendrites. This will be discussed detailed in next section.

Figure 4 shows the morphology of eutectic microstructure for (a) Al-30wt%Si, (b) Al-55wt%Si, (c) Al-70wt%Si alloys, and the collected eutectic silicon particles for (d) Al-30wt%Si and (e) Al-70wt%Si alloys after acid leaching, respectively. It can be seen from Fig. 4(a) that, for Al-30wt% Si alloy, the eutectic silicon has irregular shape, but aligning almost a line in the matrix. After leaching and sieving, fine eutectic silicon particles could be obtained, as shown in Fig. 4(d). As increasing the Si content in Al-Si alloy, there is no obvious difference in the shape and distribution for eutectic silicon grains. However, some grains with larger size exist in Al-Si alloys with high Si content (55 wt.% and 70 wt.%). Compared to Al-30wt% Si alloy, the collected silicon particles from Al-70wt% Si alloy after leaching and sieving seem to be larger (as shown in Fig. 4(d) and 4(e)).

It is crucial for solvent refining process to achieve recovery rate of refined Si as high as possible, aiming at the reduction of the production cost. The theoretical and experimental recovery rates were calculated according to equations (1) and (2), and the results are displayed in Fig. 5. From the results of the calculated theoretical recovery rates, it could be found that the theoretical recovery rate increases gradually from 66.4–93.8% with increasing the Si content from 30wt.% to 70wt.%. On the other hand, the experimental recovery rate increases from 44.6% for Al-30wt.% Si alloy to 83.7% for Al-55wt.% Si alloy, which could account for 94.9% of the theoretical recovery rate. However, further increasing the Si content of the alloy (> 55wt.%), the experimental recovery rate of primary Si dendrites decreases. When the alloy composition is Al-70wt.% Si, the experimental recovery rate drops to 68.2%. This tendency is consistent with the length evolution for the Al-Si alloy. Thus, the changed growth pattern influenced the recovery rate of refined Si. In view of production cost reduction, the optimum alloy composition is Al-50 ~ 55 wt.% Si.

4. Discussion

Based on the above results, it is clear that the growth pattern of Si primary dendrites has been changed as increasing the Si content in the Al-Si alloy. Generally, on solidification of the Al-Si hypereutectic alloy, the growth of plate-like Si primary dendrites lies on (111) planes and in [211] directions, where it occurs by the twin plane re-entrance edge (TPRE) mechanism [24]. Figure 8(a) illustrates schematically the growth model of the plate-like Si primary dendrites. In the case of Al-30wt.% Si alloy, the Si primary dendrites grew following this model, forming a thin plate-like morphology (shown in Fig. 2(a)). Due to the fragility of pure silicon or by over-energetic sieving, some thin plates were believed to be broken into fine particles (< 0.5 mm) after washing and sieving, which were classified as eutectic Si. This may be the reason why the experimental recovery rate is only 67.2% of the theoretical value.

Increasing the Si content, more Si atoms are supplied. As solidification proceeds, Si atoms diffuse to the growth front and are trapped by grain surfaces. One possibility is that the Si atoms are located at twin grain edges associated to the TPRE growth mechanism, resulting in a fast growth along < 211 > direction (length direction). The other possibility is that they are located at flat surfaces associated to the lateral growth mechanism [22], resulting in a growth tendency along < 111 > direction (width direction). For the Al-Si alloy with Si content below 50 ~ 55wt.%, both the length and width of the Si primary dendrites increased with increasing Si content, as shown in Fig. 3. This could be named coarsening process for the primary Si dendrites. The coarsened Si plates were not easily broken during sieving and washing processes, thereby improved the experimental recovery rate up to 94.9% of the theoretical recovery rate for the Al-55wt.% Si alloy.

When the Si content further increasing to more than 55wt.%, the average length of the Si primary dendrites decreased (shown in Fig. 3), indicating the advantage of the preferred growth along < 211 > direction was hindered. From the result of Fig. 2(e)-(f), more Si primary dendrites appeared, i.e. higher grain density in alloys with Si content of 60 ~ 70wt.%. During solidification, grain growth competes with each other. As the growing front with < 211 > growth direction meets neighboring grains, the growth will be hindered. This hindering effect would be enhanced with increasing the Si content, resulting in the decrease in length of the dendrites as increasing the Si content. However, the growth along < 111 > direction was not hindered since the typical two-dimension structure of the dendrites. Thereby, a multi-layered structure formed for the Al-60wt.% Si alloy (illustrated in Fig. 6), leading to the further increase in thickness.

Generally, the plate-like Si primary dendrites have a sharp tip morphology along < 211 > fast growth direction [24], which would be easily broken due to its fragile property, especially surrounded by plenty of neighboring grains. The broken tip usually has small size (< 0.5 mm, as shown in Fig. 4(b) marked as A), which could not be collected after leaching, resulting in a consumption of the refined Si. On the other hand, some crystals were peeled off from the coarsened or multi-layered dendrites due to extremely high thermal stress, as like the broken part marked B in Fig. 4(c), leading to the other type of consumption. These two kinds of broken crystal contributed to the reduction of the experimental recovery rate for alloys with Si content range of 55 ~ 70wt.%. For the further analysis, Si particles with size range of 0.2 ~ 0.5 mm was employed to characterize the broken crystals, and the statistic results are shown in Fig. 7, where the weight fractions of broken crystals to the total defined eutectic Si (< 0.5 mm) for Al-55wt.% Si, Al-60wt.% Si, and Al-70wt.% Si alloys were calculated, respectively. It can be seen from Fig. 7 that the weight fraction of broken crystals increases with increasing the Si content, indicating the enhanced broken effect at higher Si content. Thus, it is evident that the broken process has a detrimental effect on the recovery of the refined Si.

Consequently, we could summarize the growth pattern of the primary Si dendrites in the Al-Si hypereutectic alloy with various Si contents, as schematic shown in Fig. 8. In the investigated content range, i.e., 30 ~ 70wt.%, the growth of plate-like Si primary dendrites is dominated by the TPRE mechanism. For the Al-30 ~ 50 wt.% Si alloys, the Si primary dendrites grew largely along < 211 > and < 111 > directions with increasing the Si content, i.e., the primary dendrites underwent a coarsening process, resulting in an increase in experimental recovery rate of the refined Si. The highest recovery rate could be achieved for Al-50 ~ 55 wt.% Si alloys. In the case of Al-55 ~ 70 wt.% Si alloys, however, the growth along < 211 > direction was inhibited. Meanwhile, the broken effect originated from grain collision and thermal stress will be enhanced as further increasing the Si content, thereby leading to a decrease in the experimental recovery rate.

From the view of the production cost reduction, the optimum composition of the Al-Si alloy for solvent refining has determined as Al-50 ~ 55 wt.% Si, for which a desirable practical recovery rate, as well an attractive impurity removal efficiency of refined Si, could be obtained. The purity analysis will be detailed discussed elsewhere.

5. Conclusion

A series of Al-Si hypereutectic alloys with Si content of 30 ~ 70 wt.% were employed to investigate the effect of Si content on the evolution of grain morphology and recovery rate during Al-Si alloy solvent refining process. The results showed that the plate-like Si primary dendrites grown following the twin plane re-entrance edge (TPRE) mechanism have been formed in all alloy compositions. For the Al-30 ~ 50wt.% Si alloys, the evolution of Si primary dendrites was related to a coarsening process by growing along the preferred < 211 > and < 111 > directions with increasing Si content of the alloy, leading to an increase in the experimental recovery rate of the refined Si. When the Si content is at 50 ~ 55wt.%, the coarsened Si primary dendrites resulted in an extremely high recovery rate, up to 94.9% of the theoretical recovery rate. However, further increasing the Si content to 55 ~ 70 wt.%, the preferred growth along < 211 > direction was inhibited. Some broken crystals caused by grain collision and thermal stress appeared after solidification, which is named as broken process of Si primary dendrites, resulting in a decrease in the recovery rate of the refined Si. Based on the consideration of production cost reduction for Al-Si alloy solvent refining solution, it could be concluded that the optimum alloy composition is Al-50 ~ 55wt.% Si.

Declarations

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Authors' Contribution All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Mangmang Gao, Yu Zhao and Ang Gao. The first draft of the manuscript was written by Mangmang Gao and all authors commended on previous versions of the manuscript. All authors read and approved the final manuscript.

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