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Separation of primary Si and impurity boron removal from Al-30%Si-10%Sn melt under a traveling magnetic field

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Abstract: Separation of primary Si phase and removal of boron in the primary Si phase during the solidification process of the Al-30%Si-10%Sn melt under a traveling magnetic field (TMF) were investigated. The results showed that the agglomeration layer of the primary Si can be formed in the periphery of the ingot while the inner microstructures mainly consist of the eutectic α-Al+Si and β-Sn phases. The intense melt flow carries the bulk liquid with higher Si content to promote the growth of the primary Si phase which is first precipitated close to the inner wall of crucible with a relatively lower temperature, resulting in the remarkable segregation of the primary Si phase. The content of impurity B in the primary Si phase can be removed effectively with an increase in magnetic flux intensity. The results of electron probe microanalysis (EPMA) clearly indicated that the average intensity of the B Ka line in the α-Al phase region of Al-Si-Sn alloy is higher in the case of solidification under TMF than that of normal solidification condition, suggesting that the electromagnetic stirring can promote the B removal from the primary Si phase.

Key words: traveling magnetic field; Al-Si-Sn alloy; boron; solidification refining

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Crystalline silicon is one of the materials used for solar cells, accounting for over 90% of the photovoltaic (PV) materials [1]. However, the PV industry has to face a serious low-cost feedstock supply shortage due to a rapid expansion of the solar cell industry. To lower the production cost of Si solar cells, a promising way is to upgrade metallurgical-grade silicon (MG-Si) to solar-grade silicon (SoG-Si) with metallurgical treatments [2-5]. However, boron (B) element, an impurity in MG-Si, cannot be removed efficiently because of its low vapor pressure (lower than that of Si) [6] and large segregation coefficient (0.8 at 1,414 ºC) [7].

In recent years, considerable progress has been made in B removal from the MG-Si using hypereutectic Al-Si alloy solidification refining process at low temperatures [8-11]. In the alloy solidification process, the primary Si initially precipitates from supersaturated melt with decreasing temperature, during which more impurities, especially B, are enriched in the alloy by redistributing the impurities to the solid/liquid (S/L) interface. Adding pure Sn to the hypereutectic Al-Si alloy can effectively expand the crystallization temperature range to promote the growth of the primary Si [12, 13]. However, considering the diffusion kinetics of the impurities at the nearby growing Si surface, a more effective enhanced S/L segregation tendency of impurities has not been achieved.

In the present study, the traveling magnetic field (TMF) was applied during solidification of the Al-30%Si-10%Sn melt to separate the primary Si. Furthermore, the effect of the electromagnetic stirring on B removal from the primary Si during the solidification of the Al-30Si-10Sn melt was investigated.

1 Experimental procedure

Commercial purity Al (99.7 wt.%), Sn (99.99 wt.%) and MG-Si (99.7 wt.%) (all the compositions quoted in this work are in wt.% unless otherwise stated) were placed in a quartz crucible and melted by induction heating to prepare Al-30at.%Si-10at.%Sn alloy melts. The alloy melt was kept at 900 ºC for 20 min in a SiC electric

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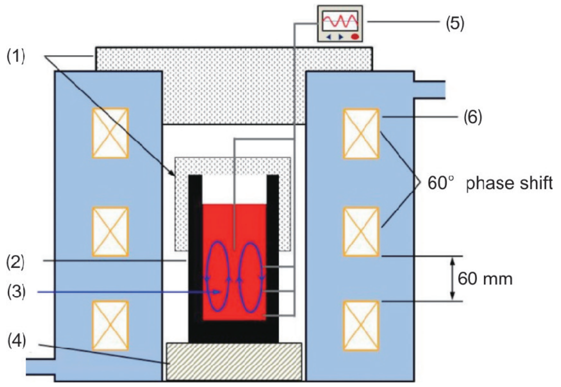
furnace, and then poured into a preheated cylindrical graphite crucible (with inner diameter 60 mm, outer diameter 80 mm, and depth 160 mm) at 900 ºC. The weight of the Al-30%Si-10%Sn alloy was controlled to be about 1,600 g for each experiment. Figure 1 gives the schematic illustration of this experimental apparatus. The thermal insulation material was applied at the top part of the graphite crucible to introduce an inhomogeneous temperature field into the liquid metal. The crucible was placed under the TMF with a frequency of 50 Hz. The magnetic field was generated using three co-coils fed from an alternating current supply providing a constant phase shift of 60° between adjacent coils. The setup gave rise to a magnetic field traveling vertically upward (TMF up) or downward (TMF down), which was described in detail by Wang et al. [14]. In this experiment, the application of TMF during solidification introduced a structure of flow field as shown in Fig. 1. The magnetic flux densities used in the present study were 0 mT, 10 mT, 25 mT, and 50 mT. The magnetic field was switched on when the melt was cooled to 870 ºC. K-type thermocouples were inserted into the melt to monitor the temperature. The samples were prepared through standard method. After polishing, the specimens were etched



(1) Asbestos, (2) Graphite crucible, (3) Structure of flow field, (4) Firebrick, (5) Temperature measurement system, and (6) TMF coils

Fig. 1: Schematic diagram of experimental apparatus

with 2% HF acid. Microstructures were observed using an optical microscope.

In order to investigate the impurity contents in primary Si, the primary Si flakes from the ingots were extracted by acid leaching to collect the refined Si, as described in Ref. [15]. The B distribution in the Al-Si-Sn alloy was examined by line analysis using an electron probe microanalysis (EPMA) with accelerating voltage of 15 kV. The B content in the primary Si phase was examined using an inductively coupled plasma mass spectrometry (ICP-MS).

2 Results and discussion

2.1 Separation of primary Si from Al-Si-Sn melt during solidification under TMF

Figure 2 shows the vertical sections of Al-Si-Sn alloys solidified under different conditions. In the case of the sample without TMF, the primary Si tends to be uniformly distributed in the whole ingot, ignoring the density difference between the primary Si and Al-Si-Sn melt, as shown in Fig. 2(a). However, when solidified under TMF with different magnetic flux densities, the primary Si phase is dramatically separated from the Al-Si-Sn melt and accumulates on the bottom and the periphery of the ingots, forming a segregation layer, as shown in Fig. 2(b)–(d).

To investigate the solidification structure at different positions, the Al-Si-Sn alloy solidified under TMF of 50 mT was chosen as a typical example. Figure 3 shows the microstructure at different positions marked in Fig. 2. In the sample without TMF, it can be seen from Fig. 3a (position 1) that the coarse plate-like primary Si phase distributes in eutectic α-Al+Si and β-Sn phase, and no intermediate compound is found. During the solidification process, the primary Si is first separated from the melt, and then binary eutectic α-Al+Si forms, followed by the solidification of the β-Sn phase, which can be identified by the solidification curve as shown in Fig. 4. When solidified under TMF (position 2 in Fig. 3b), the primary Si in the segregation layer has dramatically grown up and coarsened, which is helpful for the

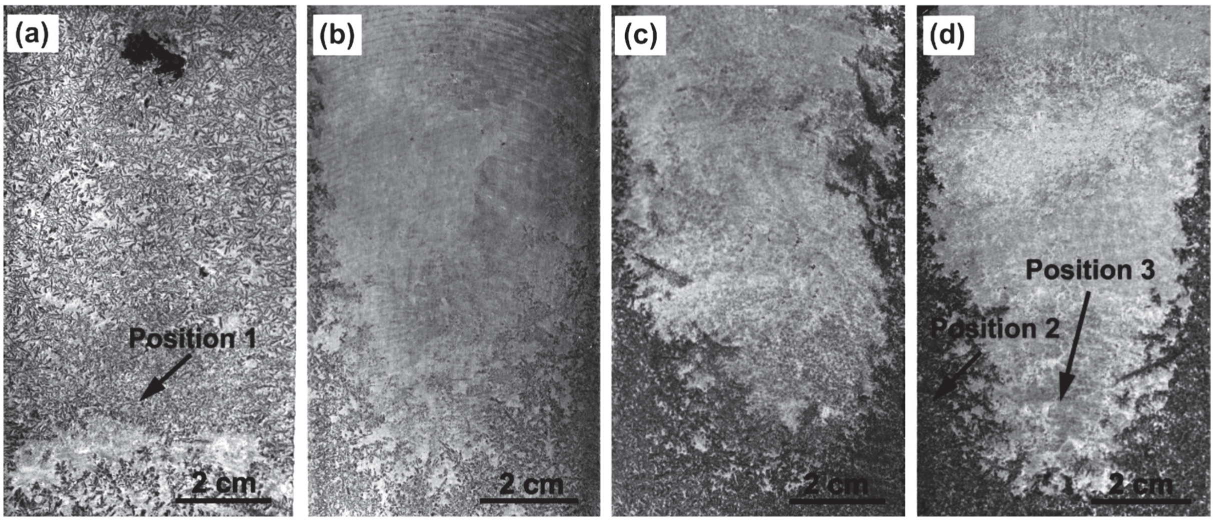


Fig. 2: Vertical sections of Al-30%Si-10%Sn alloy solidified under TMF with different magnetic flux densities: (a) 0 mT, (b) 10 mT, (c) 25 mT, and (d) 50 mT

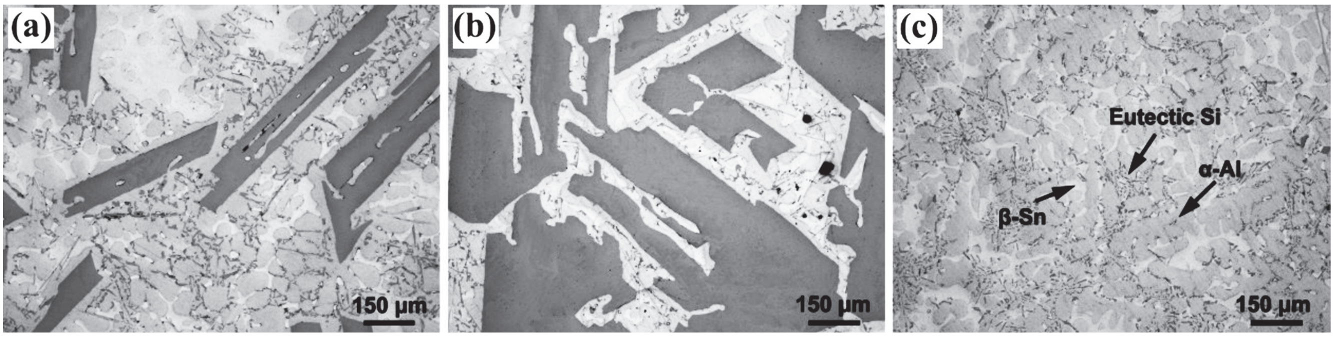


Fig. 3: Microstructure at different positions in Fig. 3: (a) position 1, (b) position 2, (c) position 3

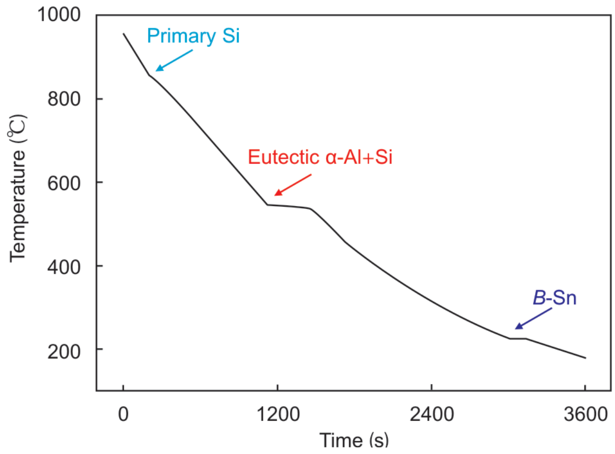


Fig. 4: Solidification curve of Al-30Si-10Sn alloy

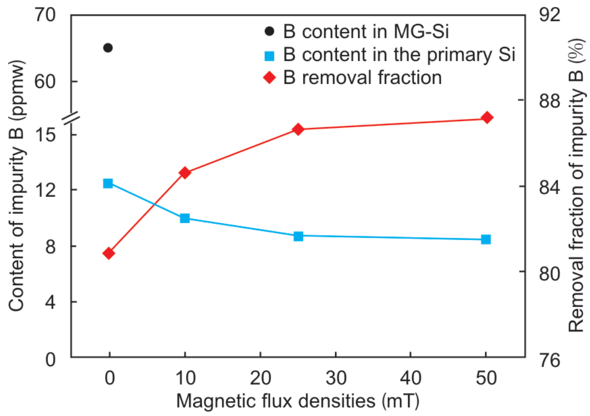


Fig. 5: B Content in primary Si phase under different magnetic flux densities

collection of primary Si after acid leaching. Figure 3(c) (position 3) reveals that the inside structure of the ingot is mainly eutectic α-Al+Si and β-Sn phase, and the primary Si cannot be found in the middle of the ingot.

The separation mechanism was described in the previous results [16, 17], and the agglomeration of the primary Si from Al-30Si-10Sn melt solidified under TMF is a complex process, which is related with the cooling conditions, flow field and crystal growth. The application of TMF during solidification of the Al-Si-Sn melt induces a recirculating flow in the radial-meridional plane, which consists of a double-vortex structure. Hence, a strong outward flow from the axis of the ingot towards the solidification front occurs where symmetrical segregation channels emerge [14, 18-20]. Such periodical flow structure, carrying the bulk liquid with higher Si content, promotes the growth of the primary Si formed close to the inner wall of the crucible where the temperature is lower. Therefore, high-density primary Si can be agglomerated on the bottom and the periphery of the ingot, which favors the separation of primary Si phases from the Al-Si-Sn melt.

2.2 Effect of electromagnetic stirring on B removal during solidification of Al-Si-Sn melt

Figure 5 shows the B content and removal fractions of the primary Si under TMF with different magnetic flux densities. The removal fraction can be calculated from the ratio of the impurity content of refined primary Si and the synthesized MG-Si. It is obvious that the impurity B can be effectively removed by normal Al-Si-Sn solidification refining (under TMF of 0 mT). The content of B reduces from 65 ppmw (in initial raw material MG-Si) to about 12.5 ppmw (in primary Si). In addition, the B content in the primary Si reduces with increasing magnetic flux density. The removal fraction of impurity B under TMF of 50 mT is extended to be about 87%, while that is 80.8% under 0 mT. This means that the solidification refining of MG-Si by Al-Si-Sn melt under the electromagnetic stirring can remove B with higher efficiency compared with normal solidification refining.

The segregation behavior of impurity elements determines the removal efficiency during alloy solidification process [15, 16]. To investigate the segregation behavior of impurity B during the growth of the primary Si, the B distribution in the Al-30Si-10Sn alloy was measured by EPMA, and the results are shown in Fig. 6. It can be clearly observed from Fig. 6(e) that the intensity of the B Kα line in the primary Si phase is low, but it increases in the α-Al phase until reaching the highest level in the β-Sn phase. This can be attributed to the transfer of impurity B to the liquid metal due to the solute redistribution [9, 10] during the movement of S/L interface towards the liquid, thus enhancing the removal efficiency of B from the primary Si.

To further investigate the effect of electromagnetic stirring on B removal, the distribution of impurity B during solidification of the Al-Si-Sn alloy without and with TMF were studied. Figure 7 shows the distribution of impurity B in Al-Si-Sn alloy under different conditions measured by EPMA. It can be seen that the average intensity of the B Kα line at the α-Al phase region of Al-Si-Sn alloy under TMF of 50 mT has a small increase by about 1.5 cps compared with that in the α-Al phase under normal Al-Si-Sn static state solidification. It may be because that the intense

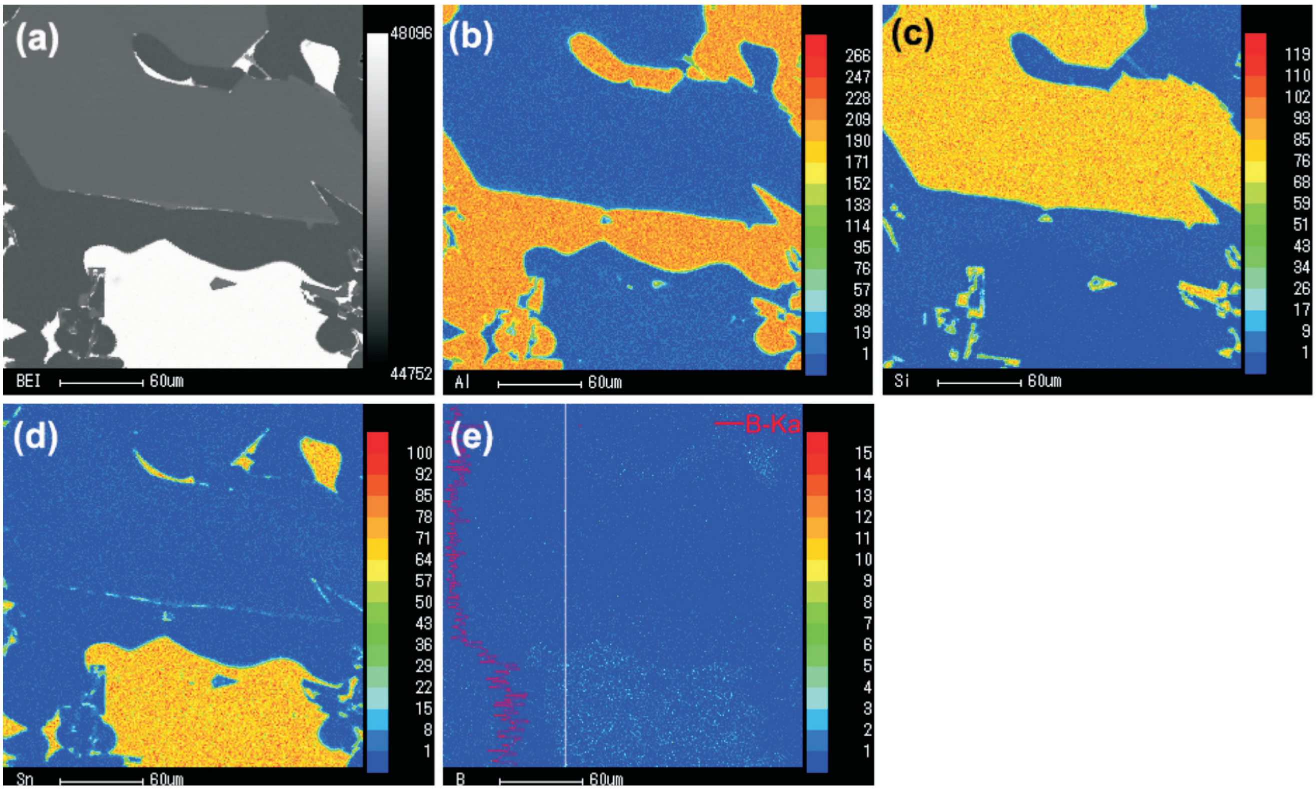


Fig. 6: B distribution in Al-30Si-10Sn alloy measured by EPMA

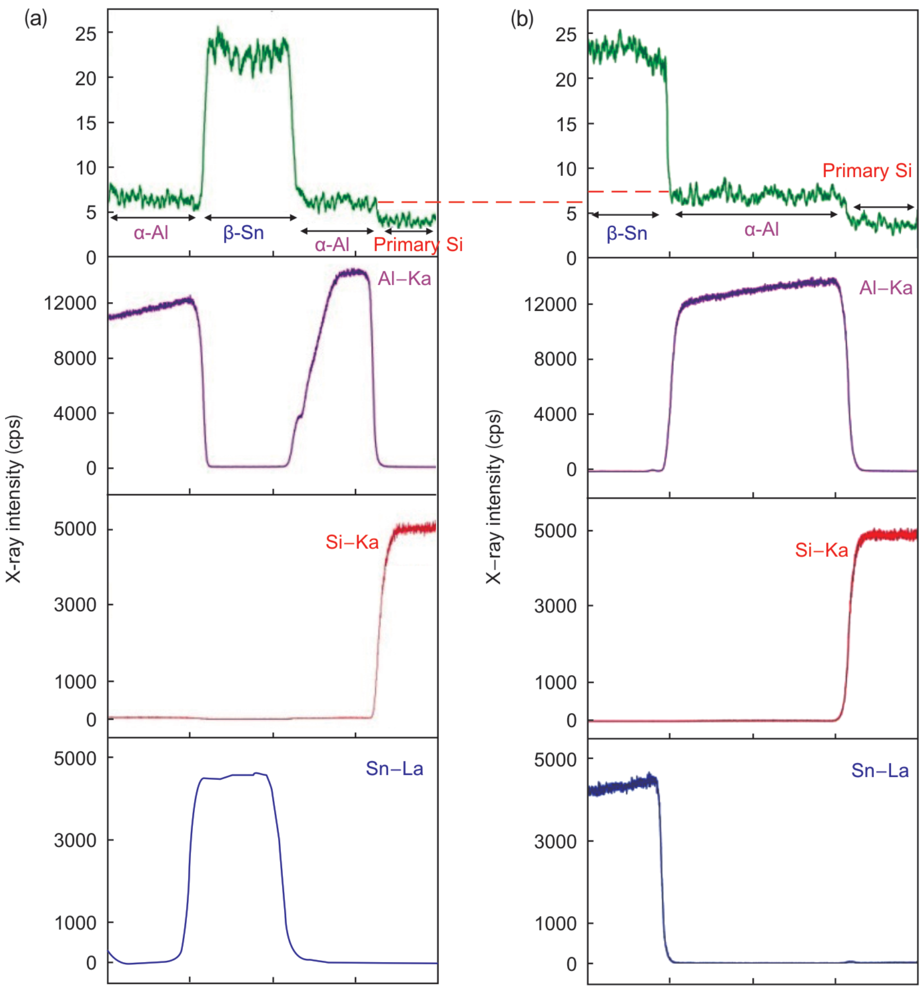


Fig. 7: EPMA line analysis of interfaces in Al-30Si-10Sn: (a) without, (b) with TMF of 50 mT

melt flow also carries away the impurities accumulated in front of the S/L interface during the growth of the primary Si, which has a positive effect on B removal [21], ultimately resulting in the increase of the removal fraction of B.

3 Conclusion

Primary Si phase separation and boron removal during the solidification process of the Al-30%Si-10%Sn melt under TMF were investigated. The results showed that the agglomeration layer of the primary Si can be formed in the periphery of the ingot while the inner microstructures are constituted mainly by eutectic α-Al+Si and β-Sn phase. The intense melt flow carrying the bulk liquid with higher Si content promotes the growth of the primary Si phase, which first precipitates close to the inner wall of the crucible with a relatively lower temperature, which results in the remarkable segregation of the primary Si phase. The content of impurity B in the primary Si can be removed effectively with increasing magnetic flux intensity. The results of EPMA clearly indicate that the average intensity of the B Kα line at the α-Al phase region of the Al-Si-Sn alloy is higher in the case of solidification under TMF than in the normal static state solidification, suggesting that the electromagnetic stirring positively influences B removal.

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