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Effect of traveling magnetic field on separation and purification of Si from Al–Si melt during solidification

Q.C. Zou [a], J.C. Jie [b,*], S.C. Liu [a], T.M. Wang [a,*], G.M. Yin [a], T.J. Li [b]

[a] School of Material Science and Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China
[b] Laboratory of Special Processing of Raw Materials, Dalian University of Technology, Dalian 116024, China

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ABSTRACT

Separation and purification of the Si crystal during solidification process of hypereutectic Al–30Si melt under traveling magnetic field (TMF) were investigated in the present study. The results showed that under a proper condition the Si-rich layer can be formed in the periphery of the ingot while the inner microstructure is mainly the Al–Si eutectic structure. 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 the crucible with a relatively lower temperature, which resulting in the remarkable segregation of the primary Si phase. The impurity contents of the refined Si can be reduced to a very low level. The typical metallic impurities have removal fraction higher than 99.5%. In addition, there is a significant difference in the P contents between the primary and eutectic Si phases, which might be ascribed to the formation of AlP phase that acts as the heterogeneous nucleation sites. Furthermore, a considerable amount of Fe-containing particles with a size about 100–300 nm is found inside the eutectic Si phase, indicating an unintended entrapment of Fe in Si.

1. Introduction

Owning to the exhaustion of traditional energy resources and increased attention on environmental protection, the exploitation of green and renewable energy is more and more valuable. Based on this background, in recent years, photovoltaic industry gets rapid development, and there is an immense need for solar-grade silicon (SOG-Si) feedstock. But up to now, most of SOG-Si raw materials are dependent on the high-cost electronic grade silicon that is produced by the modified Siemens technology. To overcome the issue of cost, the most desirable approach to produce SOG-Si is to upgrade metallurgical grade silicon (MG-Si) by metallurgical processes such as directional solidification [1], slag refining [2], plasma refining [3], and vacuum treatment [4]. This means that MG-Si will be heated and cooled for several times to ensure the efficient removal of impurities, which results in a high energy consumption.

Recently, a novel refining method for SOG-Si with MG-Si as the starting material during alloy solidification process has been proposed in Japan [5–10]. It has been demonstrated that the segregation coefficients K of most impurities, especially B and P, in the Si crystal can be dramatically reduced during Al–Si melt solidification [8–11]. As the melt solidifies, most impurities will favor to stay in the molten liquid phase because of strong segregation, thus enhancing the removal efficiency of impurities in Si crystal. However, because of the similar densities of primary Si and Al–Si melt, the high purity primary Si crystals are uniformly distributed among the Al–Si eutectics [12,13]. Although acid leaching is a promising method to selectively collect primary Si from the alloy, it will result in considerable loss of Al as well as the generation of waste acid [14]. Therefore, it is particularly important to establish a method which can separate the primary Si efficiently from Al–Si melt.

To achieve the separation of primary Si, the key factor is to control the growth of primary Si crystal, which can be achieved by introducing a forced convection in the Al–Si melt [15]. The traveling magnetic field (TMF) can induce a meridional melt flow with various flow directions, and is widely used in the metallurgical industry [16–21]. It is considered that application of TMF during Al–Si solidification can also result in a effective separation of the primary Si phase. Hence, in the present study, separation and purification of the Si crystal from hypereutectic Al–Si melt using TMF were investigated, and the corresponding separation mechanisms were discussed. Furthermore, the impurity contents of primary Si and eutectic Si were comparatively studied.

* Corresponding authors. Tel./fax: +86 411 8470 8940.
E-mail addresses: jiejc@dlut.edu.cn (J.C. Jie), tmwang@dlut.edu.cn (T.M. Wang).

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2. Experimental

Both raw materials commercial purity Al (99.7 wt%) and MG-Si (99.7 wt%) were melted in a resistance furnace to prepare Al–30 wt%Si alloy (all compositions quoted in this work are in wt% unless otherwise stated). The Al–Si melt was maintained at 1133 K for 30 min, and then poured into a preheated cylindrical graphite crucible (inner diameter: 60 mm, outer diameter 80 mm, and depth: 160 mm) at 1123 K. The weight of Al–30Si alloy was controlled to be about 750 g for each experiment. Fig. 1 shows the schematic illustration of this experimental apparatus. The thermal insulation material was placed 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 flux densities in the present study were 10 mT, 25 mT, and 50 mT. The magnetic field was switched on when the melt was cooled to 1103 K. The K-type thermocouples were inserted into the melt to monitor the temperature. The samples were prepared through standard routine method and further characterized by optical microscopy (MEF-4A) and scanning electron microscopy (SEM) equipped with an energy dispersive spectroscopy (EDS) detector.

The acid leaching treatment of the solidified Al–30Si ingots was carried out as follows. Firstly, the Si-rich layer was cut into two parts from the ingot. The two parts were dissolved in 12 mol L^{-1} HCl at room temperature for 12 h to collect the Si crystals. Then one part was used for testing the average removal fraction of impurity elements during Al–Si alloy solidification refining process. The other part was sieved through a 100 mesh screen to collect the primary Si and eutectic Si phases, to investigate the differences of impurity contents between the primary Si and eutectic Si. Secondly, the collected Si crystals were ground and immersed in aqua regia at 323 K for 24 h to remove the residue metals. Finally, the Si particles were washed with deionized water until the solution was almost neutral. The Si particles were then dried and the impurity contents were detected by an inductively coupled plasma mass spectrometer (ICP-MS, NecION 300D, PerkinElmer, America).

3. Results

3.1. Separation of primary Si from Al–Si melt during solidification under TMF

Fig. 2 shows the vertical sections of Al–30Si alloy solidified under different conditions. It can be observed that the primary Si phase tends to uniformly distribute in the ingot without magnetic field, as shown in Fig. 2(a). However, when solidified under TMF with different magnetic flux densities, the primary Si phase is separated from the Al–30Si alloy and accumulates on the periphery of the ingots to form a Si-rich layer, as shown in Fig. 2(b)–(d). In addition, the separation effect is more obvious with increasing magnetic flux intensity.

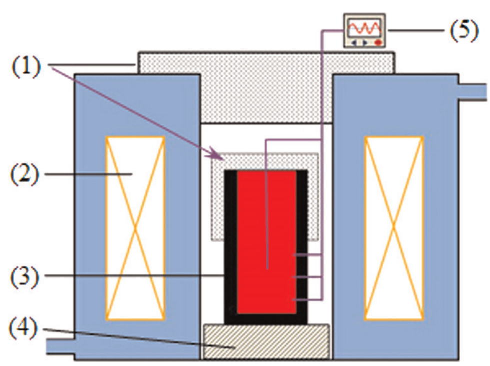

Fig. 1. Schematic diagram of the experimental apparatus: (1) asbestos, (2) TMF coils, (3) graphite crucible, (4) firebrick, and (5) temperature measurement system.

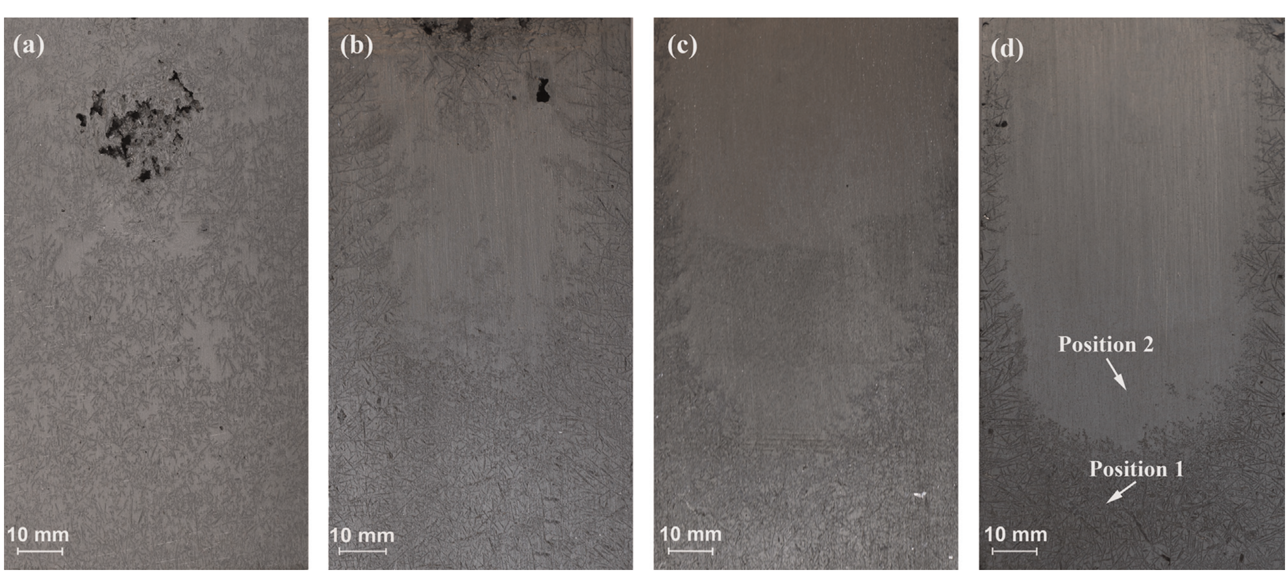

Fig. 2. Morphologies of Al–30Si ingot solidified under TMF with different magnetic flux densities: (a) 0 mT, (b) 10 mT, (c) 25 mT, and (d) 50 mT.