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Effects of AlB_2/AlP phase and electromagnetic stirring on impurity B/P removal in the solidification process of Al-30Si alloy

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ABSTRACT

To enhance the understanding of impurities B and P removal in the solidification purification process of the Al-30Si alloy, series of experiments were carried out to study the roles of AlB_2 and AlP in the nucleation of primary Si and the effect of electromagnetic stirring on the segregation behaviors of B and P. The results showed that the formed AlB_2 phase does not act as the nucleation site for the primary Si and tends to distribute in the eutectic Al-Si, which would not pollute the primary Si. The P content (< 68 ppmw) in metallurgical silicon is not sufficient to form AlP phase before the nucleation of primary Si, and thus the AlP phase can be removed effectively as it would be pushed to the front of the solid-liquid interface during the primary Si growth. It was also found electromagnetic stirring could effectively enhance the segregation behaviors of B and P during the growth of the primary Si, where the B and P contents in the primary Si were decreased with the increase of the magnetic field intensity. The effective segregation coefficients of B and P were reduced from 0.41 to 0.23 and 0.47 to 0.3, respectively, under 25 mT magnetic field compared that without electromagnetic stirring.

1. Introduction

The availability of abundant and low-cost solar grade Si (SOG-Si) feedstock is essential for the widespread use of solar cells. Over the past decade, scientists have been devoting to upgrade metallurgical silicon (MG-Si) step by step via the metallurgical process, such as directional solidification [1], slag refining [2], vacuum treatment [3], and plasma refining [4]. This means that MG-Si must be repeatedly heated to molten state at each step during refining process to ensure the efficient removal of all impurities, which results in high energy consumption.

Recently, a novel metallurgical process, namely the Al-Si alloy solidification purification at low temperature showed significant advantages in terms of both economic value and production efficiency [5–7]. The primary Si initially precipitates from hypereutectic Al-Si melt with decreasing temperature, during which more impurities (especially B and P) are enriched in the Al-Si melt because of the strong segregation behavior [8–10], thereby purifying the primary Si. However, during growth of primary Si, the non-metallic impurities B and P are not just redistributed solutes but also can form AlB_2 and AlP intermetallic compounds [11–14]. If the formed AlB_2 or AlP phase can act as the nucleation site for the primary Si or can be detained in the Si crystal during the growth of primary Si, they will cause catastrophic contamination of the primary Si. Therefore, there is an urgent need to clarify whether these intermetallic compounds can lead to the contamination of the purified primary Si. Moreover, the removal efficiencies of B and P are limited due to the impact of non-equilibrium condition in Al-Si alloy [15]. Enormous efforts have been made to improve the segregation behaviors of B and P during the growth of primary Si. One way is to reduce the solubility of B in the Al-Si melt by using small amounts of additives Ti and Hf that reacts with B to form TiB_2 and HfB_2 intermetallic compounds [16–21]. Another way is to improve the diffusion kinetics of B and P during the growth of primary Si by reducing cooling rate [22–24]. In addition, the rotating magnetic field (RMF) is used in metallurgical application for contactless melt stirring, to control the heat and mass transfer in front of the solid/liquid interface during the solidification and for crystal growth purposes [25]. However, to the best of our knowledge, there is scarcely any investigation on the effect of forced convection on the segregation behaviors of B and P between the primary Si and the eutectic Al-Si melt so far.

Here, the influence of B content on the morphology of primary Si during solidification of Al-30Si alloy was firstly investigated to clarify whether the B element and AlB_2 phase can pollute the primary Si. Furthermore, the effect of P content on the morphology of primary Si

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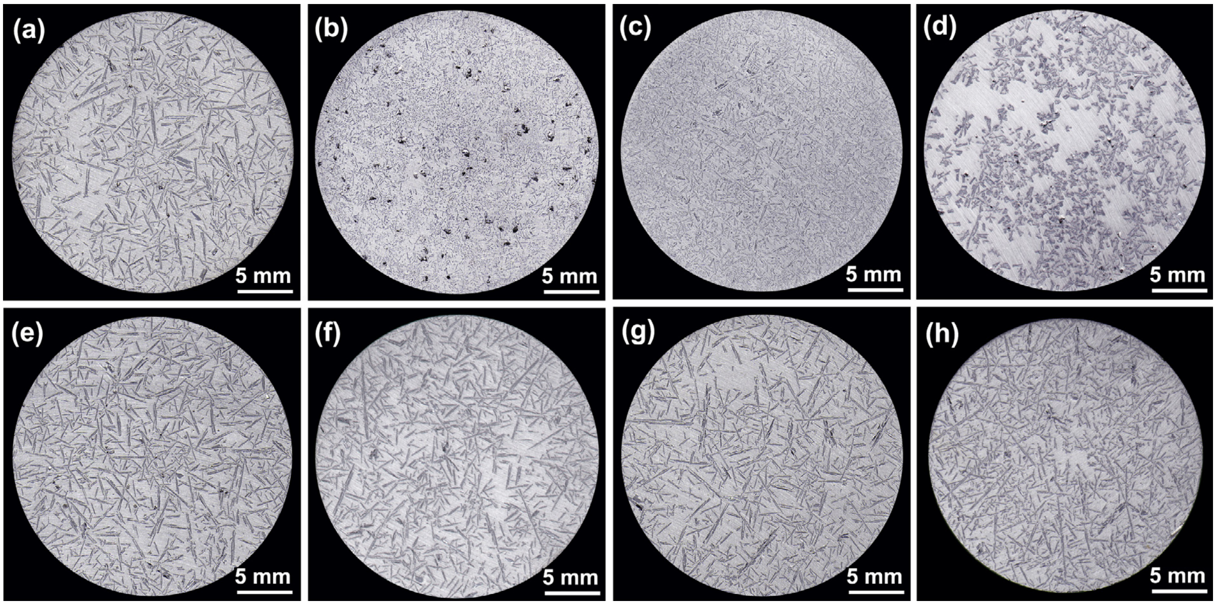

Fig. 1. Morphologies of primary Si in the Al-30Si alloys with different P, Sr, and B content: (a) unmodified, (b) 50 ppmw P, (c) 1000 ppmw P, (d) 1000 ppmw Sr, (e) 50 ppmw B, (f) 200 ppmw B, (g) 500 ppmw B, and (h) 1000 ppmw B.

was also studied to determine whether the AlP phase (formed by the existence of impurity P in MG-Si) can act as the nucleation site of primary Si. In addition, RMF was further applied in the solidification purification process of the Al-Si alloy to investigate the effect of forced convection on the segregation behaviors of impurities B and P.

2. Experimental procedure

2.1. Alloy microstructure

High purity Al (6N) and Si (6N) were weighed, placed in a quartz crucible and pre-melted by induction heating in argon atmosphere to prepare the Al-30 wt.% Si alloy melt.

2.1.1. B inoculation

To determine whether the B element and AlB_2 phase can cause the modification of primary Si, two experiments were carried out based on the contrastive study idea [26]. In the contrastive group, the Al-30Si melts were inoculated with an Al-10P master alloy and an Al-10Sr master alloy to control the P level at 50 ppmw and 1000 ppmw, and the Sr level at 1000 ppmw, respectively. In the experimental group, an Al-3B master alloy, which was synthesized by an improved halide salt reaction method [27], was introduced into the Al-30Si melts to obtain different B levels at 50, 200, 500, and 1000 ppmw. After 20 min holding at 850 °C, the above mixed melts were poured into a graphite crucible (Φ 40 mm × 50 mm, preheated to 850 °C). A K-type thermocouple, connected to a multichannel data logging system (midi LOGGER GL220, GRAPHTEC, Japan), was inserted into the center of melt to record the cooling curve.

The prepared samples were sectioned perpendicularly to the axis of the cylinder at the thermocouple controlled horizontal level, and then polished and etched for metallographic analysis. The distribution of B in the Al-30Si-1000 ppmw B alloy was further examined by an electron probe microanalyzer (EPMA; EPMA-1600, Shimadzu, Japan).

2.1.2. P inoculation

Two groups of contrastive experiments were carried out to study the effect of P content on the morphology of primary Si in different Al-Si alloys. In Al-30Si alloys, the Al-Si melts were inoculated with an Al-10P master alloy to control the P levels at 20, 50, 200, 500 and 1000 ppmw. For the study of P effect from MG-Si (99.7 wt.% purity, P content < 68 ppmw), the Al-30Si alloys were prepared in a SiC electric furnace respectively by different raw materials, i.e. the high purity Si and high purity Al, MG-Si and high purity Al, MG-Si and commercial grade Al (99.7 wt.% purity; P, detection limit), named as Al-30Si, pAl-30MG-Si, cAl-30MG-Si correspondingly. Then the melts were poured into a graphite crucible (Φ 40 mm × 50 mm; preheated to 850 °C). Metallographic specimens were cut directly from 10 mm above the bottom of the ingots, and microstructures were observed by optical microscope MEF-4A and scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS).

2.2. Solidification of Al-30Si alloy under electromagnetic stirring

A mixture of high purity Al (6N), Si (6N), and Al-30Si-1000 ppmw B master alloy (6N) (or Al-30Si-1000 ppmw P master alloy (6N)) were pre-melted in a quartz crucible by high-frequency induction heating in argon atmosphere to prepare the Al-30Si-20 ppmw B (or Al-30Si-20 ppmw P) alloy melt. Afterward, the melts were transferred to the SiC electric furnace and held at 850 °C for 20 min to make it melted uniformly. The melts were then poured into a graphite crucible (Φ 40 mm × 50 mm, preheated to 850 °C) surrounded by asbestos. In order to control the melt flow, the electromagnetic field (EMF) was applied during solidification. The melt convection was inhibited by using the static magnetic field (SMT) with a magnetic field intensity of 600 mT. The melt convection were promoted by using the RMF with a frequency of 50 Hz and magnetic field intensities of 5, 15 and 25 mT [28,29], respectively. The magnetic field was switched on when the melt was cooled to 830 °C. The cooling rate was about 2.5 °C/min.

The solidified ingots were cut into two parts along their vertical axis. One part was used for structure observation and also the B and P distribution detection by EPMA. The other part was acid treated to remove aluminum matrix for the collection of primary Si. The B and P contents in the primary Si were measured by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, American, NexION 300D).