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Growth of bulk Si from Si–Al alloy by temperature gradient zone melting

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ABSTRACT

The continuous growth of bulk Si in the Si–Al alloy using the temperature gradient zone melting (TGZM) technique is an effective method to separate the primary Si from the eutectic structure in the Si–Al alloy and to remove the majority of impurities, such as metals, B and P elements during the alloy refining process. A Si source was used to maintain the Si concentration in the alloy melt and reduce the influence of the solute-transmitting process by temperature gradient due to the precipitation of the primary Si. Bulk Si could be obtained in the Si–Al alloy through the TGZM process. With the initial temperature of 1461 K and temperature gradient of 1.81 K/mm, the actual growth rate of the bulk Si was 0.000186 mm/s. No inclusions and alloy phases were observed in the bulk Si. The removal rate of Fe impurity was 99.9% and the removal fraction of B, P and Al was 71.2%, 90.2%, 78.5% respectively.

1. Introduction

The demand for Solar-grade polysilicon (SoG-Si) has grown rapidly because the photovoltaic industry was widely developed recently [1]. The metallurgical method for SoG-Si purification was proposed to ensure a steady supply of SoG-Si as a low-cost method. The method consists of various technologies for removing different impurities, such as directional solidification [2], acid leaching [3], plasma treatment [4], vaporisation refining [5], slagging [6] and alloy refining [7].

Most metal impurities in Si have small segregated coefficients that less than 1 [8,9], which enable metal impurities to segregate from the solid Si phase and remain in the liquid Si phase easily through directional solidification. However, the impurities, including P and B [10,11], cannot be removed because of their large segregation coefficients ($k_{B\ in\ Si}=0.8$, $k_{P\ in\ Si}=0.35$). Alloy-refining method is a new type of physical metallurgical purification technology, in which Si recrystallization occurs in the supersaturated Si-based alloy melt, exhibiting a high refining efficiency at low temperature. Considerable attention has been focused on the Si–Al alloy system with low melting temperature and low cost, which can effectively decrease the contents of impurities B and P. Electromagnetic stirring [12,13] and super gravity [14,15] technology are used to enrich and collect purifying primary Si. Nevertheless, the separation of primary Si from the eutectic alloy by acid leaching [16] reduces the efficiency of these approaches because of the great loss of material (acid liquor and metal) and the complex technical route. Recently, bulk Si crystals were obtained in 44.7 mol% Si–Al melt in the temperature range of 1273 K to 1173 K by the directional solidification, and the Al content decreased to the level of its solid solubility in Si (approximately 200 ppmw at 1173 K to 1273 K) [17]. This method was also applied to other alloy systems, such as Si–Cu [18] and Si–Sn [19].

In this study, we proposed a method to continuously grow bulk Si crystal in the Si–Al alloy through the temperature gradient zone melting (TGZM) technique. The Si source and Si–Al alloy were placed in a furnace together with a temperature gradient, and a Si source was added on top of the Si–Al alloy. This method could separate the purified Si crystal effectively and reduce the cost of materials, and it was important for the realisation of the continuous growth process of bulk Si. When the Si source dissolves in high temperature and diffuses successively in the melt through the temperature gradient, sufficient Si could be provided to make the primary Si continuously precipitate, eventually forming a complete bulk Si. The research foundation for the continuous industrial production of Si alloy could be provided by this work.

2. Experimental

Initially, the MG-Si (98 wt% pure) and high-purity Al (99.99 wt% pure) raw materials were alloyed together and solidified to form the columned master alloy in an induction heating furnace with a high-purity Ar atmosphere. MG-Si particles were pre-melted to form a circular cylinder which was used as the Si source in a high-purity graphite crucible. Subsequently, the columned master alloy and the Si source were cut into suitable sizes and placed in order into a dense

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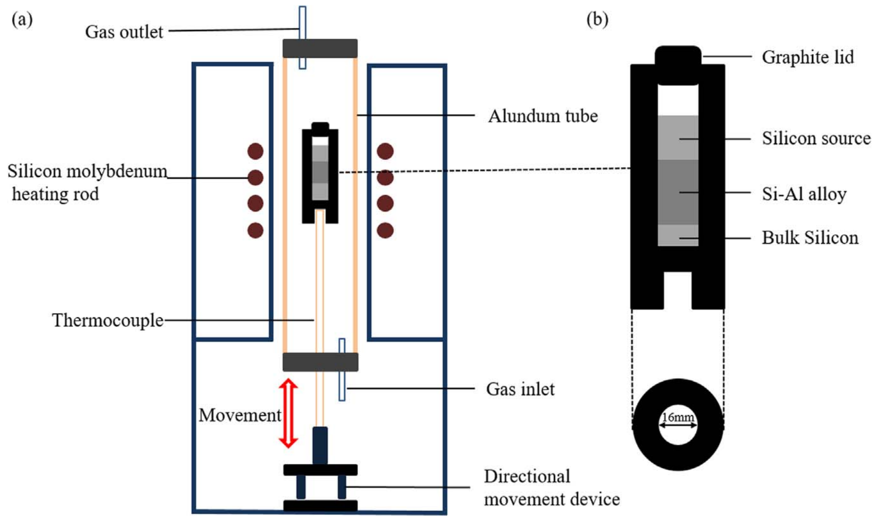

Fig. 1. Schematic diagram of the experimental apparatus: (a) Electric furnace with a PMC stepping motor; (b) Graphite crucible with the sample.

Table 1
Experimental conditions and results.

No.	Initial temperature (K)	Alloy composition	G (K/mm)	Theoretical growth rates (mm/s)	Actual growth rates (mm/s)
1	1433	61.5 mol% Si-Al	0.92	0.000091	0.000036
2	1433	61.5 mol% Si-Al	2.10	0.000208	0.000143
3	1461	65 mol% Si-Al	1.81	0.000219	0.000219
4	1461	65 mol% Si-Al	1.81	0.000219	0.000186
5	1475	66.6 mol% Si-Al	1.43	0.000190	0.000086
6	1475	66.6 mol% Si-Al	1.43	0.000190	0.000098

graphite crucible container (shown as Fig. 1b). The schematic of the experimental apparatus was shown in Fig. 1. The alumina tube was inserted in a high temperature vertical furnace with a Si–Mo heater, and a Pt30%Rh-Pt6%Rh thermocouple was used to measure the temperature changes during the whole solidification process. Before experiment, the correction of temperature gradient in an alumina tube should be done. The graphite crucible was placed in an alumina tube and heated up to 1473 K (sample 1) or 1573 K (sample 2–6). In this case, different positions in the alumina tube had different temperature gradients, and the sample was placed at a set position for 30 min in Ar atmosphere. Then, the graphite crucible was pulled down at a constant lowering rate (0.000625 mm/s) at a temperature gradient of 0.92 K/mm to 2.10 K/mm. The moving distance was approximately 10 mm, which was the thickness of the master alloy. Finally, the graphite crucible was took out quickly from the furnace and cooled to the room temperature. The experimental conditions and results were listed in Table 1.

The samples were cut parallel to the temperature gradient into two equal parts. The selected sections were ground by SiC papers and polished from 6 µm to 1 µm. The surface morphology of the alloy was examined through optical microscopy (OM, MEF4) and scanning electron microscopy (SEM, TM3030 plus, Hitachi). A bulk Si was cut from the sample 3 and was detected by the inductively coupled plasma-atomic emission spectrometry (ICP-AES, Seiko SPS7700, Japan).

3. Results and discussion

3.1. Principle of bulk Si growth from Si–Al alloy melts by TGZM

The Si–Al alloy sample was placed in a vertical furnace with a temperature gradient, and a Si source was placed on top of the Si–Al alloy. Due to the positive temperatures gradient in Si–Al alloy melt, different solute compositions in the alloy melt were obtained when the thermodynamic equilibrium was held in the solid-liquid interface. The TGZM included three procedures: dissolution of Si source, diffusion of Si atoms across the Si–Al alloy melt from the hot side to the cold side and the growth of bulk Si at the bottom of crucible. The continuous growth of bulk Si on the cold side and dissolution of Si source on the hot side of the liquid zone drove the liquid to march up the temperature gradient, as shown in Fig. 2.

A feature of crystal growth during the TGZM process is the dependence of the growth rate on the liquid-phase zone thickness, which determines the change in the contribution of kinetics and diffusion limitations in the TGZM process [20]. However, if the thickness of liquid-phase zone is large, the crystal growth is limited by the diffusion of a substance in the zone and independent of the

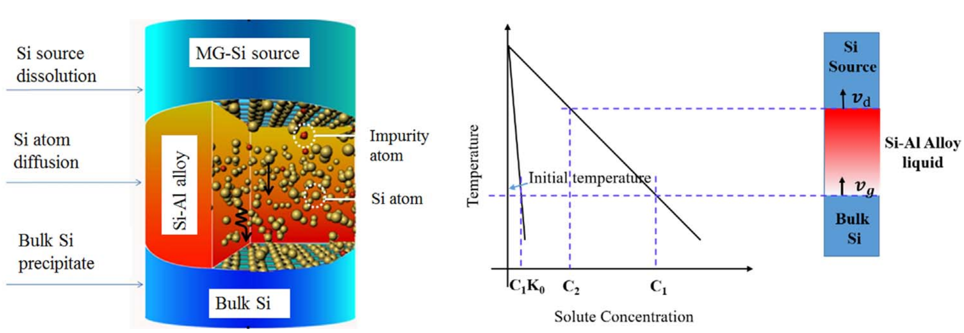

Fig. 2. Schematic diagram of the temperature gradient zone melting.