ELSEVIER Science Press
Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 27(2017) 467−474
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effects of melt viscosity on enrichment and separation of primary silicon from Al−Si melt

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Received 7 December 2015; accepted 28 November 2016

Abstract: The effects of melt viscosity on the enrichment and separation of Si crystals from Al–Si melt during an electromagnetic solidification process were investigated. Both the enrichment efficiency and the separation were found to be strongly dependent on the melt viscosity. A high melt viscosity was beneficial to the enrichment of primary silicon, whereas a low melt viscosity facilitated the separation process. A new enrichment mechanism was proposed in order to clarify the influence of melt viscosity, and an improved process for achieving high-efficiency enrichment of Si crystals via control of the melt viscosity was also proposed. Additionally, the morphology of Si crystals was found to change from spheroidal to plate-like in shape owing to the difference in viscosities in different regions.

Key words: directional solidification; electromagnetic stirring; Al−Si melt; primary silicon; separation; viscosity

1 Introduction

Exploitation of solar energy is attracting increasing attention as a solution to problems of environmental pollution and shortage of conventional (fossil) energy sources. Conventionally, solar cells are dependent on expensive semiconductor-grade silicon (SEG-Si, 99.9999999% purity), which is manufactured by the Siemens process. With the aims of producing solar-grade silicon (SOG-Si, 99.9999% purity), a modified Siemens process and a fluidized bed reactor process have recently been developed. However, the potential for cost reduction in these processes is limited because the Si productivity is low [1]. A metallurgical route, which usually includes acid leaching [2], oxidation treatment [3], vacuum melting [4], slag refining [5], directional solidification [6,7], and electron beam melting [8], has been proposed to deal with the metallurgical grade silicon (MG-Si, 98%−99.9% purity) by removing the impurities from it for the demand of SOG-Si, and it is considered as a potential method for achieving cost reduction.

In recent years, considerable progress has been made toward reducing cost further by alloying Si with other elements such as Al [9], Sn [10], Cu [11], and Fe [12]. This method has the following outstanding advantages: 1) the refining temperature is much lower than the melting temperature of Si (i.e., 1687 K), 2) the solid/liquid segregation of impurities is enhanced at low temperatures, and 3) the process is environmentally friendly.

Al−Si alloy refining [13−15] is a highly promising process for low-cost SOG-Si production and is one of the few MG-Si purification processes which is realized on the industrial scale [16]; thus, this alloy system at low temperature has received extensive research attention. Generally, Si purification using Al−Si alloy is performed in three steps: 1) fusing the mixture of MG-Si and metal Al to obtain a hypereutectic Al−Si melt, 2) cooling the melt slowly to induce nucleation and growth of primary Si, and 3) acid leaching to remove Al and other impurities for collecting Si crystals. However, considerable amounts of aluminum and silicon are wasted during the process of acid leaching. Therefore, efficient enrichment and separation of Si crystals before

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Foundation item: Project (u1137601) supported by the National Natural Science Foundation of China; Project (106112015CDJXY130007) supported by Fundamental Research Funds for the Central Universities, China

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DOI: 10.1016/S1003-6326(17)60053-0

acid leaching are crucial for achieving cost reduction and environmental conservation. Electromagnetic separation is an effective method for promoting the migration of Si crystals in order to improve their enrichment efficiency during the solidification of Al−Si alloy [17−21]. Melt viscosity is a key factor influencing the movement of Si crystals in Al–Si melt during the electromagnetic separation process [22]. However, no study has thus far been focused on the mechanism of influence of melt viscosity on the enrichment and separation of Si. The influence of melt viscosity needs to be investigated thoroughly in order to improve the enrichment efficiency of Si in Al−Si melt.

In the present work, the influence of melt viscosity on the enrichment of Si crystals is examined and a new Si enrichment mechanism is proposed in order to clarify the influence of melt viscosity. The influence of melt viscosity on the separation process is also analyzed.

2 Experimental

Hypereutectic Al−Si alloys were prepared by mixing of metallurgical-grade Si (99.9%) powder and pure Al (99.99%) powder in a graphite crucible and subsequently melting the mixture to obtain alloys in an electrical resistance-heating furnace. Finally, through adjustment of the mass fractions of Si and Al, Al−25% Si, Al−35%Si, and Al−45% Si alloys were prepared. The total mass of each sample was 80 g. The process of silicon enrichment was performed by placing samples of the prepared alloys at the center of the coil zone of a 60 kW high-frequency induction furnace and then heating the samples until they were melted completely. After the samples had been melted, they were pulled down by a pulling system. The pulling rate was controlled at 7 μm/s, and the temperature gradient was 35−40 K/cm in the axial direction of the sample. For specific experiments, the pulling distance was set to 6 cm, 8 cm, and 10 cm in the downward direction from the lower end of the induction coil. During the pulling-down process, the current intensity was controlled at 12 A. After completion of the enrichment, separation of the enriched Si crystals from the Al−Si melt was performed by removing the graphite crucible from the induction furnace and then dumping the crucible to pour out the Al−Si melt rapidly. A schematic diagram of the experimental setup is shown in Fig. 1.

After solidification, the alloy samples were cut in the longitudinal direction to examine the enrichment of primary silicon crystals. The surface of the samples was ground with SiC paper for metallographic observations. The macrostructures and microstructures of the solidified samples were observed with a SONY digital camera and Olympus PME3 light optical microscope (LOM) with an attached KAPPA image analyzer, respectively. The Si enrichment region was cut out from the sample and then subjected to atomic absorption spectroscopy (AAS) measurement for observing the Si content. X-ray diffraction (XRD, Advance D8) was used to characterize the preferential growth face of primary silicon in the enrichment zone. For the XRD characterization, the enrichment zone in different positions was cut down from the sample and polished. The XRD pattern from 20° to 120° was used to confirm the preferred growth orientation with a Cu K_α radiation resource. The viscosity of semisolid Al−Si melt was measured using a high-temperature viscometer (self-designed by Kunming University of Science and Technology), which consisted of an outer cylinder (crucible) and an inner cylinder. Both cylinders were made of graphite. The shear rate was controlled at 10 s^{-1} by adjusting the angular rotation speed of the motor. During the measurement, the samples were kept inside an argon-recirculating furnace to maintain the apparatus in an isothermal condition (±1 °C). The viscosity measurement experiment was repeated three to five times at a given temperature, and the mean values were taken as the apparent viscosities of the melts.

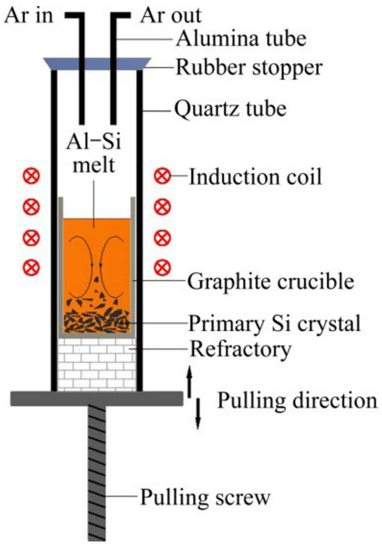

Fig. 1 Schematic diagram of experimental setup

3 Results and discussion

3.1 Enrichment of primary silicon

Figure 2 shows the cross-sections of the enriched samples, which reveal that the Si crystals agglomerated mostly in the lower part of the samples. The separation phenomenon could be attributed to the combined effect of electromagnetic stirring and the axial temperature gradient. Figure 3 shows a simulation diagram of the Si enrichment mechanism. During the enrichment process, a mushy zone formed between the melt and the enrichment zone owing to the axial temperature gradient,