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Mechanism of boron removal from Si−Al melt by Ar−H_2 gas mixtures

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Abstract: A new method about purification of metallurgical grade silicon (MG-Si) by a combination of Si−Al solvent refining and gas blowing treatment was proposed. The morphologies and transformation of impurity phases, especially for boron and iron in Si−Al melt were investigated during Ar−H_2 gas blowing treatment. The mechanism of boron removal was discussed. The results indicate that gas blowing can refine grain size and increase nucleation of the primary Si. Boron can be effectively removed from MG-Si using the Ar−H_2 gas blowing technique during the Si−Al solvent refining. Compared with the sample without gas blowing, the removal efficiency of boron increases from 45.83% to 74.73% after 2.5 h gas blowing. The main impurity phases containing boron are in the form of TiB_2, AlB_2 and VB compounds and iron-containing one is in the form of β-Al_5FeSi intermetallic compound. Part of boron combines [H] to transform into gas B_xH_y (BH, BH_2) and diffuses towards the surface of the melt and is volatilized by Ar−H_2 gas blowing treatment under electromagnetic stirring.

Key words: metallurgical grade silicon; Si−Al melt; gas blowing; boron removal

1 Introduction

The removal of boron in metallurgical grade silicon (MG-Si) is one of the most crucial tasks for upgrading to the photovoltaic silicon feedstock [1]. Several processes, such as slag refining [2], plasma treatment [3], and solvent refining [4] have been reported for this purpose.

Impurities in the MG-Si shorten the lifetime of excited carries in Si-based solar cells and disturb electric generation [5]. Hence, their removal from Si is an important issue on Si solar cells fabrication. Solvent refining is a purification process that relies on preferential segregation of impurities to a liquid, in which high purity solid silicon crystals grew from. Al as an effective solvent, has been investigated by many researchers [4,6,7]. During the Al−Si solvent refining process, the impurity elements are rejected into the Al−Si eutectic melt and the segregation behaviour of the impurity elements determines the removal efficiency. In order to improve the removal efficiency of boron from Al−Si melt, many works emphasized on thermodynamic evaluation, separation of the refined Si and kinetic factors of the Al−Si solvent refining process. The segregation coefficients of boron and phosphorus between solid Si and Al−Si melt have been calculated by many researchers with different methods [4,8,9]. Some external fields, such as electromagnetic force [10] and super gravity [11], have been applied to separating the primary Si from the Al−Si melt. Besides, the kinetic factors [12,13], such as cooling rate, Si proportion, and refining temperature, or the introduction of other additives [14,15] have been investigated to improve the purity of the refined Si. Gas blowing treatment [16,17] is an effective way to remove boron from MG-Si, but with the disadvantage of high temperature, essential hydrogen water vapour, small contact area, and closed system. However, as for the effect of gas blowing, especially for the H_2 without water vapor, the boron removal at low temperatures during Al−Si solvent refining process has not been investigated.

In the present work, a new method of solvent refining has been proposed to obtain higher removal efficiency of boron during Al−Si solvent refining. The efficiency of boron removal is evaluated by introducing into Ar−H_2 gas mixtures into the Al−Si melt and

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compared with that without Ar−H_2 gas mixtures. The distribution of boron and transformation of impurity phases, especially TiB_2, AlB_2 and VB, etc., in the Al−Si alloy after the gas blowing treatment were investigated. Mechanism of boron removal was discussed based on the experimental results.

2 Experimental

Figure 1 shows a schematic drawing of the 25 kW induction furnace used in this work. 6N pure silicon (99.9999%) was first alloyed with analytical reagent pure boron powder to about 186×10^{-6} in a high-purity graphite crucible. 90 g boron doped Si and 210 g high purity aluminum were then put into a high-purity alumina crucible with an inner diameter of 55 mm and height of 100 mm. After the crucible was positioned into the medium frequency induction furnace, the system was then filled with Ar to protect graphite crucible. Raising the temperature to melt Al−Si mixture, then a H_2−Ar mixture was blown into the melt through a 5 mm inner diameter quartz tube. The gas blowing rate was controlled at 3 L/min and the gas ratio of H_2 to Ar was 1:1 for H_2−Ar mixture. The temperature profiles of the samples were carefully controlled by adjusting the induction power of the furnace. After the gas blowing treatment, the Al−Si melt was sampled into the cold crucible from the melt by a quartz tube every 30 min and the sample was solidified rapidly at room temperature. The duration of each experiment within gas blowing was from 0 to 330 min. Then, the power was cut off and the Al−Si melt was slowly solidified to the room temperature in the furnace. Lastly, the solidified Al−Si alloy samples (containing the rapidly and slowly solidified samples) were put into acid solution to remove Al to obtain refined Si. The acid solutions were HCl solution and the duration of acid leaching was 48 h at 353 K. Then, the impurity concentrations in the refined Si were examined by inductively coupled plasma optical emission spectroscopy (ICP-OES), and the morphologies were analyzed by scanning electron microscope (SEM).

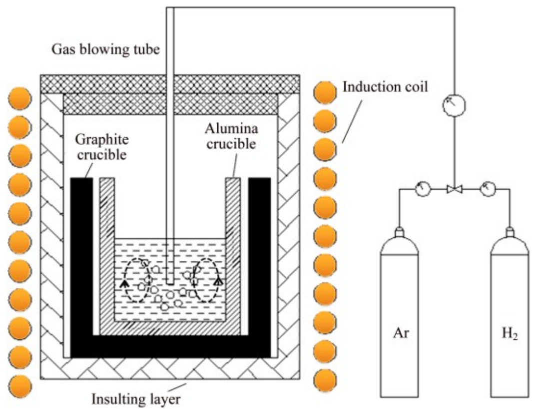

Fig. 1 Schematic drawing of 25 kW induction furnace

3 Results and discussion

3.1 Morphology of Al−Si alloy

Figure 2 shows the microstructures of the solidified Al−Si alloy with different Ar−H_2 treatment time and cooling rates. As can be seen from Figs. 2(a) and (b), the Al−Si melt was sampled into the cold crucible directly with different gas blowing treatment time. The primary silicon crystals are distributed uniformly in the alloy. The average length of the primary Si crystals in the alloy is about 500 μm without Ar−H_2 blowing. After 3.5 h

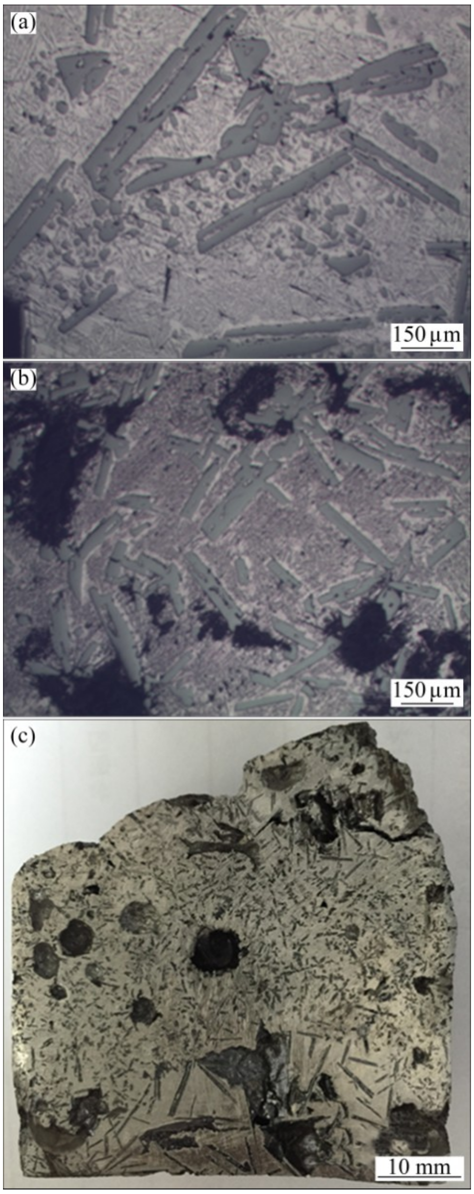

Fig. 2 Microstructures of Al−30%Si: (a) Without Ar−H_2 blowing, rapidly cooling in cold crucible; (b) 3.5 h Ar−H_2 blowing, rapidly cooling in cold crucible; (c) 5.5 h Ar−H_2 blowing, slowly cooling in furnace