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Effect of kinetics on P removal by Al-Si solvent refining at low solidification temperature

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A B S T R A C T

To determine the effect of kinetics on P removal in Al-Si-P system, three sets of experiments with different solidification temperature ranges have been carried out. High P removal rates can be confirmed. An apparent segregation coefficient is introduced to characterize the P removal in this Al-Si-P system, which are determined to be 0.0207, 0.00822 and 0.00679, when the cooling rate is 0.556 $\text{mK}\cdot\text{s}^{-1}$ and the Si contents in the melt are 39.1, 29.3, 19.4 at.%, respectively. Theoretical P contents in the primary Si phase controlled by thermodynamic factor ($\overline{X}^{T}_{\text{P in primary Si}}$) and theoretical P contents in the primary Si phase controlled by kinetic factor ($\overline{X}^{K}_{\text{P in primary Si}}$) are calculated. The results reveal that the kinetic factors have critical influence on P removal at low solidification temperature.

1. Introduction

The solar cell production, especially those based on polycrystalline Si, increases significantly with a growing demand for development of green and renewable energy. The material resource for polycrystalline Si solar cells is solar grade Si (SoG-Si). Currently, SoG-Si is mainly manufactured using the traditional Siemens process or its modified alternatives [1], which is fairly energy intensive and environment-unfriendly [2,3]. To reduce its energy consumption and pollution, new metallurgical refining processes of SoG-Si using metallurgical grade silicon (MG-Si) as a starting material have been developed, such as slag treatment [4], plasma treatment [5], vaporization refining [6] and solvent refining [7].

P is one of the major dopants in Si and should be reduced to lower than 1 ppma for solar cell application. Because the segregation coefficient of P between solid/liquid Si, 0.35 [8], is considerably much larger than those of most metallic impurities in Si, an ordinary directional solidification is not practical to remove P. On the other hand, P has high vapor pressure in molten Si [9] and can be removed from the molten Si by using vaporization refining. However, this process requires low vacuum, high holding temperature and long operation time. The high cost of the facilities and large energy consumption limit this technique from industrial application.

Solvent refining with Al-Si alloy is a very promising process to produce SoG-Si at large scale with low cost and one of the few metallurgical Si purification processes that are realized in industrial scale [10]. Compared with directional solidification of Si(1700–1800 K), solvent refining with Al-Si melt (850–1500 K) is carried out at much lower temperature, and removal of P is more efficient. The removal of P from MG-Si by solvent refining with Al-Si melt has been extensively investigated [11–13], and segregation coefficients of P between solid Si/Al-Si melt are significantly smaller than that between solid/liquid Si [14].

Our recently works have proved that kinetics [15] and trap of phosphides [16] are two very important factors controlling the removal efficiency of P at lower solidification temperature. In this work, three sets of experiments with different solidification temperature ranges have been carried out to study the effect of kinetics on P removal in the Al-Si-P system. High P removal rates can be confirmed. Macrostructure of the samples, experimental P contents in the primary Si phase and theoretical P contents in the primary Si phase controlled by the thermodynamic factor/kinetic factor with varying Si contents are studied. The results in this research show that the kinetics is the control factor of the P removal in this Al-Si-P

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system, and might suggest a new method to improve the refining process of SoG-Si.

2. Experimental

To avoid the effect of other elements that may be brought in by MG-Si and commercial Al, the Al-Si alloys were prepared by mixing of high purity raw materials: Si (solar grade, 6N), Al (99.96%) and high purity Si-P master alloy. A total of 80 g raw materials were put in an alumina crucible (O.D. = 35 mm, Depth = 70 mm). The initial P content was controlled to 890 ppma in the whole sample. Three sets of experiments were carried out in this work, the parameters of each experiment are summarized in Table 1.

The experimental process was described in our previous publication [16]. The crucibles were placed in an electric resistance furnace, heated to 1473 K in Ar atmosphere, and held for 3 h. After that, the samples were cooled down quickly to 10 K above the liquidus temperature (1250 K for Al-39.1 at.% Si melt, 1123 K for Al-29.3 at% Si melt, 960 K for Al-19.4 at% Si melt) and cooled to 850 K (eutectic temperature) with a pre-determined cooling rate ($0.556\ \mathrm{mK\cdot s^{-1}}$). Then the solidified sample was taken out from the furnace and leached in diluted HCl and HNO_3. After the acid leaching, larger primary Si flakes were collected, rinsed with deionized water, dried and separated from smaller eutectic powders.

The separated primary Si flakes of each sample, which were considered as refined primary Si, were measured by sieve analysis. The macrostructure of the Al-Si alloy ingots were obtained using an optical image scanner. The chemical compositions of the primary Si flakes were tested by inductively coupled plasma optical emission spectrometrys (ICP-OES).

3. Results and discussion

3.1. Macrostructure of Al-Si ingots

Fig. 1 shows the longitudinal sections of each sample. Because the experiment is not carried out under vacuum, all the samples contain some gas bubbles in the alloy. The primary Si flakes display needle-like morphology. For the primary Si flakes concentrated near the side surface of the samples (especially in S-3), the process of the primary Si crystals growth can be seen, that is, the primary Si flakes nucleate from the margin of the alloy (cold end), then grow towards the middle of the melt until meet other primary Si flakes. The length of the primary Si flakes is about 5–10 mm. And with higher Si content, the thickness of the primary Si flakes becomes much larger.

To evaluate the size distribution and average size of the primary Si flakes, a sieve analysis can be used. Cumulative size distribution of the primary Si flakes and fineness number (*FN*) of each sample are examined. The *FN* defined by American Foundry Society, presents the average particle size along with its distribution and a larger *FN* means finer flake size. This is explained by the following Eq. (1):

$$FN = \frac{\sum_1^n (S_i \times W_i)}{\sum_1^n W_i} \tag{1}$$

where S_i is the fineness modulus of each sieve, W_i is the weight of the remaining flakes in the sieve, and n is the number of sieves.

Fig. 2(a) shows the cumulative size distribution of the primary Si flakes of each sample (mass percent). When the Si content increases, the fine flakes in the sample occupy a larger mass percent. Fig. 2(b) shows the *FN* of each sample. From sample S-1 to S-3, the *FN* decreases with increase of the Si content, which means the average size of the primary Si flakes increase with increase of the Si content. Because under higher Si content environment, more Si atoms can easily transfer to the boundary layer and build up on the growth interface.

3.2. P removal in the refined primary Si

Fig. 3(a) shows the P content in the primary Si phase from each sample examined by ICP-OES. With the increasing Si contents, the P contents in the primary Si phase fall from 21.7 ppma in sample S-1, to 8.1 ppma in sample S-2, and 6.3 ppma in sample S-3. Considering the initial P content in each sample, which is 890 ppma, relatively high P removal rates are confirmed. Because the higher Si content leads to a higher solidification temperature, these results indicate that the P removal is more effective under low solidification temperature.

During the solidification process, mass transfer in the solid Si phase occurs only by diffusion, the diffusion coefficient of P in solid Si is $3 \times 10^{-13}\ \mathrm{cm^2/s}$ at 1373 K, which is a quite small value compared with that of other metal elements (usually in the range of 10^{-4}~$10^{-6}\ \mathrm{cm^2/s}$) [17]. Because of that, it can been considered as that there is no P diffusion in the solid Si phases. When a temperature gradient exists in the liquid, thermal convection will occur, because of the difference in density between cold and hot melt. Therefore, mass transfer in the liquid phase is carried out not only by diffusion but also by convection. In this case, the impurity contents in the liquid phase are partial mixing.

An apparent segregation coefficient, $k_{\mathrm{P\ app}}$ is introduced to characterize the P removal during the whole solidification temperature range, an equation similar to Scheil equation is derived for the calculation of the solid composition as a function of f_S:

$$X_{\mathrm{P\ in\ primary\ Si}} = k_{\mathrm{P\ app}} X_{\mathrm{P\ ini}} (1 - f_S)^{k_{\mathrm{P\ app}} - 1} \tag{2}$$

where $X_{\mathrm{P\ in\ primary\ Si}}$ is the P content (mole percentage) in the primary Si phase, $X_{\mathrm{P\ ini}}$ is the initial P content (mole percentage) in the whole sample, and f_S is the fraction of the primary Si phase (mole percentage).

Considering that the total amount of solute in the solid must be conserved, a formula is obtained by integration of Eq. (2):

$$\int_0^{f_S} k_{\mathrm{P\ app}} \cdot X_{\mathrm{P\ ini}} \cdot (1 - s)^{k_{\mathrm{P\ app}} - 1} \mathrm{d}s = \overline{X}_{\mathrm{P\ in\ primary\ Si}} \cdot f_S \tag{3}$$

Table 1
List of experiments.

Exp. No.	Initial Si content in whole sample (at.%)	Cooling rate ($\mathrm{mK\cdot s^{-1}}$)	Initial P content in whole sample (ppma)
S-1	39.1	0.556	890
S-2	29.3		
S-3	19.4		