



Solvent extraction of phosphorus from Si-Cu refining system with calcium addition



Liuqing Huang^{a,c}, Abdolkarim Danaei^c, Sridevi Thomas^c, Pengfei Xing^b, Jintang Li^a, Xuetao Luo^{a,*}, Mansoor Barati^c

^a Fujian Key Laboratory of Advanced Materials, College of Materials, Xiamen University, Xiamen 361005, PR China

^b School of Materials and Metallurgy, Northeastern University, Shenyang 110004, PR China

^c Department of Materials Science and Engineering, University of Toronto, Toronto, ON M5S 3E4, Canada

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ABSTRACT

Enhanced removal of P from Si-Cu alloy was obtained by Ca addition. The effectiveness of Ca addition on the phase reconstruction and P gettering in Si-50 wt%Cu alloy was investigated. It was shown that the introduction of Ca can achieve the phase reconstruction of Si-50 wt%Cu alloy by the formation of CaCu_2Si_2 and $\text{CaCu}_{11}\text{Si}_5$ phases, which were precipitated in the Cu_3Si phase. Dense P was found to homogeneously precipitated in the CaCu_2Si_2 phase, indicating that the increase in the amount of the CaCu_2Si_2 phase would collect more P. It was found that the extraction fraction of P was proportional to Ca content in Si-50 wt% Cu alloy. The removal fraction of P was increased from 27% to 82% when the Si-Cu system was doped with 5 wt% Ca. The thermodynamic analysis of P removal was investigated, showing that the Ca addition could effectively decrease the segregation coefficient of P between solid Si and the Si-Cu melt. It was concluded that Ca could be used as an impurity trapper to facilitate the P removal in the Si-Cu alloy.

1. Introduction

Given the growing demands for renewable energy sources, increasing attention has been focused on green and renewable solar energy. Solar cells module is the basic component of every photovoltaic (PV) power plant. Both industry and academia are dedicated to working on increasing the power conversion efficiency (PCE) and reducing the costs of solar cells. Recently, the polycrystalline silicon solar cells that have reached a PCE of 21.9% [1]. The dominant manufacturing process of solar grade silicon (SoG-Si) is the modified Siemens process. To develop low-cost and mass-producible techniques, unprecedented progress in the production of SoG-Si by the metallurgical process has been made in recent years. As the raw material, metallurgical grade silicon (MG-Si) is derived from silica ores, which can be reduced by a carbothermic reaction. The distribution of impurities in MG-Si mainly depends on their different segregation behaviors. It is known that the nonmetallic impurities have higher segregation coefficients than that of metallic impurities [2]. For metallic impurities, directional solidification [3] and acid leaching [4,5] can be applied to remove the impurities gathered at the grain surface or boundaries. For nonmetallic impurity boron (B), slag treatment [6–8], electron beam [9], plasma refining [10], and gas blowing [11,12] are used to remove B by the oxidation

reaction. For nonmetallic impurity phosphorus (P), vacuum refining is a feasible process to extract P from Si melt due to the difference in saturated vapor pressure [13]. However, a further reduction in cost and improvement in productivity are still necessary.

Solvent refining is a promising method for the refinement of MG-Si [14]. The solvent metal should meet two requirements. One is that Si-metal alloy has a low melting point; another is that impurities in the Si-metal alloy have low segregation coefficients between solid Si and alloy melt. Many metals have been chosen as solvent such as aluminum (Al) [15], copper (Cu) [16], iron (Fe) [17], tin (Sn) [18], or nickel (Ni) [19]. To further decrease the segregation coefficient of impurity, a multiple solvent refining technique was developed [20–24]. However, the separation of solvent metal is an important issue for solvent refining. Based on the intrinsic property of the Si-metal alloy, several methods such as rotating magnetic field [25], heavy media separation [26], and acid leaching [27] have been used to remove the alloy phase. The solid solubility of Cu in Si is much smaller compared to Al and Sn [28], and the Si-Cu phase is easy to be removed from Si by heavy liquid separation due to the significant difference in density between Si and Si-Cu phases [16]. Hence, Cu can be used as a promising solvent in the refining of MG-Si. In our previous work [29,30], a combination of Si-Cu solvent refining and other metallurgical methods was used to upgrade

* Corresponding author.

E-mail address: xuetao@xmu.edu.cn (X. Luo).

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MG-Si. After the treatment, the final concentration of B in Si could be reduced to below 0.5 ppmw while the removal fraction of P was not satisfactory. To further improve the purification efficiency, much attention has been paid to the introduction of a small amount of solvent metal as impurity getter, which can target a certain impurity. For example, titanium (Ti) was chosen as impurity getter to redistribute B in MG-Si by forming a TiB₂ compound. Through the work of Yoshikawa et al. [31], a small amount of Ti was added to Si-Al alloy and its effect on B removal was studied. It was reported that TiB₂ is a strongly stable compound, which can be rejected to the Si-Al melt prior to the precipitation of the Si dendrites. Lei et al. [32] investigated the effect of Ti content and refinement parameters on the enhanced removal of B from Si. The mechanism of B removal has been investigated by Chen's group, showing that the formation of TiB₂ particles before the precipitation of primary Si is the reason for the enhancement removal of B [33,34]. For P removal, calcium (Ca) was chosen as the getter to redistribute P. In the work of Min and Sano [35], it had been reported that Ca₃P₂ is a stable compound, and its stability is deduced from the phosphide diagram calculated by FactSage™ software. To confirm the affinity of Ca for P, Morita [36] conducted experiments and found that Ca₃P₂ was segregated in the grain boundaries of silicon and easily removed by acid leaching. The thermodynamic analysis indicated that the interaction coefficient between Ca and P was a large negative value. Shimpo et al. [37] reported that ~80% P in MG-Si could be removed by 5.17 at.% Ca addition. Hu et al. [38] added Ca to Si-Sn alloy to achieve the phase reconstruction process. The removal fraction of P was reached 86% when Ca was added to the Si-Sn alloy. The effect of Ca addition on the formation of P-containing phase in the Si-Al system has been studied [39,40]. The results suggested that P was rejected by the Si solidification front and then concentrated in the CaAl₂Si₂ phase.

In this study, Ca was used as an impurity getter to enhance P removal from Si-Cu alloy. The influences of Ca addition on the phase reconstruction and P distribution in Si-Cu alloy are experimentally investigated. Moreover, the existing state of P in the Si-Cu-Ca alloys are speculated. Finally, the effect of Ca addition on the enhancement removal of P and its segregation behavior are studied.

2. Experimental

The preparation of Si-Cu(-Ca) alloys was carried out in a horizontal furnace. Forty-gram of MG-Si lumps (99% purity, Becancour Silicon, Inc.) and 40 g Cu granules (> 99.9% purity, Sigma-Aldrich) were put into a graphite crucible. Meanwhile, 2.5 g copper phosphorus shot (Cu:P = 85:15 wt%, Alfa Aesar) were doped into the mixture to increase P concentration in the alloy (total mass ~82 g). The mixture was heated at a rate of 5 K/min in the furnace under a flowing argon atmosphere and held for 3 h at 1823 K. Subsequently, the samples were cooled down to room temperature at a rate of 10 K/min. Following this, the prepared Si-50 wt%Cu alloy was ground into fine powder by an oscillating mill (MM400, Retsch Company). Inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher Scientific iCAP 6300) was used to measure the concentration of impurity in the samples. The ICP-OES results for the prepared Si-Cu alloy are summarized in Table 1.

Twenty grams of Si-50 wt%Cu alloy powders was mixed with x g (x = 0.2, 0.5, and 1.0) calcium granules (99% purity, Aldrich) and then melted in the same furnace under same conditions. To separate the alloy phase from the prepared alloys, acid leaching was applied. The leaching acid contained reagent grade HNO₃ (68.0% to 70.0%, Caledon

Laboratory Chemicals), HCl (36.5% to 38.0%, Caledon Laboratory Chemicals), and HF (48%, GFS Chemicals). The leaching took place in 100 mL Teflon beakers, which were placed on a magnetic stirring apparatus. The mixture was stirred by a Teflon stirrer (400 rpm) at 343 K for the whole leaching process. A three-stage leaching process was used in this study, the detail is described in our previous work [29]. At the end of each stage, the solution was centrifuged at 5000 × g for 5 min using a centrifuge (Thermo Scientific Sorvall Legend X1R). The final products were diluted in deionized water and centrifuged for several times until the pH value of the solution was 7.

3. Results and discussion

3.1. Microstructure of Si-Cu alloy with Ca addition

The microstructures of Si-Cu alloy before and after Ca addition are characterized by scanning electron microscope and energy-dispersive spectroscopy (SEM-EDS, JEOL 6610LV). Fig. 1 shows the microstructure of the prepared Si-50 wt%Cu alloy without any Ca addition. The microstructure of Si-Cu alloy only contains Si and Si-Cu phases. With the 2.5 wt% Ca addition, two new phases were found to appear at the Si-Cu phase (Fig. 2). The primary phase was rod-like Cu-Si-Ca-P, the secondary phase was needle-like Cu-Si-Ca. Table 2 summarizes that the results of EDS analysis which suggests that the composition of these phases likely be Cu₃Si (Spectrum 1), CaCu₂Si₂ (Spectrum 2), and CaCu₁₁Si₅ (Spectrum 3). It is worth noting that the relatively high P content was measured in the CaCu₂Si₂ phase.

According to the work conducted by the Shimpo et al. [37], P-containing phases adjacent to CaSi₂ in Si-Ca-P alloy were identified as Ca₃P₂ by XRD. Hu et al. [38] reported that P was distributed evenly in CaAl₂Si₂ embedded in the Ca-alloyed MG-Si; however, no Ca₃P₂ was detected by XRD. In this study, the concentration of P in the Si-Cu alloy before Ca addition was measured as 1622 ppmw. To confirm the P-containing phases in the Si-Cu-Ca system, the XRD analysis (Rigaku MiniFlex 600) was also applied. As shown in Fig. 3, the Cu₃Si phase was indeed the possible phase which appeared in the four samples (Si-Cu-x wt% Ca, x = 0, 1, 2.5, and 5). With the increasing Ca content, the intensity of Ca-containing phases (CaSi₂, Ca₂Si, and CaCu) increased while the intensity of Cu₃Si decreased. In the XRD pattern of Si-Cu sample, some small peaks can be observed in the same region of Ca-based compound peaks in other samples. Since the Ca content in Si-Cu alloy was 402 ppmw, the small peaks might come from contaminations or some oxides. However, the presence of P-containing phase could not be confirmed due to the detection limit of XRD and its relatively low content in the samples.

To predict the possible phase transition in the Si-Cu-Ca-P system, a quaternary phase diagram was calculated by FactSage™ software. As shown in Fig. 4, Ca_xSi_y (CaSi, Ca₂Si, and CaSi₂) and Ca₃P₂ appear in the high-Ca region. Although the existence of P-CaCu₂Si₂ phase had been confirmed in Fig. 2, no Si-Cu-Ca-P compound phase was found in this diagram. Based on the above discussion, two possible mechanisms can be proposed for the P-containing phases transition in the Si-Cu-Ca alloy. One is that Ca₃P₂ formed and coprecipitated with other phases such as CaSi₂ and CaCu; another is that P was rejected to the Si-Cu-Ca melt and then dissolved in the CaCu₂Si₂ phase as the melt solidified.

3.2. Existing state of phosphorus in Si-Cu alloy with Ca addition

To figure out the existing state of P in Si-Cu-Ca solvent system, the distributions of P in Si-Cu and Si-Cu-Ca alloys were examined by an electron probe microanalyzer (EPMA, JEOL JXA8230). Fig. 5(a) shows the EPMA mapping analysis of an alloy phase in the Si-50 wt%Cu alloy. It was shown that the Ca and P are relatively concentrated in the Si-Cu phase compared to the Si phase. Fig. 5(b) shows the EPMA mapping analysis of the Si-50 wt%Cu alloy with a small amount of Ca addition. It was found that the intensity of P and Ca in the CaCu₂Si₂ phase are much

Table 1

ICP-OES analysis of Si-50 wt%Cu alloy (unit: ppmw).

Sample	P	B	Fe	Al	Ca	Mg	Mn
Si-50 wt%Cu	1622	27	2705	1788	402	192	45

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