



Enhancement in extraction of boron and phosphorus from metallurgical grade silicon by copper alloying and aqua regia leaching



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ABSTRACT

The feasibility and optimization of an enhanced boron and phosphorus extraction process, from metallurgical grade silicon (MG-Si), consisting of solvent refining and acid leaching were studied comprehensively. MG-Si was alloyed with copper (Cu), following which, the removal of boron and phosphorus from the Si–Cu alloy by acid leaching was investigated. The results showed that the Cu-alloying process led to the concentration of boron and phosphorus in the Si–Cu alloy phase, which was confirmed to be an important part of their removal. Based on the analysis of acid sensitivity of the Si–Cu alloy phase, it was found that aqua regia was an effective leaching agent for removing the Si–Cu alloy phases from Si grains compared to HCl and HNO₃. Addition of copper resulted in the increase in the extraction yield of boron and phosphorus from MG-Si from 21.0 to 58.7% and 23.2 to 42.2%, respectively. The selected Si–Cu powders were within a size range 74–106 μm and the leaching was conducted at 70 °C for 5 h via a three-step sequential acid leaching procedure. Furthermore, the leaching kinetics of boron and phosphorus using aqua regia was observed to be controlled by interfacial transfer and product layer diffusion.

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1. Introduction

Solar energy is the most abundant and clean source of renewable energy. With the development of the photovoltaic industry, the production of solar cells is increasing rapidly. By far, the most prevalent bulk material for solar cells is crystalline silicon (c-Si), also known as solar grade Si. Over 80% of solar cells are made of polycrystalline Si (Braga et al., 2008). Polycrystalline Si cells are less expensive, yet less efficient than those made from monocrystalline Si (Lee et al., 2015). Recently, an increased interest in environmental protection and a reduction of manufacturing prices have urged the countries to explore more practical and economical methods. Thus, metallurgical purification methods for the production of solar grade Si have been introduced (Mukashev et al., 2009). These methods include acid leaching (Sakata et al., 2002), solvent refining (Yoshikawa and Morita, 2012), vacuum refining (Zheng et al., 2011), and slag treatment (Jung et al., 2014).

Noteworthy, the impurity distribution depends on the segregation behavior of impurities in metallurgical grade Si (MG-Si), which directly affects their subsequent extraction. The metallic impurities, such as iron

(Fe), aluminum (Al), and calcium (Ca), are primarily located at the Si grain boundaries or the grain surfaces owing to their small segregation coefficients (Tan et al., 2014). Nonmetallic impurities, namely boron (B) and phosphorus (P), gather inside the Si grain with high segregation coefficient, which restricts their exposure to the acid or removal by directional solidification (Jiang et al., 2014; Sim et al., 2006). Therefore, slag treatment has been proposed to remove B via oxidation reactions and P can be removed from molten Si by vacuum refining based on vapor pressure difference. However, these methods involve rigorous equipment requirements and high energy consumption. Thus, the removal of B and P from MG-Si has remained a challenging task.

Solvent refining, a purification process has been employed to overcome the above mentioned barriers. In this process, Si recrystallization takes place from the supersaturated melt depending on the segregation behavior of impurities (Hu et al., 2013a,b). Given the low melting points and low segregation coefficients of the impurities present between the solid Si and the alloy melt, metals such as Al, Fe, tin (Sn), and copper (Cu) are typically used as impurity getters (Li et al., 2014; Ma et al., 2013). In our study, Cu was selected as the impurity getter due to its low solubility in the solid silicon and the large difference in their densities (Olesinski and Abbaschian, 1986). The main problem involved in solvent refining is the difficulty in separating primary Si and solvent metal. Conventional separation methods involve gravity sedimentation

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(Mitrasinovic and Utigard, 2009) and electromagnetic force (Yoshikawa and Morita, 2005). The gravity separation method is suitable for systems in which there is a large density difference between Si and solvent, such as the Si–Cu and Si–Fe systems. In the study of Morita et al., an electromagnetic field was applied to separate Si crystals grown from a Si–Al melt during solidification. These methods have their own disadvantages, such as low efficiency and limited effect on removal of small inclusions. However, acid leaching is a feasible and low-cost method for refining MG–Si at the industrial scale. Several researchers have reported that alloying followed by acid leaching is an effective route to purify MG–Si. Recently, alloying with titanium (Ti) or Ca followed by acid leaching was found to significantly improve the removal efficiency of B and P from MG–Si. Shimpo et al. melted Si–P–Ca alloy and then leached using aqua regia, it was found that 80% P was removed by the addition of 5.17 at.% Ca (Shimpo et al., 2004). Yoshikawa et al. used Ti as an additive to remove B from Si–Al alloy, and then leached with a mixture of HCl + HNO₃ + H₂SO₄ (Yoshikawa et al., 2005). Johnston et al. studied Ti and Ca metals as impurity getters in purification of MG–Si, focusing on the removal of B and P (Johnston and Barati, 2013). In addition to Ti and Ca, other metal elements have been investigated as well. Margarido et al. studied the refining of Si–Fe alloy using a two-step leaching procedure: first stage involved the use of HCl and the second stage employed HCl + FeCl₃·6H₂O. The leaching of main metallic impurities (Fe, Al, and Ca) was found to depend on the composition of the phases and nature of their distribution (Margarido et al., 1993). Visnovec et al. used a mixture of HNO₃ + HCl to purify Si–Cu alloy after gravity separation. It was determined that the overall impurity level in purified Si was reduced from 5277 to 225.5 ppmw (Visnovec et al., 2012). Although, these studies have been conducted for removing impurities by the addition of the above-mentioned elements, the corresponding mechanisms contributing to a higher removal efficiency of B and P have been rarely touched. Furthermore, little attention has been paid in literature to the investigation of the effect of lixiviant on the separation and purification of alloy phase during leaching process.

The main objective of the current study was to demonstrate that Cu alloying in combination with acid leaching could be effectively used for purifying MG–Si, in particular, for removing B and P. In this study, MG–Si was first alloyed with Cu to trap B and P, and then the purified Si was recovered by acid leaching. Various parameters of the process including particle size of the alloy powder, leaching reagent, time, and temperature were comprehensively studied. Moreover, a modified cracking shrinking model was applied to analyze the acid leaching kinetics.

2. Materials and methods

2.1. Materials

The raw material, MG–Si lumps, with a purity of 99% was provided by Run Xiang Co., Ltd., China. The contents of the main impurities in MG–Si are listed in Table 1. Cu powders (particle size: 74–106 μm) and reagent-grade HCl, HNO₃, and HF were purchased from Sinopharm Chemical Reagent Co., Ltd. The initial MG–Si and the prepared Si-50 wt.% Cu alloy were crushed to a size of <1 mm by jaw and roll crushers, respectively. Then, five particle size ranges were selected by sieving: 0–74, 74–106, 106–149, 149–178, and >178 μm. The MG–Si powders with a particle size of <1 mm were used in the preparation of Si-

50 wt.% Cu alloy. The MG–Si powders with a particle size of 74–106 μm were used in the acid leaching experiments.

2.2. Alloying and solidification process

Fig. 1(a) shows a sketch of apparatus used in this process. For the preparation of Si-50 wt.% Cu alloy, MG–Si powders (particle size: <1 mm) were mixed with Cu powders to form the mixture of Si-50 wt.% Cu (MG–Si/Cu mass ratio = 1:1). The mixture was then melted in a tube furnace (total alloy mass of ~100 g). For this, the mixture was heated to 1550 °C at the rate of 5 °C·min⁻¹ in an argon atmosphere, and then held for 2 h to allow for homogenization of the melt. The temperature was continuously measured using a WRe5–WRe26 thermocouple and was controlled within ±10 K. The mixture was subsequently cooled at a rate of 5 °C·min⁻¹.

2.3. Acid leaching

As shown in Fig. 1(b), ten gram samples of MG–Si and Si-50 wt.% Cu alloy powders were mixed with 100 mL of leachant in a Teflon beaker with mechanical stirring, respectively. The extraction was done via a three-step sequential acid leaching procedure:

Step 1: 2 M HCl/HNO₃/aqua regia.

Step 2: 2 M HNO₃ + trace HF.

Step 3: 1 M HNO₃.

The experimental variables included the leaching reagent (used in the first step), particle size, time, and temperature. After acid leaching, the solution was filtered and rinsed thoroughly with de-ionized water until the solution was neutral and then it was dried.

2.4. Characterization

Concentrations of impurities in the samples were measured by inductively coupled plasma-atomic emission spectrometry (ICP–AES, Optima 2000DV, PerkinElmer Inc., US). Moreover, distributions of the elements in MG–Si before and after alloying with Cu were studied by an electron probe micro analyzer (EPMA, JXA-8100, Japan Electronics Co., Ltd., Japan). Finally, the microstructural evolution in the Si–Cu alloy powders after the first step of leaching with HCl/HNO₃/aqua regia was detected by scanning electron microscopy and energy dispersive spectroscopy (SEM and EDS, SU70, Hitachi Co., Ltd., Japan).

3. Results and discussion

3.1. The microstructure of MG–Si before and after Cu alloying

According to the research results reported by Santos et al., the composition of the MG–Si used in the acid leaching experiments affects on the extraction of impurities (Santos et al., 1990). Therefore, it is essential to investigate the effect of Cu alloying on the concentration of B and P in MG–Si. The values listed in Table 1 indicated that the initial concentration of B and P in raw material was 3.12 and 17.14 ppmw, respectively. After Cu alloying, the concentration of B and P in Si changed to 2.67 and 12.34 ppmw, respectively. Fig. 2(a) shows the micrograph and EPMA map of the impurity precipitated phase in the used MG–Si. Ca, although a major impurity, was barely detectable, in most cases as small spots. This is because Ca-containing phases are brittle and could be removed during sample preparation. Therefore, Si–Fe based phase is the main impurity phase observed in Fig. 2(a). The micro-analysis led to the detection of at least five phases that appeared to have different qualitative composition. It was found that B and P did not easily co-precipitate and form compounds owing to their segregation behavior in MG–Si. Fig. 2(b) shows the micrographs and the EPMA map analysis of the Si–Cu alloy phase in Si-50 wt.% Cu alloy. It is found that the intensities of B and P in the alloy phase are higher than those in the Si phase. The results indicated that the solidification sequence of the liquid alloy

Table 1
Impurity concentrations (ppmw) in the raw materials used in the study.

Sample	B	P	Fe	Al	Ca	Ti	Mn	Ni
MG–Si	3.12	17.14	10.74	100.76	29.89	88.14	5.704	14.86
Cu	2.14	8.93	13.94	19.01	1014.11	11.17	1.04	2.96
Si-50 wt.% Cu	2.67	12.34	10.83	113.14	258.13	45.776	4.919	6.282

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