Science Press

Trans. Nonferrous Met. Soc. China 17(2007) s1030−s1033

Transactions of Nonferrous Metals Society of China

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Removal of iron and aluminum impurities from metallurgical grade-silicon with hydrometallurgical route

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Received 15 July 2007; accepted 10 September 2007

Abstract: A new method for production of solar grade silicon(SoG-Si) at low cost from metallurgical grade silicon (MG-Si) via vacuum metallurgical technique was proposed, which is a promising process to feedstock solar energy silicon material independence of traditional Siemens method. In this procedure, pre-treatment of MG-Si using hydrometallurgical routes to remove the metallic impurities such as iron and aluminum to reduce the production cost is an important process. The influences of acid agents, acid concentration, reaction time and temperature and particle size of raw material ground on the removal efficiency of iron and aluminum impurities were investigated, respectively. The results show that the optimum operation conditions for leaching in acid C are: acid concentration 6 mol/L, temperature 60 ℃, time 4 d, diameter for raw material 50 μm. The removal efficiencies of impurities iron and aluminum are up to 85% and 75%, respectively.

Key words: solar grade silicon; metallurgical grade silicon; hydrometallurgy; purification

1 Introduction

Solar energy is one of the ideal renewable energy resources because of the non-pollution, non-mover parts, the universality of resource and non-exhaustion for ever, according to the environmental protection nowadays and the requirement of the sustainable development[1−2]. The crystalline silicon has the main status as the basal material of the solar cells in the future of 20 years, because of the advantage of the high-stabilization efficiency, low environmental loading, permanence of capability and so on[3]. The Siemens process and the decomposition of the silicane are two major routes to manufacture silicon with high purity at expensive cost for both photovoltaic and electronic industries. So it is very important to research new procedures, which is independence of the traditional silicon production.

Most of the metallic elements presented as impurities in MG-Si have a small segregation coefficient in silicon, as listed in Table 1. Thus, in spite of the high solubility of impurities in the molten silicon, they have small solubility in the solid and result in concentrating at the grain boundaries. Upon pulverizing the MG-Si, fracture occurs mainly at grain boundaries, exposing the impurities as active reaction interfaces in acid solutions. The major advantage of acid leaching for MG-Si purification is that it could be realized at low temperature with low energy consumption and simple instruments to reduce cost, compared with other refining processes[4].

Some new techniques in production of SoG-Si in resent years have been proposed and studied [5−13]. A novel process was proposed by the authors to produce solar grade silicon from MG-Si via vacuum metallurgy at low cost[14] . In this procedure, the pretreatment of MG-Si to remove some metallic impurities is an important process to simplify purification in the next steps.

Foundation item: Project (50674050) supported by the National Natural Science Foundation of China; Project (2006BAE01B08) supported by the Sustentation Project of Science and Technology of China; Project (20060674004) supported by PhD Programs Foundation of Ministry of Education of China

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In this paper, we reported the main results of removal effect for iron and aluminum impurities in the purification of MG-Si produced by carbothermic reduction of quartz in the furnace from a company in Yunnan Province of China (CCYP), by leaching of the ground material with different acid solutions as a function of their concentration, leaching temperature and leaching time and particle size of MG-Si, respectively.

2 Experimental

2.1 Characterization of MG-Si

MG-Si produced by CCYP has been analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and the results are listed in Table 1. The major metallic impurities are iron (0.15%), aluminum (0.054%) and calcium (0.032%). Other impurities are titanium, boron, vanadium and phosphorus. The non-metallic impurities such as boron, carbon and phosphorus could not be directly purified by means of acid leaching, which has been discussed in Refs.[15−16]

Table 1 Chemical composition and segregation coefficients in MG-Si from CCYP

Element	Concentration/ $(mg \cdot kg^{-1})$	Segregation coefficient[7]
Fe	1 500	6.4×10^{-6}
Ca	320	1.6×10^{-3}
P	112	0.35
V	10	4×10^{-6}
Al	540	2.8×10^{-3}
B	18	0.8
C	1 000	7×10^{-2}
Ti	12	3.6×10^{-6}

2.2 Microstructure

The microstructural analysis of MG-Si was investigated using scanning electron microscopy- energy dispersive spectrometer (SEM-EDS) that enabled a qualitative analysis of main elements presented, shown in Fig.1. The impurities among silicon grains were observed. When the cast MG-Si is pulverized, breakage occurs mostly at the grain boundaries. Thus if MG-Si lumps are pulverized to a particle size that is equivalent to the size of the polycrystalline grains, a major portion of the metallic impurities presented on the surface of the grains is exposed, which enhances the reaction of MG-Si pulverized in acid solution.

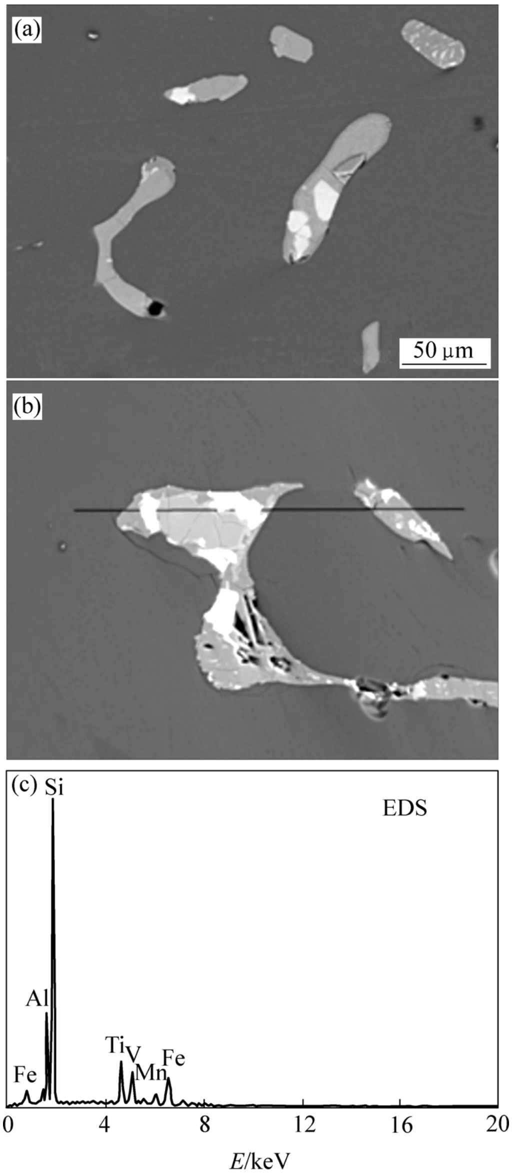

Fig.1 SEM/EDS images of MG-Si from certain company in Yunnan Province: (a), (b) SEM images; (C) EDS image

2.3 Leaching trials

1) Sample preparation

Prior to the leaching experiments, the MG-Si from CCYP was crushed and ground, then sieved to give fractions with different particle sizes in order for leaching trials.

2) Leaching experiments

Leaching trials were done with aqueous thermostat. After each experiment, the solid was filtered and washed with dilute acid and distilled water before drying. The iron-ion and aluminum-ion in the solid and in the liquid were analyzed by ICP-AES, respectively.

3 Results and discussion

A large number of leaching trials were performed in order to study the effects of different acid concentration, temperature and time of the leaching process, particle size of pulverized silicon on the removal efficiencies of impurities such as iron and aluminum.

3.1 Effect of acid agents and acid solutions

The removal efficiencies of impurities iron and aluminum with different acid agents and concentrations are shown in Fig.2 and Fig.3, respectively. The removal efficiencies of impurity iron are about 65% and 50% in acid A and acid B solutions, respectively. Otherwise, it is up to 80% in acid C solution, which concludes that the removal result of impurity iron achieved in acid C solution is higher than those in acid A and acid B. Furthermore, compared with different concentrations of acid C, the removal efficiency of impurity aluminum by acid leaching shows that the optimum concentration of acid C is 6 mol/L.

The main reason is that the average activity coefficient of acid C is larger than those of both acid A and acid B, and the average activity coefficient of acid C is improved significantly with increasing concentration[17].

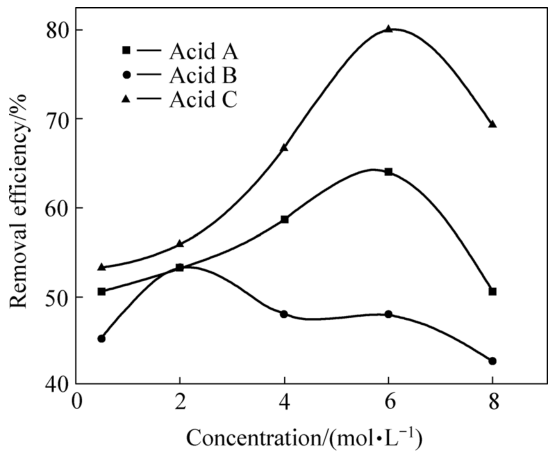

Fig.2 Removal efficiencies of impurity iron by acid leaching for different acid agents and concentrations at 20℃

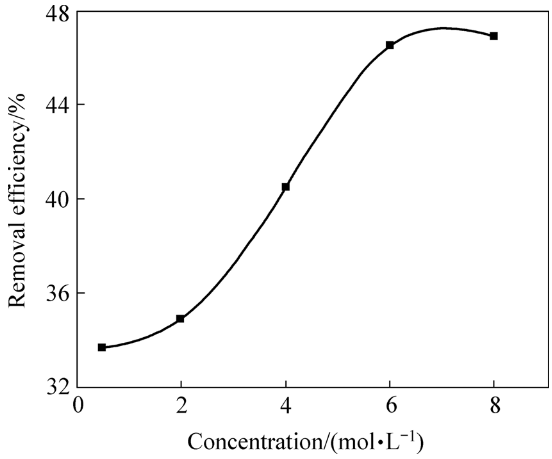

Fig.3 Removal efficiencies of impurity aluminum by acid leaching for different concentrations of acid C

3.2 Effect of reaction temperature

The reaction rate can be improved with high temperature, because the collision probability of molecules in the reaction system can be accelerated. So, we can shorten the reactive time via enhancing reaction temperature. The influence of temperature on the removal efficiencies of impurities iron and aluminum is shown in Fig.4. The removal efficiencies of these two impurities in acid C solution at 20 ℃ are very low, and increase with the temperature. The removal efficiencies are about 85% and 63.7% for impurities iron and aluminum, respectively. And then, the effect is not obvious, which suggests that the optimum temperature is 60 ℃.

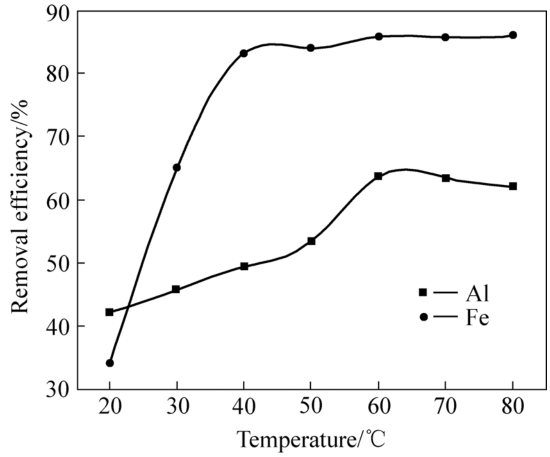

Fig.4 Removal efficiencies of impurities iron and aluminum by acid leaching in acid C at different temperatures

3.3 Effect of reaction time

Reaction time is an important factor in the process. Referring to the cost of acid leaching process, it is found that the removal effect continuously increases with the increase of reaction time, as shown in Fig.5. However, prolonging reaction time will increase the load of the acid leaching process and decrease the product of silicon.

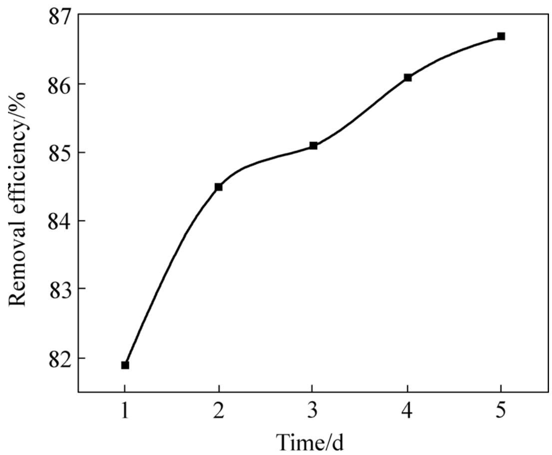

Fig.5 Removal efficiencies of impurities by acid leaching in acid C for different leaching time

It is suggested that the reaction time should be 4 d.

3.4 Effect of MG-Si particle size

The effect of particle size on the purification for the cases of leaching with acid C solution is shown in Fig.6. It is found that the removal efficiencies of impurities iron and aluminum impurities are improved significantly with decreasing particle size. The requirement of improved grinding of MG-Si is well below the diameter of the polycrystalline MG-Si for obtaining pure silicon. Our results indicate that many friable phases containing impurities, concentrated in the finer fraction during sieving, are not so easily removed by acid leaching. A similar grain size effect is found for most of the other minority impurities. In general the removal efficiencies are similar for most metallic impurities such as Ca, Ti and V, except with high segregation coefficient impurities such as B and P, which can be removed by other techniques.

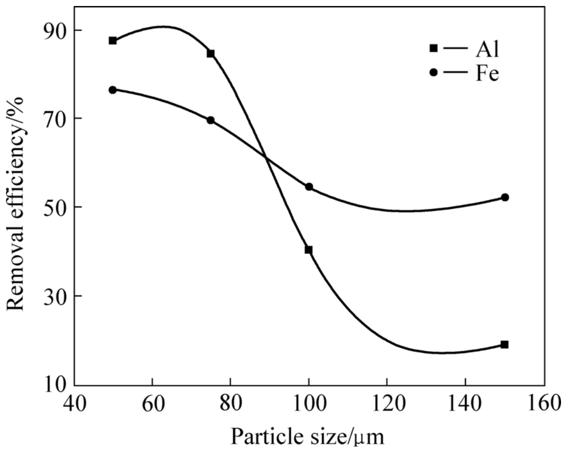

Fig.6 Removal efficiencies of impurities iron and aluminum by acid leaching for different particle sizes

4 Conclusions

1) The optimum operation conditions for leaching in acid C are: acid concentration 6 mol/L, temperature 60 ℃, time 4 d and diameter for raw material ground 50 μm.

2) The removal efficiencies for impurities iron and aluminum in MG-Si, are up to 85% and 75%, respectively.

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(Edited by HE Xue-feng)