

Recovery of high purity silicon from SoG crystalline silicon cutting slurry waste

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Abstract: The recovery of high-purity Si from the cutting slurry waste of SoG-Si was investigated. The composition and size distribution of cutting waste were characterized. The Si-rich powders were obtained from the cutting waste using a physical sedimentation process, and then further purified by removing impurity using acid leaching. The effects of process parameters such as acid leaching time, temperature and the ratio of solid to liquid on the purification efficiency were investigated, and the parameters were optimized. Afterwards, the high-purity Si ingot was obtained by melting the Si-rich powders in vacuum furnace. Finally, the high purity Si with 99.96% Si, 1.1×10^{-6} boron (B), and 4.0×10^{-6} phosphorus (P) were obtained. The results indicate that it is feasible to extract high-purity Si, and further produce SoG-Si from the cutting slurry waste.

Key words: SoG-Si; cutting slurry waste; high-purity Si; recovery; physical sedimentation; high temperature melting

1 Introduction

Solar energy becomes one of the most important renewable clean energies in 21st century due to the limitations in conventional energy resources and the growing challenges about climate changes and environmental pollutions [1–5]. To fabricate the solar cell, polycrystalline silicon wafers with thickness of 180 μm are obtained from the solar grade crystalline silicon (SoG) ingots. A SoG-Si ingot is sliced by a multi-wire saw with an ethylene glycol containing silicon carbide (SiC) abrasives [6]. More than 40% of SoG-Si becomes powder and goes into the slurry waste in process of wafer slicing [1,7,8]. In last decade, the global photovoltaic (PV) industry has been rapidly developed. The rapid development of PV industries causes the dramatic increase of the SoG-Si cutting loss slurry. In 2011, around 2.3×10^8 kg of SoG-Si was produced in China, and thereby about 3×10^8 kg of Si slurry waste was created, which induced the serious environmental pollutions. The SoG-Si cutting slurry waste exists in the form of slurry mixed with the cutting fluid, Si particles,

abrasive SiC particles and the metals worn down from the saw wire. If the lost Si can be effectively recycled from the slurry waste and be re-supplied as Si feedstock to the field of solar cells fabrication again, it will save the shortage of solar grade Si materials and bring in enormous environmental and economic benefit.

The recycle and application of the slurry waste have drawn strong attention in last decade [9–23]. The separation of SiC and ethylene glycol (cutting fluid) from the cutting slurry waste has been industrialized [9–11]. However, the effective recycle of high-pure Si from the slurry waste is still a challenge. Therefore, efforts have been given to recycle polycrystalline Si from the cutting slurry waste using different methods [11–15]. BILLIET and NGUYEN [16] described methods of centrifuging, decanting, filtration and froth flotation, then high energy electrical discharge techniques to recover crystalline Si from kerf loss slurries. WANG et al [17–19] reported the recovery of Si from the slurry waste using a process including chemical treatment, heavy fluid-gravity centrifugation, high-temperature treatment and directional solidification. WU and CHEN [20] used an electrical field to separate Si and SiC. LIN and TAI

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[21] reported a so-called phase-transfer separation method, and TSAI [22,23] investigated the effects of electrical fields, operation time and baffle plates on the separation of Si and SiC in recycling slurry wastes.

In this work, a method to fabricate high-purity Si from the cutting slurry was proposed, which was a process consisting of conventional physical sedimentation, acid leaching, filtration and high temperature melting. Finally, the high-purity Si ingot with 99.96% Si, 1.1×10^{-6} B, and 4.0×10^{-6} P (mass fraction) was obtained using the method. The effects of the process parameters on the purification efficiency have been investigated. The results provide a possibility to produce SoG-Si from the cutting waste.

2 Experimental

The SoG-Si cutting slurry waste was obtained from REC, Norway. The cutting slurry consists of Si, SiC, metal fragments (mainly iron fragments) and ethylene glycol. Before the materials were shipped, most of the ethylene glycol has been removed from the slurry. The received cutting waste was first heated at 300 °C for 30 min to remove the rest of the ethylene glycol. The heated cutting loss waste was used as the starting material in this work and referred to sample S₁. The sample S₁ was first characterized using X-ray diffraction (XRD), X-ray fluorescence (XRF), chemical analysis and particles sizes analysis.

The separation of Si and SiC was performed using the conventional physical sedimentation method, in which water was used as the sedimentation solution. The sedimentation process was carried out in a 1000 mL volumetric cylinder at different sedimentation time and ratios of solid to liquid. After the physical sedimentation process, the solution enriched with Si particles was obtained. The Si-rich powders (represented as S₂) were obtained from the solution using vacuum filtration followed by alcohol and de-ionized water washing for 3–4 times and post-baking at 80 °C. The iron and iron oxide in the Si-rich powders S₂ were removed using an optimized acid leaching process to get Si-rich powders S₃. The Si-rich powders S₃ were then pressed into pellets, placed in a graphite crucible, and heated to above 1550 °C in argon atmosphere for a given time to get Si ingot.

The particle size distributions (PSD) of the samples were determined by a static light-scattering analyzer (Mastersizer2000, Beijing instrument plant, China) using an aqueous solution containing 0.1% (mass fraction) alcohol as a dispersing agent. The amounts of Si, SiC, Fe, B and P in the samples were determined by XRF, chemical analysis method and inductively coupled plasma mass spectrometry (ICP-MS). The particles

morphology and the microstructure of Si ingot were observed by scanning electron microscopy (SEM, SUPRA 35, LEO) equipped with energy disperse spectroscopy (EDS). The phases in the materials were identified by X-ray diffraction (XRD) with Cu K_α radiation. The amounts of Si, B and P in the Si ingot were determined by XRF, chemical analysis and ICP-MS, respectively.

3 Results and discussion

3.1 Characterizations of cutting waste

Figure 1 shows the XRD pattern of the heated cutting slurry waste S₁. The main peaks in the XRD pattern can be indexed to SiC, Si and FeO. The peaks corresponding to the SiC have the highest intensities, indicating that the SiC is a dominated phase in the cutting loss waste. The XRF and chemical analysis and ICP-MS show that the sample S₁ consists of 63.3% SiC, 31.2% Si, 5.3% FeO, and 0.2% other impurities (mass fraction). ICP-MS analysis shows that the sample also contains 22×10^{-6} B and 15×10^{-6} P.

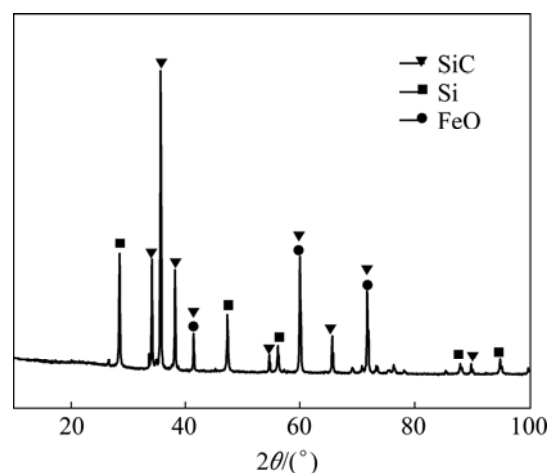


Fig. 1 XRD pattern of heated cutting loss waste S₁

Figure 2 shows the particles size distribution (PSD) of the sample S₁. The particles in the sample S₁ have sizes in the range from 1.0 to 23.8 μm. Two distributions peaked at 1.8 and 6.6 μm have been found in the PSD curve, indicating that the sizes of Si and SiC might be different. The volume fraction of the particles with sizes of 1.0–4.1 μm is about 40%, and that of the particles with sizes of 4.1–23.8 μm is around 60%. It has also been found from SEM observation that the particles with sizes larger than 10 μm and smaller particles with sizes between 1 and 4 μm exist in the sample. EDS analysis shows that most of the smaller particles are Si and most of the larger particles are SiC, indicating that the size distributions peaked at 1.8 and 6.6 μm are mainly

attributed to the Si and SiC particles, respectively. Of course, the smaller SiC particles and larger Si particles also coexist, though the volume fraction is very low.

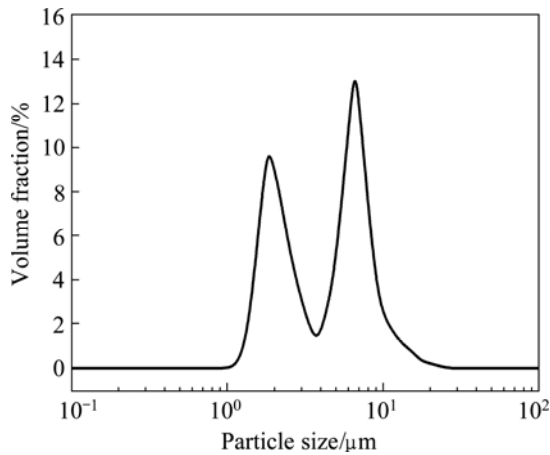


Fig. 2 Particle size distribution of heated cutting loss waste S_1

3.2 Separation of Si particles from cutting waste

The sample S_1 consists of larger SiC particles and smaller Si particles. It is well known that the densities of SiC and Si are 3.16 and 2.33 g/cm³, respectively. The large density difference between SiC and Si infers that the separation between Si and SiC could be realized by a gravity sedimentation process. Assuming the particle in a solution is a regular sphere with a diameter of D_p , and the sedimentation obeys Stokes' law [24,25], the stable sedimentation velocity (u_{pm}) of the particle can be calculated as follows:

$$u_{pm} = \frac{(\rho_p - \rho)}{18\mu} D_p^2 g \quad (1)$$

where g is the gravitational acceleration; ρ_p is the density of the particle; ρ is the density of the solution; and μ is the viscosity of the solution. It is clear that the settling velocity of a particle in a solution depends on the particle size, the density difference between particle and solution, and the viscosity of the solution. The ratio of the sedimentation velocity of the SiC to Si particles could be calculated by

$$\frac{v_{SiC}}{v_{Si}} = \frac{D_{SiC}^2 (\rho_{SiC} - \rho)}{D_{Si}^2 (\rho_{Si} - \rho)} \quad (2)$$

where v_{SiC} and v_{Si} are the sedimentation velocities of the SiC and Si particles, respectively; ρ_{SiC} is 3.16 g/cm³; ρ_{Si} is 2.33 g/cm³; D_{SiC} and D_{Si} are the particle diameters of the SiC and Si particles, respectively. When the sedimentation is performed in water, the settling velocity of the Si particles with size of 1.8 μm is 2.35 μm/s, the settling velocity of the SiC particle with size of 6.6 μm is 51.22 μm/s, the v_{SiC}/v_{Si} (peak) is 19.6, meaning that the separation between SiC and Si in the cutting waste could be realized in water. Of course, due to the interaction and

complex size distributions of Si and SiC particles, the real sedimentation process will be affected by sedimentation time and the ratio of solid to liquid.

Figure 3 shows the Si contents in the Si-rich powders S_2 , which were obtained at different sedimentation time and ratios of solid to liquid. It is clear that the Si-rich powders S_2 obtained at smaller ratio of solid to liquid have higher Si content. At a certain ratio of solid to liquid, the Si content in the sample S_2 firstly increases with the sedimentation time, and then reaches its maximum at the sedimentation time of 4–5 h. Figure 4 shows the Si recovery rates at different sedimentation time and ratios of solid to liquid. At all the ratios of solid to liquid, the Si recovery rate decreases with increasing the sedimentation time, and the larger ratio of solid to liquid is benefit to the increase of the Si recovery rate. Considering both the Si content in sample S_2 and the Si recovery rate, the best all-over separation efficiency between Si and SiC particles can be reached at the solid to liquid ratio of 0.08 and the sedimentation time of 5 h. The Si-rich powders S_2 obtained at such conditions consist of 79.0% Si, 12.8% SiC, 6.84% Fe, 21×10^{-6} B and 16×10^{-6} P.

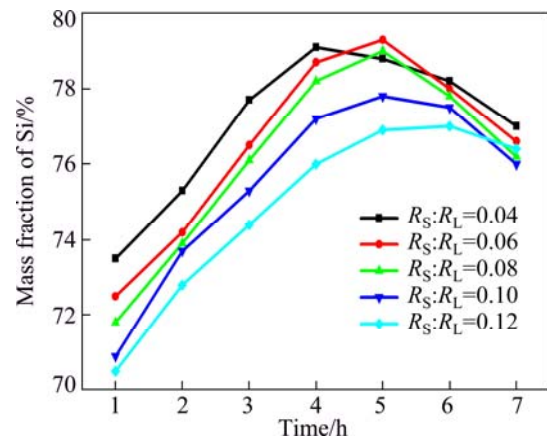


Fig. 3 Si content in Si-rich powders S_2 obtained at different sedimentation time and ratios of solid to liquid ($R_S:R_L$)

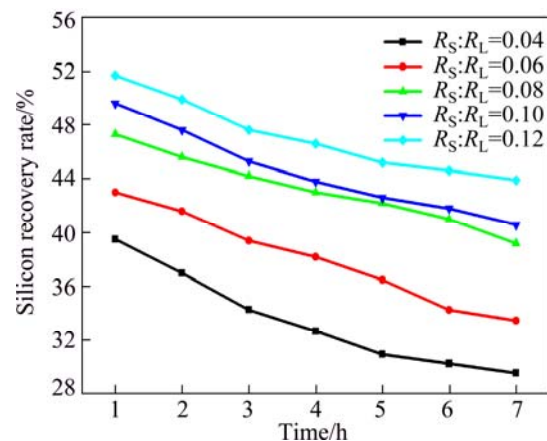


Fig. 4 Si recovery rates at different sedimentation time and ratios of solid to liquid ($R_S:R_L$)

3.3 Removal of iron from Si-rich powders

The iron in the Si-rich powders S_2 can be removed using acid leaching. The effects of the leaching time, leaching temperature and HCl concentration on the removal efficiency of iron have been investigated. The optimized acid leaching process parameters are the leaching temperature of 70 °C, leaching time of 3 h, HCl concentration of 15%, the leaching liquid to solid ratio of 4:1, and the stirring velocity during acid leaching of 150 r/min. At such optimized conditions, the iron content in the Si-rich powder reduces to 0.22%. The removal efficiency could be as high as 97%. The Si-rich powders S_3 obtained after acid leaching have 85.0% Si, 13.8% SiC, 0.22% Fe, 10×10^{-6} B, 8×10^{-6} P, and 0.93% other impurities. It can be concluded that the acid leaching process could realize the removal of iron in the Si-rich powders.

3.4 High temperature melting of Si-rich powders

The above powders S_3 were then pressed into pellets. The Si ingot was obtained by melting the pellets in a vacuum furnace. Figure 5 shows the photos of the Si ingot. The Si can be found at the bottom of the crucible, and SiC moved to surface of Si ingot during melting processing. Figure 6 shows the XRD pattern of the Si ingot. All the Bragg peaks in the XRD pattern can be indexed to Si. No any other phases have been found in the detect limitation of the XRD. Figure 7 shows the SEM image of the Si ingot. EDX analysis shows that area marked as A is Si, and the white phase marked as B consists of 65% Si, 25% Fe and 9% Al (mole fraction). The Si ingot has 99.96% Si, 1.1×10^{-6} B, and 4.0×10^{-6} P (mass fraction). The amounts of Si, B and P in the



Fig. 5 Photos of Si ingot: (a) Cross section; (b) Surface

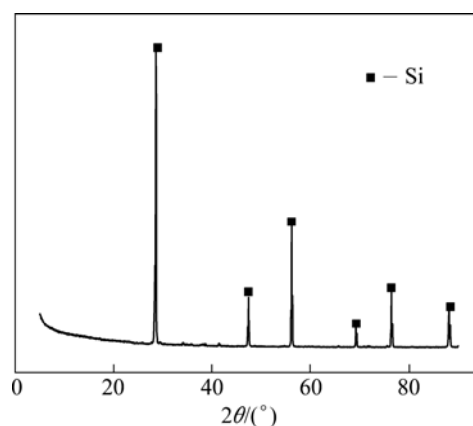


Fig. 6 XRD pattern of Si ingot

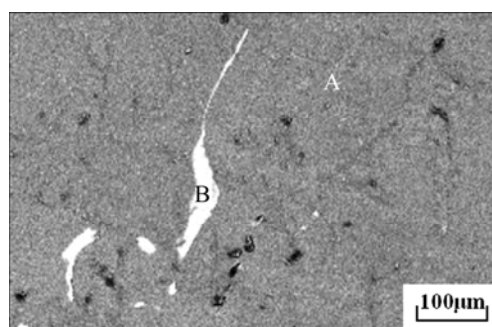


Fig. 7 SEM image of Si ingot

metallurgy grade Si (MG-Si) are 98%–99%, 20×10^{-6} – 60×10^{-6} and 120×10^{-6} – 200×10^{-6} , respectively. It is still very clear that the purity of the Si ingot is much better than that of MG-Si, and the amounts of B and P in the Si ingot are much lower than those in the industrial Si. Of courses, the contents of B, P, Fe and Al in the Si ingot are still higher than those in the solar grade Si. Among those impurities, the Fe could come from the cutting wire, i.e. cutting loss slurry, and the B, P and Al mainly come from SiC abrasives and the graphite crucible used for melting the Si-rich powders. It is expected that the level of B and P can be further reduced in a large scale industrial process or by a quartz crucible. The metal in the Si could be removed using directional solidification. Therefore, producing SoG-Si from the cutting loss waste is feasible.

4 Conclusions

1) The SoG-Si cutting waste from REC Norway has been characterized. The cutting loss waste consists of 63.3%SiC, 31.2%Si, 5.3%FeO, 22×10^{-6} B, 15×10^{-6} P and 0.2% other impurity. The particles have sizes in the range from 1.0 to 23.8 μm. Two distributions peaked at 1.8 and 6.6 μm have been found in the particle size distribution curve. The peaks ranging from 1.0 to 4.1 μm are attributed to the Si particles, while the peaks ranging from 4.1 to 23.8 μm mainly consist of SiC particles.

2) The separation of Si from the cutting waste could

be realized using a physical sedimentation process in water. The Si-rich powders S_2 obtained at the optimal sedimentation parameters (the volume ratio of solid to liquid is 0.08, and sedimentation time is 5 h) consist of 79.0% Si, 12.8% SiC, 6.84% Fe, 21×10^{-6} B and 16×10^{-6} P.

3) The Fe, B, P in the Si-rich powders S_2 could be removed using the HCl acid leaching. The iron removal efficiency could be reached 97% at the optimal conditions (leaching time is 3 h, leaching temperature is 70 °C, acid concentration is 15%, stirring velocity is 150 r/min, and the volume ratio of liquid to solid is 4:1), and B and P contents in Si-powders S_3 decrease from 21×10^{-6} to 8×10^{-6} and 16×10^{-6} to 10×10^{-6} , respectively, compared to those of Si-rich powders S_2 .

4) The high purity Si with 99.96% Si, 1.1×10^{-6} B and 4.0×10^{-6} P was obtained by melting the Si-rich powders. It could be feasible to produce SoG-Si from the Si cutting slurry.

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太阳能晶体硅切割废料中高纯硅的提取

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摘 要: 研究从太阳能晶体硅切割废料中制取高纯硅。分析切割废料的组成、粒度分布等, 利用物理沉降法对废料中的硅粉进行富集, 然后经酸洗除杂。研究酸洗工艺参数如酸洗时间、温度、固液比等对提纯效率的影响, 并优化工艺参数。最后将酸洗除杂的硅富集料进行真空高温熔炼获得含 99.96%Si、 1.1×10^{-6} B 及 4.0×10^{-6} P(质量分数)的高纯硅。结果表明: 从晶体硅切割废料中回收太阳能多晶硅是未来的一个重要发展方向。

关键词: 太阳能多晶硅; 切割废料; 高纯硅; 回收; 物理沉降; 高温熔炼

(Edited by Chao WANG)