Removal of Fe, B and P impurities by enhanced separation technique from silicon-rich powder of the multi-wire sawing slurry

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Abstract

The silicon-rich powder, which was separated by tuning the particle surface potential combined with centrifugation, contains varied impurities like iron, boron and phosphorus. To remove these impurities, the process of pre-dispersion and magnetic separation was attempted. The aggregates in the silicon-rich powder were dispersed by surface potential tuning combined with microwave treatment. According to the DLVO theory and experimental results, the electrostatic repulsion of the particles was largest when the pH value of solution reached 13.0, and the fine silicon-rich particles can be kept sufficiently dispersed at this pH, which was good for the further separation by magnetic field with the 90% removal of iron impurity. The residual iron impurity can be further completely removed by the microwave acid leaching with the mixing acid solutions of hydrofluoric and hydrochloric acid. By combining these enhanced purification techniques, other bothersome impurities such as boron and phosphorus can also be reduced to the requirements of solar grade polysilicon. This work is good for the recycling of silicon scrap materials to the solar grade polysilicon.

Keywords:

wiresawing slurry; silicon-rich powder; pre-dispersion; magnetic separation; microwave acid leaching.

1. Introduction

Solar energy, which has many advantages in comparison with conventional energy sources, shows great potential for the sustainable development of modern society. The major developed countries are actively developing various new technologies to utilize the solar energy. Among them, the most popular one is based on the solar photovoltaic effect by which the solar energy can be converted to electric energy[1]. Till today, the photovoltaic modules are mainly composed of single crystal silicon and polysilicon wafers, which is very typical in the solar energy industry.

Currently, in the Si-wafer industry, the method of manufacturing polycrystalline silicon wafers is the multi-wire sawing way, which makes the silicon ingot cut into hundreds of thin pieces by the cutting wires at high speed reciprocation motions. During the cutting wire process, the silicon carbide was used as abrasive and the polyethylene glycol as dispersing agent. The thickness of Si-wafers in the range of $180\sim 240\mu\text{m}$, or even thinner to $100\mu\text{m}$. Although the diameter of the cutting wires was also reduced to $100\sim 140\mu\text{m}$ nowadays, there is still at least 40% of the high purity silicon ingot lost into the cutting waste slurry[2, 3]. The polysilicon consumption all over the world in 2014 was around 240000 tons, so it can be estimated that about 100000 tons of silicon was wasted as the slurry during the multi-wire sawing process. It is quite natural to have the idea, whether this slurry can be used to extract the silicon to the high purity in a cost-effective way, and make it reused in SoG-Si production[4]. Obviously, this work is quite worth doing for lowering the production cost of the solar silicon battery, while there are at least two challenges must be solved, i.e., the first one is to separate the Si/SiC mixture powder effectively to obtain the Si-rich powder, and the second one is to remove the tiresome harmful impurities such as boron, phosphorous to the SoG-Si requirements. If these two problems can be solved in a good way, the huge silicon slurry can be reutilized in a high-value way.

Many studies have been carried out on the separation of the Si and SiC mixture powder from the cutting slurry, and for further purification of the obtain Si-rich powder, most economic and effective process in by hydrometallurgical leaching, usually by using acid. While in the real leaching process, the aggregation of the fine

Si particles would prevent the sufficient removal of the contained impurities, so the most important step before the leaching is actually how to make the powder dispersed as much as possible, which will determine the purification efficiency of the acid leaching. The present study is focusing on this problem and proposed a simple and easy way to dispersed the fine Si-particles. Based on this idea, the removal of typical impurities of iron, boron and phosphorous was tested to evaluate the effectiveness of this method [5-12].

The impurities of boron and phosphorus could reduce the photoelectric conversion efficiency of the silicon battery, and also the most difficult ones to be removed by traditional pyrometallurgical processes due to their very high equilibrium segregation coefficient of 0.8 and 0.35 respectively. As for the removal of these two impurities in the slurry, hydrometallurgical leaching process is the best candidate technique [13-15]. There are quite frequently reported that the acid leaching can remove the impurities in the silicon powders since 1927[16, 17]. In our previous work, it was evaluated that the iron content in the Si-rich powder after centrifugation reached 5.68%, so it can be estimated that removal of this iron by individual acid leaching would consume large amount of acid. Therefore, in present study we prefer to try the magnetic separation technique to find out if the acid consumption would be reduced. Furthermore, how to reduce the residual boron and phosphorous in the Si-rich powder after acid leaching process to a permissible level, is still a big challenge and will also be investigated in this study.

In a word, the novel process proposed to remove the impurities of iron, boron and phosphorus from the Si-rich powder in this study includes the three main steps, i.e., predispersion, magnetic separation and the microwave acid leaching.

2. Experimental

2.1 Materials

The silicon wiresawing waste was kindly donated by Liaoyang Silicon Co. Ltd. in Liaoning Province of China and the most of the polyethylene glycol (PEG) had been removed by washing in the factory. The silicon carbide and the silicon powders are

the major constituents of the waste, besides, small amount of the metal chips also included in. It was analyzed that the content of boron and phosphorus in the cutting wastes was much beyond the standards of SoG-Si, which extremely affect recovered high purity silicon reused.

The silicon-rich powders, obtained by the process of tuning the particle surface potential combined with centrifugation, and the detailed experimental procedures can be referred to the previous work of our research [18]. All the acid and alkaline reagents used in the study is of analytical purity.

2.2 Analytical techniques

The silicon-rich powder samples were dissolved by the equal volume mixed of nitric acid (3mol/L) and hydrofluoric acid (2mol/L), and the agitatingly dissolving time was about 3 hours until there was no bubble emerged. The concentrations of iron, boron and phosphorus in the filtered solution were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (OPTIMA 7000DV). Scanning electron microscopy (SEM, Cambridge S-360) instrument was used to observe the morphology of the particle samples. Transmission electron microscopy (TEM, JSM-2010) can observe the fine structure of the samples. The Energy Dispersive X-ray Spectroscopy (EDS, Cambridge S-360) was used to analyze the elements distribution of the particle surface. The particle sizes distribution of the samples are analyzed by LMS-30 Laser Mastersizer made in Janpan.

2.3 The impurities' content of silicon-rich powder sample

The contents of the impurities in the silicon-rich powder sample should be determined. One gram of the silicon-rich powder sample was collected in a plastic beaker and 100 ml mixing acid with 0.10mol/L hydrofluoric acid and 0.20mol/L nitric acid was added to dissolve the silicon and other metals. The solution was stirred constantly until no bubbles emerged, meaning that the dissolving reaction was essentially completed. The insoluble particles which is mainly composed of SiC were filtered and washed with the deionized water for 5 times to remove the residual acid. The filtrated solution was collected and added to the volume of 200 ml by deionized

water. The content of Fe, B and P in the filtrated solution were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy(ICP-AES).

2.4 Suspension ratio of the particles in the solution

The samples of 0.5g silicon-rich powder with 80ml deionized water was placed in a cylinder and tuned the solution pH value to 7.0, 8.5, 10.0, 11.5 and 13.0 respectively by using aqueous solution of 10%(v/v) ammonia, then increasing the solution volume to 100ml by adding deionized water. These cylinders were shaken uniformly and placed for 5 hours. By using the same method, the samples were prepared for different sedimentation time of 10 hours, 20 hours and 30 hours. The upper solution of 90 ml in the cylinder was pumped out, and the residual solution was poured into an evaporation dish which was weighed and recorded as M_z . The solution in the evaporation dish was dried by the dry oven with the temperature of 50°C , then weighed and recorded as M .

The suspension ratio of the particles (recorded as x) in the solution can be calculated according to the following equations:

$$x = \left(1 - \frac{M-M_z}{0.5} \right) \times \frac{10}{9} \quad (1)$$

3.Results and Discussion

3.1 The aggregation of silicon-rich powders

The aggregation of fine particles in the silicon wiresawing waste powders may be caused by the frictional effects in the cutting process, or the drying and dehydration process. As shown in Fig.2, the particle size distribution of the silicon-rich powders is quite different before and after drying. It appears that the diameter range of the particles is 0.39~3.02 μ m before drying, while after drying, this range change to 0.39~9.95 μ m. This means that the Si-rich particles will aggregate through the drying process. The aggregation process of fine particles may include in the impurities in to the formed aggregated particles, obviously leading to the difficulty of releasing these impurities in to the leaching solution as well as the leaching efficiency. So it is very important to study the formation mechanism of these aggregates, in order to design the appropriate approaches to remove these impurities.

Fig. 1 Particle size distribution of the Si-rich powder before and after drying.
(a. before drying, b. after drying)

The aggregation of fine particles generally divided into the soft and hard types. The soft aggregation was directly caused by molecular force, capillary force and electrostatic attraction among the surface molecules or atoms of the particles, so the formatted aggregates have relatively low hardness. As to the hard aggregation, the chemical bonding existed like oxygen bridges between the particles, so the bonding strength of the fine particles are strong enough to make the aggregates having high hardness. As for the concrete formation mechanism, the crystal bridge theory and the hydrogen bond theory could be used to explain the particle aggregation during the drying process[19].

Figure 2 shows the silicon-rich powders obtained by the centrifugal process which have the aggregations. It can be seen that many tiny particles with the average diameters of 1μm aggregated into a large particle. Obviously, the aggregation is not good for the sufficient extraction of the those impurities contained in the inner part of the large particle, and pre-dispersion of these aggregation particles would be helpful for the effective removal of impurities.

Fig. 2 SEM photographs of Si-rich powder

3.2 Dispersion of silicon-rich particles

The aggregated particles can be effectively dispersed by the mechanical energy (such as milling, ultrasonic wave). The effect of the ultrasonic treatment on the particle dispersing is illustrated in Fig.3. It can be seen that the particle diameter range significantly decreased after the ultrasonic treatment. It can be understood that the ultrasonic treatment, the aggregates suspended in the solution would be fractured by the cavity effect, mechanical effect and high-temperature effect of the ultrasonic waves. Every mass point of the water molecules can produce high frequency vibrations when the ultrasonic travels through the water and may break the particle aggregation into pieces.

Fig.3 Particle size distribution of the Si-rich powder

(a. without ultrasonic waves treatment, b. ultrasonic waves treatment for 30min)

Usually, the physical dispersion method such as the mentioned above cannot completely disperse the aggregated particles. Based on the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, it was well known that the particles in the water have the micro-structures of electric double layers over their surfaces[20]. When the diffusion layers of the particles overlap between each other, the electrostatic repulsive would weaken the bonding strength of the particles and disperse them. The stability of suspension system, whether the suspended particles in the aggregated state or disperse state, is essentially decided by Van der Waals force power and electrostatic repulsion force power of electric double layer of each particles. In a frank word, the zeta potential of the particles represents the surface repulsive forces between the suspended particle, indirectly reflecting the dispersion degree of the particles in the suspension[21]. As to Fig.4, both of the silicon particles and the silicon carbide particle zeta potential would increase with the pH value increasing above pH 3.2. And once the pH value over 10, the electrostatic repulsion force between particles reached maximum and showed a maximum particle dispersion effect.

Fig.4 Zeta potentials values of Si and SiC particles in the aqueous solutions at different pH values

The suspension ratio of the Si-rich fine particles can further prove the effect of pH value on the particles dispersion in the solution. The silicon-rich powders would settle to the bottom when kept settling for a certain period of time. The suspension ratio is

the fraction of the suspended particles in the solution. Fig.5 shows that the suspension ratio is quite different under different pH conditions. The suspension ratio reached 85% only after 5 hours settling in the solution at pH 7, and reduced to about 10% when settled after 30 hours. When the pH value is 13, even after settling for 30 hours, the suspension ratio is still kept at 95%, meaning that even in such a high pH value, the surface potential of each fine particle is large enough to keep the particle suspended in the solution. Obviously, the dispersed state of these fine particles is quite favorable for the smooth release of the included impurities such as iron, boron and phosphorus.

Fig.5 The suspension ratio of the silicon-rich powders at different pHs

Fig.6 shows the variation of the silicon-rich particle diameter range after the alkalization treatment. As demonstrated above, the alkalization treatment favorable for the dispersion of the silicon-rich powders. And especially for the particles combined the effect of ultrasonic waves and the electrostatic repulsion, the diameter range from $0.65 \sim 9.39 \mu\text{m}$ to $0.33 \sim 2.55 \mu\text{m}$. So it can be seen that by combining the dispersion effect of zeta potential of the fine particles and ultrasonic treatment, the dispersion of the fine particles would reach the optimal results, and can be recommended as the effective means for predispersion before the separation treatment.

Fig.6 Particle size distribution of the Si-rich powder

- (a. Si-rich powder in water, b. Si-rich powder in alkaline solution of pH 13,
c. ultrasonic wave of the Si-rich powder in alkaline solution of pH 13)

3.3 Existence form of iron and magnetic separation efficiency

In silicon-rich powders, the content of iron is analyze to be more than 5.68%(m/m). The iron scraps included into the silicon wiresawing waste may exist in the three types. The first type is individual metal iron particles, which can be adsorbed by the magnetic field. The second one is the finer iron fragments adhered to silicon or silicon carbide particles, which may be caused due to the friction effect during the multi-wire sawing motion, some iron particles were adsorbed on the surface of the silicon or SiC particles. For these two types of iron scrap, the particles can be removed by magnetic separation by utilizing their magnetic effect. The EDS results confirm the existence forms of iron particles, was shown in Fig.7. The particles in the red circle corresponds to the white circle on Fig. 7(a) which are the individual irons. And the red squares on the Fig 7(b,c) is the range of the EDS.

Fig. 7 EDS patterns of iron included in the Si-rich powder

(a. individual iron particles,

b.c. finer iron fragments adhered to silicon or silicon carbide particles)

As the results shown above, it can be seen that by combining the effect of ultrasonic waves and the electrostatic repulsion, the silicon-rich particles can be well dispersed. So if these dispersed fine particles can be subjective to the magnetic separation, the optimal separation efficiency may reached through the magnetic field, in which the ferromagnetic substance can be adsorbed by magnetic field, and non-magnetic substances such as Si and SiC powder were collected for further purification, as shown in Fig.8.

Fig. 8 The schematic of magnetic separation process for predispersed Si-rich suspension

The dispersed silicon-rich suspension was pumped uniformly to the magnetic separation equipment with a peristaltic pump, then the ferromagnetic substance and non-magnetic substances can be separated by the magnetic field. The dispersive degree of the particles would affect the yield of the silicon powders. Fig.9 shows the proportion of these two substances with different dispersing way. Without the dispersive process, most of the particles were absorbed by the magnetic field, and only 20.98% particles could pass smoothly the magnetic field. Due to the aggregation, the iron scraps, silicon particles and a few silicon carbide particles are not the individual form particles. The percent of magnetic substance decreased to 23.05% after the pH adjusted by adding aqua ammonia.

Fig.9 The content of iron in the Magnetic substance and Non-Magnetic substance(a. without predispersion, b. predispersion by ultrasonic waves treatment, c. predispersion by alkalization treatment combined ultrasonic waves treatment)

The content of ferromagnetic substance and non-magnetic substances is different with the different dispersive ways and the results were listed in Table.1. The removal ratio of iron reached more than 90% by the pre-dispersion and magnetic separation process, and especially for the alkalization treatment combined ultrasonic waves treatment, the removal ratio reduced to 0.48% after the magnetic separation. Thus, the acid consumption for the further leaching process can be drastically reduced.

Table.1 The result of the magnetic separation

Predispersion Methods	Fe % wt. in Non-Magnetic Substance	Fe % wt. in Magnetic Substance
Ultrasonic	0.52	18.42
Alkaline +Ultrasonic	0.48	21.33

The silicon-rich powders, which had been treated by the pre-dispersion and magnetic separation process, also contain impurities, especially boron and

phosphorous. The microwave acid leaching method was attempted to remove these residual impurities. The leaching agent is a mixed acid of hydrochloric acid and hydrofluoric acid for a certain concentration. The contents of the main impurities before and after acid leaching process were showed in Table.2. It was shown that the content of boron and phosphorous after leaching cannot be detected. It is confirmed that the impurities of dispersed particles can be exposed well to the acid leaching agent for the sufficient dissolving. Besides, the coordination effect of fluoride and chloride with the impurities may also cause a better erodibility with the metal ion.

Table.2 The contents of main impurities for different samples after treatment

Samples	Fe	B	P
Si-rich powder	56771	143	239
After magnetic separation	4823	21	39
After acid leaching	No detection	No detection	No detection

4. Conclusion

The fine Si-rich powder tends to aggregate during the cutting and drying processes, which will bring the trouble to the further removal of impurities included in. Surface potential of the Si and SiC particles was tuning by vary the solution pH, which dispersed the fine particles drastically due to the strong repulsive force. If combining with the ultrasonic treatment, the particles would be dispersed better. So after above predispersion, magnetic separation can more effectively remove the iron impurities, with the 5.68% of the initial content of iron in the silicon-rich powder reduced to 0.48%. The residual impurities of boron and phosphorus were almost removed completely by the microwave acid leaching with mixed acids of hydrochloric acid and hydrofluoric acid as the leaching agent. This work provides a simple and effective process to remove the impurities in the Si-rich powders which were derived from the cutting slurry, and the results can also be referred by the silicon scrap recycling for SoG-Si industry.

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