Recovery of silicon powder from kerf loss slurry waste using superconducting high gradient magnetic separation technology

Changqiao Yang¹ · Suqin Li¹ · Ruiming Yang¹ · Jiaxing Bai¹ · Zijie Guo¹

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Abstract A major challenge in recycling of silicon powder from kerf loss slurry waste is the complete removal of metal particles. The traditional acid leaching method is costly and not green. In this paper, a novel approach to recover high-purity Si from the kerf loss slurry waste of solar grade silicon was investigated. The metal impurities were removed with superconducting high gradient magnetic separation technology. The effects of process parameters such as magnetic flux density, slurry density, and slurry flow velocity on the removal efficiency were investigated, and the parameters were optimized. In one lot of control experiments, the silicon content was increased from 90.91 to 95.83%, iron content reduced from 3.24 to 0.57%, and aluminum content from 2.44 to 1.51% under the optimum conditions of magnetic flux density of 4.0 T, slurry density of 20 g/L, and slurry flow velocity of 500 mL/min. The result indicates that the superconducting high gradient magnetic separation technology is a feasible purifying method, and the magnetic separation concentrate could be used as an intermediate product for high-purity Si powder.

Keywords Silicon powder · Kerf loss slurry waste · Superconducting high gradient magnetic separation technology · Metal impurities removal · Purification

Introduction

Conventional energy shortage and environmental concerns have made the solar energy industry popular globally. Solar energy has many unique advantages. It is inexhaustible, renewable, and pollution-free [1, 2]. The rapid development of photovoltaic industries leads to a shortage of polysilicon, which is the material of choice to fabricate photovoltaic converter, and its price has multiplied [3–5]. In the next few decades, there is no other material to replace polysilicon as the main material for photovoltaic industry. To fabricate the solar cell, polycrystalline silicon rods are sliced into 0.2–0.7 mm-thick silicon wafers with multi-wire cutting, in which the wire diameter is usually 0.2–0.5 mm, which is about the thickness of the silicon wafer [6]. While the theoretical calculation tells that 44% of the rod polysilicon material becomes powder and goes into the slurry waste in the process of wafer slicing, the actual loss is usually 50–52% in real process [7]. Each year, about 3800 t (according to the current global polysilicon production data) of solar grade polysilicon material has been lost in the slicing process, which amounts to \$4.5 billion based on the current unit price of \$120/kg. Effective recycling of the lost silicon material will alleviate the shortage of solar grade silicon with significant economic and environmental benefit.

The conventional processes to reclaim silicon powder from kerf loss slurry waste are distillation-centrifugal separation, electrophoresis, gravitational settling [8], high-temperature treatment [9], etc. Jin et al. [10] patented a reclaim procedure: acid pickling and solid–liquid separation are carried out with the slurry waste, the obtained liquid then goes through a distillation–condensation–dehydration series, before the solidification product is treated with nitric acid and hydrofluoric acid to get the Si and SiC materials. Sousa et al. [11] used a thermal

✉ Suqin Li
lisuqin@metall.ustb.edu.cn

¹ School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 10083, China

plasma process to recycle silicon kerf loss for solar grade silicon feedstock. Their result shows that the deoxidation rate of the final silicon ingot was as high as 80% and the initial carbon concentration was reduced by 85%. Wang et al. [12] applied nitric acid to dissolve iron and a centrifuge separator to remove most of SiC before the Si was reclaimed and purified with high-temperature processing and directional solidification. To some extent, this method was suitable for industrial scale production, but there are some limitations. Acid corrosion of the surface of centrifuge may occur after long-term use of acid treatment. Lin et al. [13] reported about the use of centrifuge to separate Si and SiC from slurry waste. They used acetone at first to remove suspending agent and binder, and nitric acid to dissolve iron, before a centrifuge was used to separate Si and SiC. Silicon powder of 90.8% purity and 74.1% recovery rate were achieved with the following experiment conditions: solid volume concentration of 6.5%, medium liquid density of 2.35 g/cm³, 60 min churning time, and 60 min centrifuge time. Further high-temperature process is needed as the purity of the reclaimed powder is not up to the solar grade standard, since Si and SiC particles have different density, surface charge, and particle size. Wu and Chen [14] used electrical field and gravity to separate Si and SiC particles. The obtained silicon powder still contains metal impurities elements such as Fe, Al, etc., from the wear-and-tear of the cutting wire, and the subsequent purification to achieve solar grade purity, which is still in stage of research at present, is a significant challenge.

The superconducting high gradient magnetic separation (HGMS) technology, which was developed from the conventional ferromagnetic technique, is a new physical separation technology. It is a simple, energy-efficient, inexpensive, and non-destructive technique with high efficiency and no secondary pollution [15]. The prominent feature of superconducting HGMS technology is the high magnetic flux density which the maximum reach 5.5 T [16]. The high saturation magnetic matrix is filled in the uniform background magnetic field, so that the magnetic flux density gradient is greatly increased. A higher magnetic flux density gives higher separation efficiency [17], so the superconducting HGMS is more suitable for capturing fine weakly magnetic particles. The first fully developed superconducting HGMS process was implemented in the Kaolin Clay industry to help clean and brighten the china clay. Dwari et al. [18] applied a low-intensity wet magnetic separator to concentrate iron resources from low grade siliceous iron ore. It obtained a concentrate of 67% Fe by recovering 90% of iron particles below 200 µm size. Li et al. [19] analyzed the effect of a high gradient magnetic field on the distribution of the solute Si. They found that a high gradient magnetic field is capable of separating the solute Si and the primary Si phase from matrix. However, superconducting HGMS technology has

yet to be used for separation and purification of Si powder from the kerf loss slurry waste.

The purpose of this study is developing an economic mass production technology for recovery and purification of Si powder from the kerf loss slurry waste. To that end, the effects of process parameters were investigated. The influencing factors and mechanism of magnetic separation were analyzed and discussed.

Experimental

The raw material used in experiments was the primary silicon powder prepared from the kerf loss slurry waste by centrifugation at Henan Solar Energy Silicon Products Company, China. The primary silicon powder was ash black with slightly metallic luster, consisting of Si and metal fragments (mainly iron fragments). The phases in the powder were identified by XRD (D/max 2550PC, Japan Rigaku Co., Ltd) with Cu K α radiation, and the particles morphology and microstructure were observed by SEM with EDS (ZEISS EVO 18 Special Edition, Germany Carl Zeiss Jena). The amount of Si, Fe, Al and other elements were determined by XRF (Axios mAX, Netherlands PANalytical) with 4.0 kW, 160 mA.

The separation between metal fragments and Si powder was performed using the superconducting HGMS method. Figure 1 shows a process flow diagram of the superconducting HGMS system used in our experiment. The superconducting device designed by Institute of High Energy Physics, Chinese Academy of Sciences, consists of two superconducting magnets and a high gradient reactor. The two superconducting magnets are used to generate a high-intensity magnetic field, while the high gradient reactor is filled with magnetic matrix (steel wools) which can raise the gradient

Fig. 1 Schematic diagram of superconducting HGMS

of the magnetic field and increase the magnetic force acting on magnetic particles.

The prepared slurry was fed into the high gradient reactor via the inlet. Metal particles are captured by steel wools and non-magnetic particles (silicon powder) are to be exported with the slurry through the outlet. The slurry was collected with beaker and dried in a drying oven at 105 °C, and then, their chemical constituents were examined. The steel wools were fetched out from high gradient reactor when the magnetic separation process was finished. Rinse off the metal particles adsorbed on the steel wools with a high-pressure water gun. To study the influence of various parameters of superconducting HGMS technology, the experiments were carried out for various parameters such as magnetic flux density, slurry density, and slurry flow velocity. In conducting this inquiry trial, each test needs to be repeated twice, and then, the average of the three experiments is taken as the experimental results.

Results and discussion

Characterization of raw materials

The raw material was grinded and sieve graded as 45 µm particle for the experiment. Figure 2 shows the XRD pattern of the raw material in which the main peaks are indexed as Si and Fe₃O₄. The Si peaks have the highest intensity, indicating that Si is a major phase in the raw material. The major metal impurity particles are Fe₃O₄.

Fig. 2 XRD pattern of raw material

Table 1 Chemical composition of raw material by XRF (%)

Si	Fe	Al	Ca	Ti	V	Ni	P	Mn	S	Zr	Ba
90.91	3.24	2.44	0.81	0.66	0.49	0.22	0.20	0.08	0.06	0.06	0.04

The chemical composition of sample is shown in Table 1. XRF analysis shows that the sample consists of 90.91% Si, 3.24% Fe, 2.44% Al, and other impurity elements. Figure 3 shows the particles morphology and distribution of elements. Si particles are of irregular shape with sharp edges, and their size is bigger than other impurity particles. Figure 3 also clearly shows the dominance of Si particles and the fact that impurity elements such as Fe, Al, and Ca exist independently and do not associate with Si particles. This is critical in physical separation and removal of the impurity particles, especially the iron impurities.

The effect of magnetic flux density on metal impurities removal

The effect of magnetic flux density on the removal performance was investigated with the superconducting HGMS separator, at different magnetic flux densities ranging from 0 to 5.0 T. Other settings are: steel wools filling ratio 10%, slurry density 10 g/L, and slurry flow velocity 300 mL/min. The result is shown in Fig. 4, which gives an optimum value of 4.0 T and a maximum Si content of 94.01%. The Si content increases with magnetic flux density until the latter hits the point of 4.0 T, where the Si content starts to decrease with further increase of magnetic flux density. Compared with the Si content, Fe content follows the opposite trend. Before 4.0 T, the Fe content decreases with magnetic flux density. The minimum Fe content is 0.66%, and the removal rate is 79.63%, which is rather significant. However, Al content has changed little around 1.53%. Compared with the initial content, the Al content was reduced by 36.89%.

Magnetic separation is a physical separation method based on the magnetic differences of the materials. In a magnetic field, a particle is under the influence of the magnetic force and composite stray force (such as gravity, inertia force, fluid drag force, etc.). For effective separation of magnetic materials, the magnetic force F_m (act on the magnetic particle) must be greater than the overall composite stray force F_c [20]. The formula of F_m is

$$F_m = \frac{\chi}{\mu_0} VB \text{ grad}B = \frac{4\chi}{3\mu} \pi r^3 B \text{ grad}B, \quad (1)$$

where χ is the magnetic susceptibility of the particle, μ_0 is the vacuum magnetic permeability, V is the particle volume, B is the magnetic flux density, $\text{grad}B$ is the magnetic flux density gradient, and r is the particle radius.

Fig. 3 SEM images of raw material

Fig. 4 Effect of magnetic flux density on the removal performance

Fig. 5 Relationship between magnetization and magnetic field intensity of hematite

From Eq. (1), F_m mainly depends on the physical properties of the particles (magnetic susceptibility), magnetic flux density, and magnetic flux density gradient. In the process of magnetic separation of the fine weakly magnetic particles, large magnetic force is needed to capture them from the slurry, and usually, the efficiency is improved with increased magnetic flux density and magnetic flux density gradient. However, this is true only within a certain range. Take the iron ore, for example: in room temperature, hematite is basically paramagnetic, with a rather weak ferromagnetism. The relationship between magnetization and magnetic field intensity is shown in Fig. 5.

From Fig. 5, the curve has constant slope above a certain magnetic field intensity (usually 2.2×10^6 A/m, this

value is different for different minerals). The magnetization is given as [21] follows:

$$M = M_0 + \chi_\infty H, \quad (2)$$

where M and M_0 are the magnetization and the magnetization in vacuum, respectively, χ_∞ is the magnetic susceptibility under infinite magnetic field intensity, and H is the magnetic field intensity.

The formula of magnetic susceptibility is as follows:

$$\chi = \frac{M}{H} = \frac{M_0}{H} + \chi_\infty. \quad (3)$$

From Eq. (3), it is clear that iron-bearing mineral's magnetic susceptibility decreases with the increase of magnetic field intensity when the latter goes above a certain value. In the experiment, this threshold is 4.0 T. Going back to Eq. (1), F_m decreases with the decreasing χ when the magnetic flux density is greater than 4.0 T. The efficiency of iron impurities removal is decreased due to decreased F_m , which explains the turning point 4.0 T in Fig. 4. The slight Al content reduction may be attributed to Al particles mixing up with magnetic particles, and captured and carried away with the latter by the steel wools. Magnetic flocculation and mechanical mingling of particles may play a role in it.

The effect of slurry flow velocity on metal impurities removal

The velocity of slurry flowing through the magnetic medium determines the shear force exerted on the particles deposited on the surface of steel wools, which affects the recovery rate and the grade of the product. To investigate its effect on removal efficiency, the slurry flow velocity was changed from 300 to 700 mL/min. The previously found optimum magnetic flux density of 4.0 T was used in all following experiments. Steel wools filling ratio was kept constant at 10% and slurry density 10 g/L. The result is shown in Fig. 6.

Figure 6 shows the influence of flow velocity on the separation efficiency of Fe and Si particles. Better separation efficiency was observed at low velocity. When the velocity goes above 500 mL/min, Si content drops rapidly, while the Fe content increases. In the range of 300 to 700 mL/min, the effect of flow velocity on Al content is small. Si, Fe, and Al contents are 95.26, 0.61, and 1.51%, respectively, at the slurry flow velocity of 500 mL/min.

In the capture process, besides magnetic force F_m , magnetic particles are also under the influence of the fluid drag force F_D and gravity F_G . While F_G can be neglected for micro-sized particles, F_D is given by [22] the following:

$$F_D = 6\pi\eta r(v_f - v_p), \quad (4)$$

Fig. 6 Effect of slurry flow velocity on the removal performance

where η is dynamic viscosity coefficient of slurry, r is the radius of the particle, and v_f and v_p are slurry flow velocity and particle velocity, respectively.

The capture efficiency of magnetic particles (or magnetic separation efficiency) can be judged qualitatively by the ratio of F_m and F_D (R). F_m should be higher than F_D for separation to occur, and the larger the R value, the higher the efficiency. R is given by the following:

$$R = \frac{F_m}{F_D} = \frac{\frac{4\chi}{3\mu} \pi r^3 B \text{ grad} B}{6\pi \mu r v} \quad (5)$$

$$= \frac{2}{9\mu} \cdot \frac{\chi r^2}{\eta} \cdot \text{grad} B \cdot \frac{B}{v},$$

where $\frac{\chi r^2}{\eta}$ is a characteristic of slurry. It is easy to capture the large size and strongly magnetic particles when the slurry density is a fixed value (η is a fixed value). $\text{grad} B$ is a characteristic of the magnetic matrix (steel wools). The higher the magnetic flux density gradient generated by magnetic matrix, the easier it is to capture the magnetic particles. $\frac{B}{v}$ is a process parameter for magnetic separation. Particle properties and magnetic matrix properties are usually fixed, so B and v are the main factors to play with. In a sense, it can be said simply that R is proportional to B and inversely proportional to v . There is combined optimum value for B and v for the best separation efficiency.

During the magnetic separation process, the magnetic particles would face increased viscous resistance when the slurry flow velocity was increased. This would adversely affect the capture of magnetic particles by steel wools leading to lower Si content and higher Fe content. With superconducting HGMS, the slurry flow velocity should be kept low to help steel wools capture the magnetic particles. High slurry flow velocity will work against the separation of Si

Fig. 7 Effect of slurry density on the removal performance

and Fe from primary silicon powders. On the other hand, people also want to raise the slurry flow velocity for process capacity. As can be seen from the test results (Fig. 6), the best separation efficiency was obtained under the slurry flow velocity of 500 mL/min.

The effect of slurry density on metal impurities removal

The effect of slurry density on the removal performance was investigated at magnetic flux density of 4.0 T and slurry flow velocity of 500 mL/min. The result is shown in Fig. 7.

As can be seen from Fig. 7, the slurry density has a feeble effect on the removal performance when it is lower than 20 g/L. The Si content is increased from 95.26 to 95.83%, and the Fe content dropped from 0.61 to 0.57%, as the slurry density goes up to 20 g/L. When the slurry density is greater than 20 g/L, Si content falls rapidly and so does the removal performance. Al content does not change with the increase of the slurry density and stays around its average value of 1.51%.

The magnetic particles and the non-magnetic particles inevitably mix up with each other during the separation process. The separation efficiency reaches the peak value when this mixing up was minimum [23]. The distance between solid particles changes with the slurry density. The higher the density, the smaller the distance, and the greater the slurry viscosity, the more load of magnetic matrix. The selective separation would then be hindered, while the non-selective magnetic agglomeration enhanced. When the slurry density becomes very high, the number of the particles (both magnetic and non-magnetic) in a unit volume would be so large that the probability of them (both magnetic and non-magnetic) being captured by steel wools becomes big. The increased degree of physical mixing may also deteriorate the separation efficiency. The increased thickness of adsorption

Table 2 Chemical composition of concentrate by XRF (%)

Si	Fe	Al	Ca	Ti	V	Ni	P	Mn	S	Zr	Ba
95.83	0.57	1.51	0.71	0.58	0.50	0.19	0.21	0.05	0.06	0.06	0.03

Fig. 8 SEM images of raw material and magnetic concentrate. **a** Raw material, **b** magnetic concentrate, and **c** a single particle of concentrate

layer of captured magnetic particles on the steel wools surface would also reduce its ability to attract more magnetic particles. In Fig. 7, the optimum separation efficiency was obtained at the slurry density of 20 g/L.

Comprehensive condition experiment

Under the optimal parameters, i.e., a magnetic flux density of 4.0 T, a slurry flow velocity of 500 mL/min, and a pulp concentration of 20 g/L, the Si content was boosted from 90.91 to 95.83% after once superconducting HGMS test and the content of impurity elements (Fe, Al, etc.) were reduced to varying degrees. Chemical analysis results are shown in Table 2. How to separate the trail elements will be our future work.

Morphology and microstructure analysis

The morphologies changed from the raw material to magnetic concentrate are shown in Fig. 8, where Fig. 8a is for the raw material and b is the magnetic concentrate. In Fig. 8a, the particles vary significantly in grain size and shape, with many scattered tiny ones. After the separation purification, the small scattered particles have been effectively removed, and the morphology becomes more uniform, as shown in Fig. 8b. EDX analysis shows that Si content is significantly increased, while the contents of impurity elements (Fe, Al, Ca, etc.) are reduced notably. Figure 8c is the SEM image of a single particle of magnetic concentrate at the magnification of 10000, and EDX analysis shows the Si granular matrix and some of the tiny Fe-containing particles sticking on the Si grain surface. EDX analysis fails to identify other impurity elements (such as Al, Ca) besides Fe due to their content are very low. It is thus clear that the superconducting HGMS technology is efficient at separation and purification of silicon reclaimed from kerf loss slurry waste.

Conclusion

The superconducting HGMS technology is proved to be an effective way for purifying silicon powder reclaimed from kerf loss slurry waste. The control experiment results confirm that the fine weakly magnetic particles can be removed and silicon powder purified.

Three main factors affecting the separation efficiency were analyzed with single factor tests to find the optimum process parameter values. Under the optimum process settings (magnetic flux density of 4.0 T, slurry flow velocity of 500 mL/min, and slurry density of 20 g/L), Si concentrate with purity as high as 95.83% has been produced from kerf loss slurry waste with a starting Si content at 90.91%. Fe content is reduced from 3.24 to 0.57% and Al content from

2.44 to 1.51%. The remarkable efficiency of this superconducting HGMS technology can greatly reduce the burden on downstream processing steps (such as acid leaching) to get high-purity (more than 99.9%) silicon powder.

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