Recycling of Abrasives From Wasted Slurry by Superconducting Magnetic Separation

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Shigehiro Nishijima, Yoshinobu Izumi, Shin-Ichi Takeda, Hiroki Suemoto, Atsushi Nakahira, and Shin-Ichi Horie

***Abstract*—Abrasives have been recovered from the slurry wasted of the factory where the silicon wafers for solar battery are processed. The slurry consists of oil and abrasives and is used in the wire saw. The viscosity of the slurry is carefully controlled to maintain a high cutting performance though it tends to be high as the silicon powder is accumulated in the slurry. The cutting performance of the slurry decreases as the amount of the silicon powder increases. The abrasives, however, still have enough performance to cut the silicon wafers. Iron segments of the wire saw were found to attach to the SiC abrasives. The iron segments magnetize the abrasives in the mechanochemical process and thus reduce the cutting performance of the abrasives. Due to the iron segments presence the abrasives with poor cutting performance could be separated from the slurry by means of superconducting magnetic separator. After the magnetic separation a centrifugal separator was used to separate the silicon powder. It was confirmed that the superconducting magnetic separation is applicable to this practical application.**

***Index Terms*—Abrasive, magnetic separation, slurry, silicon, wafers, solar battery.**

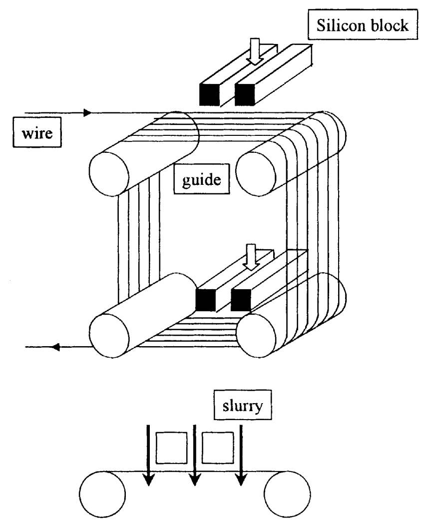

Fig. 1. A schematic of wire-sawing machine

I. Introduction

In MAGNETIC separation, magnetic particles are separated or collected by means of magnetic forces originated by the gradient magnetic field [1]. The research and development of magnetic separation have been made [2]–[6] and the method is now applied, for example, to the purification of clay [7]. Since the recent development of superconducting magnets cooled by a cryocooler, the high magnetic field can be easily produced without liquid helium. The superconducting magnet system with cryocooler has promoted a new research and development within superconducting magnetic separation [8]–[10]. We have tried to develop the superconducting magnetic separation system for the environmental preservation and/or the recycling of resources. Valuable resources to be recycled show usually low magnetic susceptibility and hence the magnetic separation has not been applied commercially even under the high magnetic field produced by superconducting magnets. A magnetic seeding technique has been developed for separating and recycling nonmagnetic materials such as biological, nonmetallic or liquid materials [11].

In this work, a superconducting magnetic separation has been applied to the recycling of wasted slurry from solar battery factory. It was found that an alternative technique to magnetic seeding can be applied successfully to obtain the recycling the abrasives in the slurry: The open gradient superconducting magnet system. This open gradient superconducting magnetic separation system was confirmed to be commercially available.

II. Wasted Slurry From Solar Battery Factory

The wire saw is used for cutting the silicon blocks to produce wafers for the solar battery (Fig. 1). The silicon blocks are pressed toward the wires on which the slurry (a mixture of abrasives and viscous oil), is poured. The abrasives move with the wire due to the viscous oil and cut the silicon. The silicon powder generated during the cutting process accumulates in the slurry. The silicon powder increases the viscosity of the slurry hence decreasing the cutting productivity and accuracy. To solve the problem a certain amount of new slurry replaces the used one periodically. The replacement increases the running cost of the wire saw and causes a large amount of industrial waste (approximately 200 L/day). The wasted slurry was usually got rid off by the industrial waste disposal contractor.

The composition of the slurry before and after use is presented in Table I. Before use the slurry consists of abrasives

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TABLE I
CHEMICAL COMPOSITION OF SLURRY BEFORE AND AFTER WIRE-SAWING

【Before Use】

	grain	oil	slurry
Weight %	55	45	100
Volume %	25	75	100
Density	3.21	0.87	1.45
Viscosity (mPa·s)		20	100

【After Use】

	grain	oil	silicon	others	slurry
Weight %	43	42	12	3	100
Volume %	20	72	7	1	100
Density	3.21	0.87	2.30	4.82	1.47
Viscosity (mPa·s)		20			180

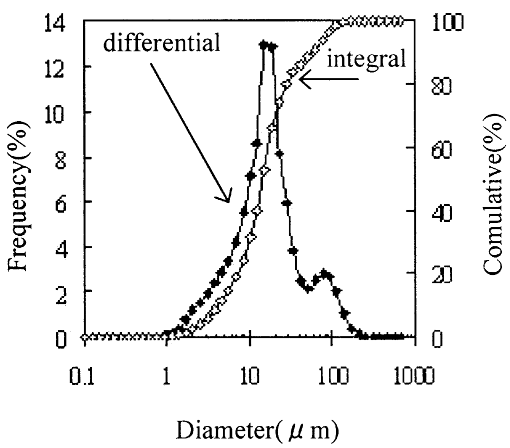

Fig. 2. Particle size distribution of particulate materials involved in waste slurry

and oil. The density of the slurry is approximately 1.45 g/cm^3 and the viscosity is 20 mPa·s. After wire sawing the viscosity is 180 mPa·s, and the cutting accuracy is worse. The silicon powder increases the viscosity of the slurry and its fraction may be as high as approximately 12% in weight.

Fig. 2 shows the particle size distribution (PSD) in wasted slurry. Particles having the diameter of 100, 15 ,and 2 μm show high content. The particles with 15 μm in diameter are the SiC abrasives. Those with 2 μm are fragments of SiC, wire saw and silicon powder. The diameter of the abrasives before use ranges from 5 to 25 μm and the mean diameter is 15 μm. It was admitted that most of the abrasives were not broken during the cutting and are reusable. The particles having 100 μm diameter are flocculated SiC.

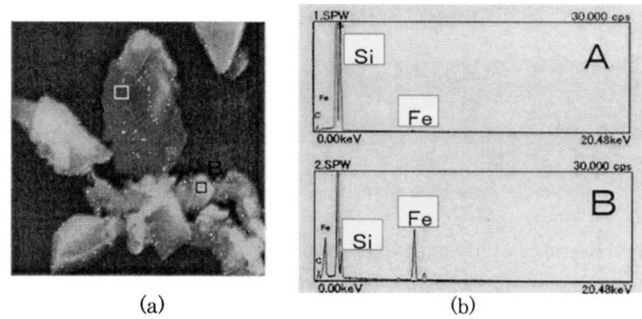

Fig. 3. SEM photograph of abrasives involved in wasted slurry, (b) Elemental analysis of the abrasive surface.

Fig. 3(a) shows the SEM observation of SiC abrasives in the wasted slurry. It was confirmed that the abrasives were not broken. The oil in the slurry was found not to be oxidized and to be reusable. When the abrasives and/or the oil are recovered from the wasted slurry, the expenses for waste disposal and for buying the new slurry are reduced. Though centrifugal separation is able to recycle the abrasives, the abrasives separated by this method do not show high cutting performances. It was needed to clarify why this happens and to establish other economical methods to recycle the abrasives in the wasted slurry.

III. SUPERCONDUCTING MAGNETIC SEPARATION

In order to elucidate the cause why the centrifugally separated abrasives do not show high cutting performances, XRD patterns of the separated abrasives are also studied and shown in Fig. 3(b). It was found that the iron segments adhere to the abrasives especially area "B" in the figure. The iron segments of the wire saw adhere to the abrasives through mechanically assisted chemical reaction. It is known that the cutting performance of the abrasives decreases when other matter attaches to their surface. Consequently the poor cutting performance of the centrifugally separated abrasives is ought to be mainly caused by the attached iron segments. The amount of the iron attached to the abrasives was estimated to be approximately 1% by weight. It was also found iron within the solid matter of the slurry represents about 4% by weight. It suggests that fragments of iron from the wire saw also accumulate in the solid matter of the slurry. This iron fragments present within the slurry are thought to be the other cause of its lower cutting performance, as the centrifugal separation can not divide them from the iron attached SiC, hence they are put together in the recycled slurry.

The following process is proposed to recycle the abrasives from the wasted slurry i) the iron attached SiC or the iron fragments are separated magnetically; ii) the centrifugal separation is performed on the remaining slurry to separate the silicon powder and the abrasives.

The recycling of the oil can also be made by the centrifugal separation. A superconducting magnetic separation was decided to be introduced to answer the following demand; i) to solve the problem of the decrease in the cutting performance, ii) to fit the various types of cutting process (the amount of iron attached to the abrasives depends on the cutting process), iii) to increase the flow speed by about ten times in near future.

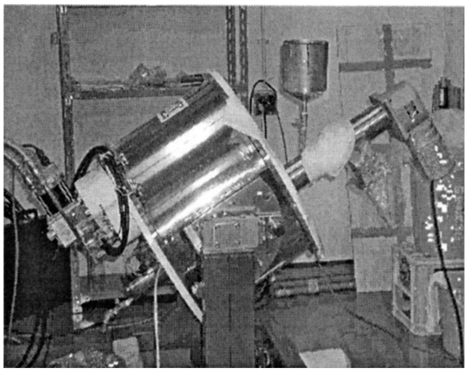

Fig. 4. The superconducting magnet equipped with a separation canister attached to the warm bore.

TABLE II
SPECIFICATIONS OF CRYOCOOLED SUPERCONDUCTING MAGNET SYSTEM

Warm bore	100 mm
Inductance	38H
Operating Current	120A(at *10T)*
Stored Energy	286kJ(at 10T)
Axial Length	460 mm
Outer Diameter	680 mm
Weight	250 kg

TABLE III
RESULTS OF MAGNETIC SEPARATION (2 T); (a) AMOUNT OF WASTED SLURRY, (b) RECOVERED SLURRY AND (c) CAPTURED SLURRY

	Volume (mL)	Solid Content (g)	Abrasive content(g) (g)	SiC Fragment (g)	Iron Content (g)	Ms (T/kg)
a	3,000	2,200	1,716	418	66	10.7
b	2,500	1,700	1,376	324	0	0.346
c	500	500	340	94	66	53.4

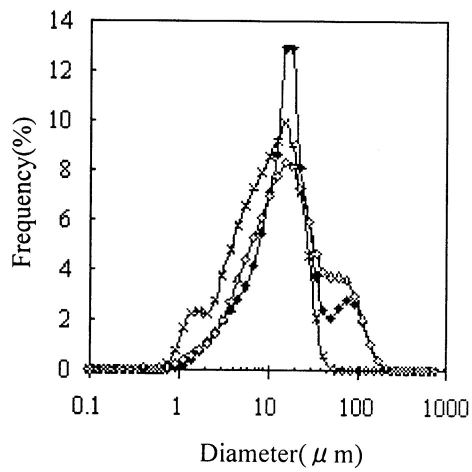

Fig. 5. Particle size distribution of particulate materials discharged from outlet of chamber after magnetic separation (5T).

Based on the amount of the iron attached to the abrasives and on the iron fragments in the solid matter in the slurry, 0.02 m/s of the flow speed, 2 T of external field and 10 T/m of magnetic field gradient are estimated to be needed.

IV. DEVELOPMENT OF THE MAGNETIC SEPARATOR

The gradient of the magnetic field needed for the separation can be generated by a open gradient superconducting magnet. A separating system as shown in Fig. 4 was developed. The superconducting magnet is tilted by 30 degree and the separation canister was installed in the warm bore. The specifications of the superconducting magnet system are presented in Table II. The wasted slurry is stored in the slurry reservoir and then introduced to the separation canister. The iron attached abrasives and the iron fragments are captured on the wall of the canister by the open gradient magnetic field while the slurry flows in the separation chamber. To stir the slurry a screw device is installed in the canister. The slurry without iron which can be recycled is discharged from the outlet of the canister. The external field is then decreased to remove the iron attached abrasives and the iron fragments.

V. EXPERIMENTAL PROCEDURE AND RESULTS

Separation tests for the wasted slurry obtained from the industrial factory were performed using the separator shown in Fig. 4. To change the magnetic gradient, magnetic field strength was set at 2 in one test and 5 T in another. An amount of 3 L of wasted slurry was used for separation tests. This slurry was flew down the screw inside the canister toward the outlet at a rotating speed of 6 rpm (which was the rotation used in all the tests presented in this paper). Preliminary test for the original slurry (as received from the factory) showed that the viscosity was too high to achieve separation with an economically reasonable flow rate, so the actual separation test was done after adjustment of the viscosity with dilution of the slurry by a thinner ($\mathrm{slurry} : \mathrm{thinner} = 4 : 1$ by volume) to obtain a final viscosity of 50 mPa·s. The adopted flow rate was 0.02 m/s, which was set to the economically desired separation rate, using the valve just beneath the slurry reservoir.

Table III shows the results obtained from the recovery test at a magnetic field strength of 2 T. The amount of wasted slurry processed was 3 L and the recovered amount of it was 2.5 L, corresponding to a recovery of abrasives of about 80%. Magnetization of the recovered slurry was found to be smaller than that of the originally wasted slurry. This reduction of the magnetization hints that the magnetic component involved in the slurry was separated. The same tendency of magnetization change after magnetic separation was obtained at 5 T.

In order to clarify the efficiency of the magnetic separation and to make sure if the particle size of the abrasives was still maintained even after sawing, PSD was measured for both before and after a separation performed at 5 T. The obtained distribution is shown in Fig. 5. The distribution obtained for the 2 T case is similar in tendency to the 5 T case, but as the latter allows better PSD curves it is the one cited for discussion. The PSD curves suggest that the peak at 100 μm corresponds to the flocculated particles size of SiC, which will be easily deflocculated by shear flow. It is worth noting that PSD of the captured slurry

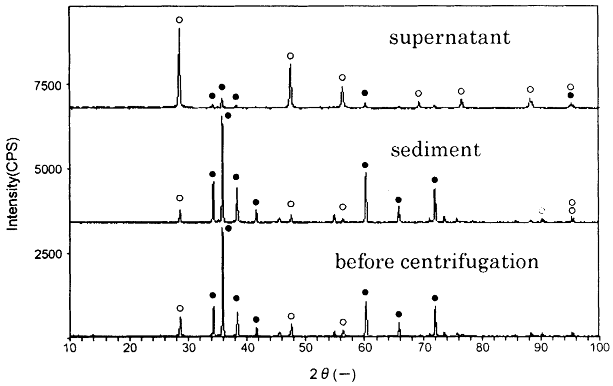

Fig. 6. XRD patterns of abrasives and silicon particle separated by centrifugation after magnetic separation.

after separation has a new peak below 10 μm region and the peak corresponds to the iron fragments (SiC broken particle with iron in some extent also could be included in this PSD region). This conclusion is supported by the fact that, in the captured slurry, only the iron component increases after separation as shown in Table III. Hence, the particles having a peak at 15 μm in PSD curve are inferred to be SiC particle with iron component. Summarizing: the results on the PSD curves demonstrate that magnetic separation technique can separate the particles even with iron in small content.

We have encountered also some difficulty to use the recycled slurry after dilution using thinner, because of the high viscosity presented by the resulting slurry. Thus the material for dilution should be changed from thinner to other material or other technique should be applied to reduce viscosity. The idea that heating the slurry to 60°C can reduce viscosity was drawn from the viscosity change with temperature observed for the same oil used in this slurry. Therefore, magnetic separation of the wasted slurry after heating up to 60°C was made at 2 T, and subsequently centrifugation at 2000 rpm was performed for the slurry discharged from the outlet of the canister. Fig. 6 shows the XRD patterns obtained from the slurries before and after centrifugation. It is clear that the solid component of the slurry before centrifugation was silicon and SiC particle. On the other hand, the upper and lower portions of the slurry after centrifugation were found to be silicon in supernatant and SiC particle in sediment, respectively. It was also found that centrifugation at higher rotation rate such as 3000 rpm can have capability to even separate silicon fragments, and result in recycling the oil separated from the slurry.

Summing up, a scenario for recycling the wasted slurry from solar battery factory was tested. It was confirmed that the procedure proposed here, which is comprised of magnetic separation, adjustment of the oil temperature, and centrifugation, can be practically operated. When the treatment rate of wasted slurry is higher than 700 L/day, this technique is to be employed with matching economical demand and hence superconducting magnet separation is found to be used in practical applications.

VI. Conclusion

A fundamental study was performed on the application of superconducting magnetic separation technique to recycle wasted slurry from the solar battery factory. It was shown the applicability of this technique to treat the wasted slurry of abrasives. From the results presented in this work, several conclusions concerning the use of magnetic separation technique can be drawn:

1) Since the wasted slurry contains not only nonmagnetic abrasives but also SiC abrasives (mechanochemically reacted with iron during wire-sawing), the latter particles, which decreases the cutting performance, can be easily recovered by magnetic separation.
2) The iron fragments coming from the wire during sawing also can be recovered by magnetic separation.
3) SiC abrasives can be divided from silicon fragments using centrifugation after magnetic separation, which can lead the way for recycling the SiC abrasives wasted from solar battery factory.
4) When the rotating rate of centrifugation was changed to a high rate such as 3000 rpm, and after the magnetic separation step, separated oil can be obtained from the wasted slurry, with better results than the ones obtained by only using centrifugation.

Summarizing: superconducting magnetic separation technology is able to recover the SiC abrasives and oil from the wasted slurry successfully, and thus establishing a viable recycling system of the wasted slurry from the semiconductor factory.

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