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Study on Manufacturing of Recycled SiC Powder from Solar Wafering Sludge and Its Application

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Slurry containing SiC powder and oil is used to cut ingots with a wire in a solar cell wafering process. The slurry, which is generally recycled due to its high price, produces a residue known as sludge during the recycling process. The sludge is mainly composed of SiC, Si, and oil. This study proposed a method to remove Si and oil from sludge to obtain a high-purity SiC powder of approximately 98.5% in an economically feasible manner. Additionally, this study utilized the recycled SiC powder to develop a porous SiC ceramic heat sink with thermal conductivity of about 10W/mK and showed that the heat sink can be used as an efficient apparatus to release heat of electronics.

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NOMENCLATURE

cp = centipoise
D_x = percentile particle size distribution
h = hour
wt % = weight percent

1. Introduction

In line with development of the photovoltaic industry, not only the polysilicon and ingot manufacturing industry but also a relevant process and parts industry has been emerging.[1] For the solar cell wafering process, a slurry that includes SiC powder and oil is used to cut silicon ingots with a wire-sawing machine.[2,3] In other words, when a wire, whose main component is Fe, passes through the slurry and pushes the ingot at a constant pressure, the slurry is pushed onto the surface of the wire and the ingot is cut off by SiC particles inside the slurry. At this time, the process causes the formation of a slurry that consists of oil, Si of the ingot component and SiC powder of the cutting fluid. This slurry is normally recycled to be reused due to its high price.[4]

Fig. 1 illustrates the slurry recycling system intended to recycle the cutting fluid, SiC, which is used for cutting the silicon ingot. In the system, waste separated after the second decanter is called sludge. Domestically, silicon ingot wafering is estimated to produce approximately 7000 tons of sludge monthly. Out of the produced sludge, a solid phase, except the oil of lubricating coolant, accounts for almost 50%, with an amount of 3,500 tons. As other fine powder including cut off Si occupies about 20% of the solid phase, SiC byproduct actually amounts to about 2,800 tons, and out of this, approximately 85% can be recycled to be reused for the wafering process. Therefore, Sic materials of 420 tons are disposed of as waste monthly and 5,040 tons annually, which is equal to disposal of USD

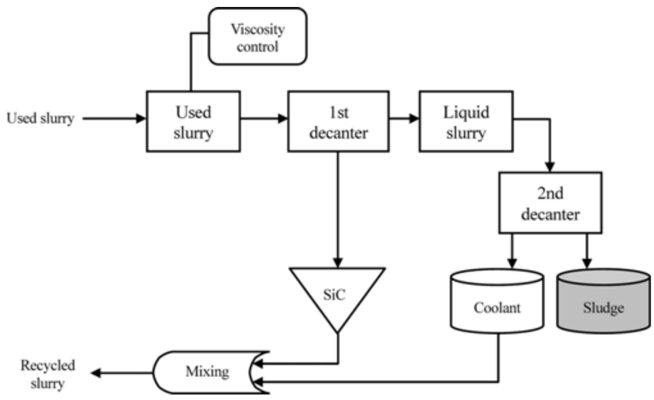


Fig. 1 Slurry recycling system

25.2 million worth of material ($5/kg). Accordingly, research has been actively conducted to recycle disposed SiC materials.

Wang et al.[5] proposed a way of efficiently removing SiC through an Al-Si alloying process and Lin etc.[6] used a centrifugation approach to separate silicon kerfs and silicon carbide abrasives. Wang et al.[7] proposed a novel approach of directional solidification for separating submicron particles. Joyce and Schmid[8] analyzed the impurities in silicon that were recovered from silicon kerf with pyrometallurgy. Wu and Chen[9] found that Si and SiC could be separated by electrophoresis and gravitational settling. Meanwhile, Lin et al.[10] successfully recovered 99.1 wt%-pure Si by using a two stage phase-transfer separation process. Tsai[11] suggested Al_2O_3 as abrasives instead of SiC and identified the possibility of separating Si/Al_2O_3 mixtures with electrophoresis and gravitational settling. Yoko and Oshima[12] proposed a new way of recovering Si from silicon sludge by using supercritical water in a semi-batch reactor.

The current drying method with a certain amount of Si-kerf to obtain SiC powder is limited to producing only low value-added slurry or fire-proofing material owing to low purity of SiC. High-purity SiC is thus required for the recycled powder to be used as a material for high value-added industries, such as structural materials or electronics parts. Kwon et al.[13] developed a method to synthesize β,-SiC powder from the large amount of silicon sludge produced by the solar cell industry based on a direct carbonization synthesis method and additionally indicated the possibility of its use as a structural material or filtering material on the basis of SiC's characteristics, including high-temperature strength, wear-resistance, corrosion-resistance, and high thermal shock.

This study was aimed at developing a technology to economically mass produce recycled SiC powder, whose SiC content is equal to 99% of that of fresh SiC, from solar silicon sludge. To that end, this study developed an approach of efficiently separating Si that condenses onto and remains in SiC particles even after the washing process. In addition, the recycled high-purity SiC powder was used to develop a porous SiC ceramic heat sink whose performance was verified through application to the cooling of the heat source of electronic goods.

2. Experimental Methods

2.1 SiC Separation and Refinement Process

Fig. 2 displays the SiC separation and refinement process. A large amount of Si fine powder and oil component of sludge can be removed through the first stage of the washing process, because the Si fine powder, whose size is 1 μm and below, is very slow in terms of precipitation speed due to its smaller percentage compared to SiC particles. The sludge and additive water were mixed in a proportion of one to one (1:1) during the two iterations of washing. However, as it was difficult to remove Si condensed onto SiC, an alkaline reagent of KOH or NaOH was added before 30 or 40 min -long agitation and the subsequent washing processes. In the second stage of filtration, applied to reduce the moisture of the washed slurry, proper size of filter pores is selected to additionally remove the remaining Si fine powder. In the third stage of drying, a microwave dryer to remove moisture in a short period of time was used.

The slurry used in the experiment was manufactured by mixing cooling oil(diethylene glycol) and SiC powder of Nanko[1] in a weight ratio of one to one (1:1).

2.2 Thermal Conductivity Measurement and Thermal Performance Experiment of Recycled SiC Heat Sink

After manufacturing a Sic heat sink used for releasing heat of electronics with the recycled SiC powder, a laser flashing method[2] was used to measure thermal conductivity. The laser flash method was originally developed to measure thermal diffusivity of solids. However, various methods have been proposed to measure the thermal diffusivity of many materials. Fig. 3 presents a schematic diagram of the thermal performance experiment. The experiments on thermal performance of aluminum and porous SiC heat sinks were conducted by using LED light as a heat source. A natural convection experiment was carried out without running a fan inside an acrylic box with the top open (1 m × 1 m × 0.5 m) and a forced convection experiment was conducted with the fan running.

3. Results and Discussion

3.1 Precipitation Experiment

Table 1 shows the variation of precipitation time according to additive water amount by using the slurry with a combination of SiC powder and diethylene glycol. The time required to reach 98% SiC precipitation becomes shorter as the water content increases. In the case of the initial washing process where the slurry and water were mixed in a volume ratio of one to one (1:1) to approximate the conditions of Sample 4, the time taken to reach the precipitation level is about 4.5 hours. During the second washing process, most parts of the supernatant originating from the previous washing process were drained out and then the sludge was added by water in a ratio of one to one (1:1) to correspond to Samples 5 and 6. In this case, about 3.5 hours are required to reach the precipitation level. During the following wash process, which was almost equal to Sample 6, with addition of NaOH, precipitation was reached after approximately 2 hours.

Fig. 4 shows the results of the analysis of particle size of the

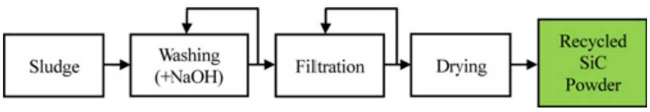


Fig. 2 SiC separation and refinement process

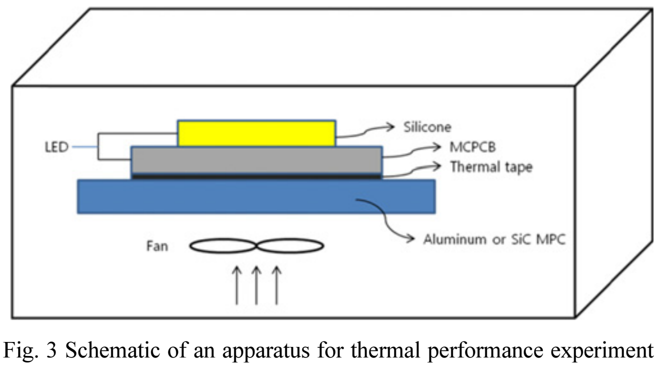
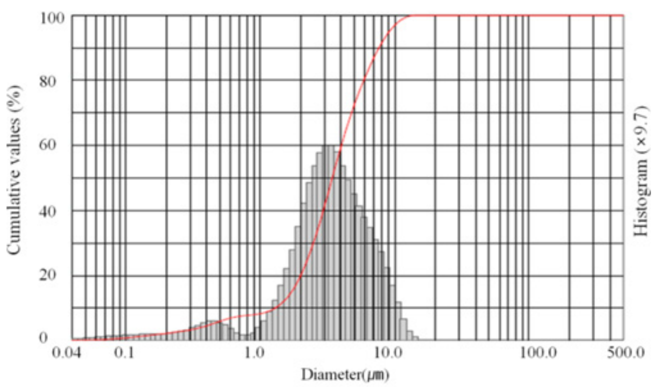


Fig. 3 Schematic of an apparatus for thermal performance experiment

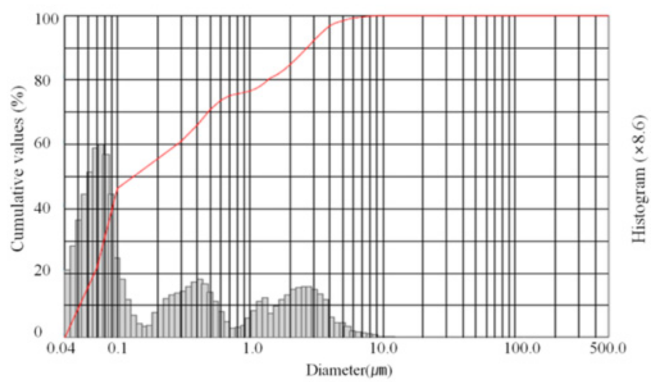
supernatant that was poured out after the second washing process. As seen in Fig. 4(a), the particle volume distribution is nearly normal with a range between 1 μm and 10 μm and the particle diameter corresponding to a cumulative value of 97% is about 10 μm. However, as seen in Fig. 4(b), the particle diameter corresponding to a cumulative value of 97% is about 4.4 μm with respect to the particle number depending on the particle size, indicating that the particles inside the supernatant are mostly below 4.4 μm in diameter. Also, it was found that particles of 1 μm and below account for more than 70% of the total particles when they were counted. Therefore, Nanko's SiC powder, used in the experiment, has shown about 4.3 μm of D_6, 10.1 μm of D_{50} and 21.2 μm of D_{97}, indicating that most parts of the Si fine powder were separated through the washing process. D_6, D_{50}, and D_{97} represent the 6 %, 50% and 97% point in the cumulative undersize particle size distribution, respectively.

Table 1 Variations of SiC Precipitation percentage with additive water

Items \ Sample no.	1	2	3	4	5	6
Water content	15%	30%	45%	60%	75%	90%
Oil content	85%	70%	55%	40%	25%	10%
Density(g/ml)	1.08	1.06	1.04	1.02	1.00	1.00
Viscosity at 25°C & 100rpm(cp)	27.0	17.4	11.1	8.5	6.9	3.9
Reaching time for 98% SiC precipitation(h)	72	24	8.5	4.5	2.5	2.0
SiC precipitation percentage after 8 hours(%)	63	93	97	98	99	100



(a) Cumulative values and histogram of particle size distribution (in volume/undersize)



(b) Cumulative values and histogram of particle size distribution (in number/undersize)

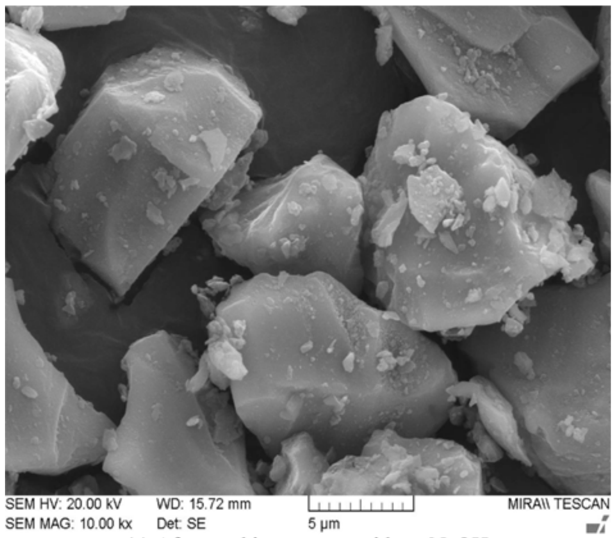
Fig. 4 Distributions of particle size and number after washing with water

A simple washing process, however, is not sufficient to wash off submicron-sized Si fine powder that condenses onto and remains on the SiC particle surface inside the sludge. As illustrated in Fig. 5(a), for the slurry that is subjected to the washing process only, relatively small-sized Si particles adhere to relatively large-sized SiC particles. In order to remove these Si particles, NaOH is added in the final washing process. According to Fig. 5(b), after the addition of NaOH, the Si fine powder is almost removed during the washing process.

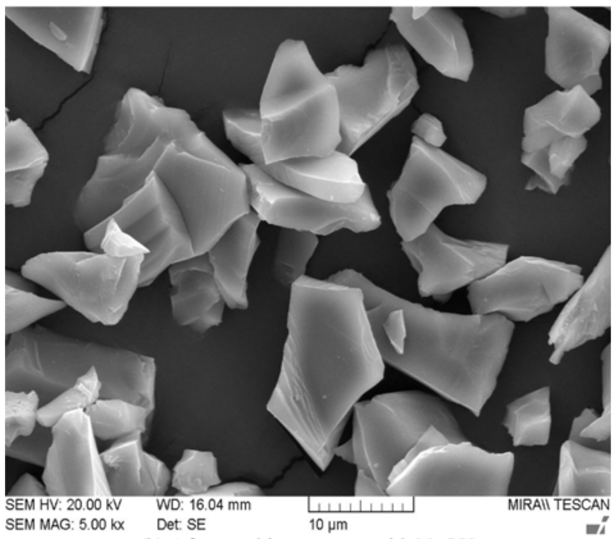
3.2 Filtration Process

The washing is generally followed by filtration designed to reduce the moisture content of the sludge before the sludge goes through the drying process. Fig. 6 shows the sludge state of filtration with moisture of about between 40 and 50% and particle size of about 10 μm.

Meanwhile, out of the solid components of the sludge considered in this study, excluding the liquid components, SiC accounted for at least



(a) After washing process without NaOH



(b) After washing process with NaOH

Fig. 5 SEM photograph of particle distributions

50% in terms of weight. Consequently, when passing through the filter, the sludge produced significant frictional heat caused by high pressure and, accordingly, the filter temperature reached almost 60°C, nine or ten hours after the beginning of filtration. As it is generally desirable to use a membrane filter at a temperature of 70°C or below, the need for a cooling system was recognized. As a result, a water-cooled jacket was installed outside of the sludge tank with the aim of controlling the temperature rise, and the cooling system was operated when the sludge temperature reached 60°C Fig. 7 displays the variation of sludge temperature with time in the filtration apparatus equipped with the cooling system, indicating that the temperature of the sludge is controlled within a range of 60°C ± 4°C. Operating experiments were performed four times over a period of two weeks in total to ensure stability of the experiment apparatus.

Fig. 6 Sludge after filtration

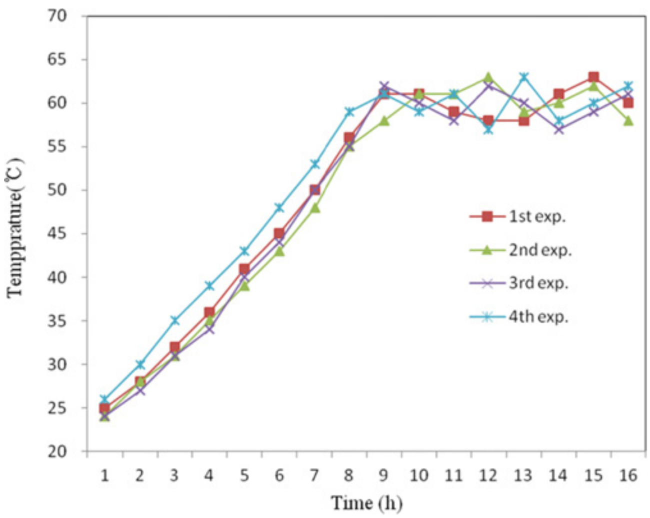


Fig. 7 Variation of sludge temperature with time

3.3 Drying Process

With regard to properties of the sludge passing through the filtration apparatus, it is combined with a fine powder having a mean size of 10 μm and mainly water-containing liquid. A very small amount of liquid is mixed with the oil content that is not completely removed. Issues related to drying of the sludge used in this study included the following: (i) any increase in the amount of sludge to be dried caused a delay in drying the inside of the sludge, and (ii) the sludge formed into a mass after being dried. In order to resolve these issues, a microwave drying approach was adopted. Fig. 8 shows numerous pores resulted from the process of drying the sludge with the microwave. According to characteristics of the microwave drying, the sludge is heated at high temperature for a short period of time and its inside and outside regions are dried simultaneously while moisture escapes at a rapid pace, which consequently leads to the generation of those pores.

3.4 Flushing Performance with Respect to the Water Inflow

Table 2 describes the variation of the powder characteristics according to powder manufacturing methods to enhance the purity. The first powder that originates from the sludge is pulverized with its oil being removed after heat treatment at temperature of 270°C in an electric furnace without going through any process. The first powder is almost black in color, quite similar to that of the initial sludge, and the SiC content resulting from the crucible process amounts to 74.9wt%. The included Si fine powder contributes to lowering the mean value

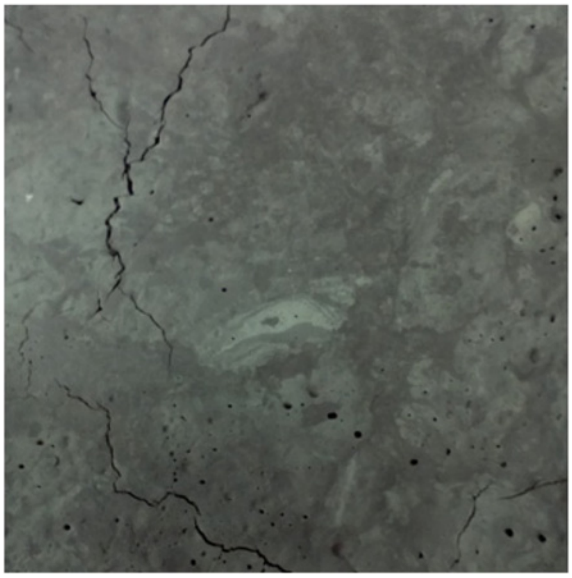


Fig. 8 Pores on the surface of the sludge after microwave drying

Table 2 Variation of powder characteristics with manufacturing method

Powder manufacturing method / Powder characteristics	Drying only	Water washing and drying	Water washing, water washing with NaOH and drying	Fresh SiC (#1500)
Powder color	Black	Light Brown	Light Green	Green
SiC content (wt%)	74.9	97.1	98.5	99.3
Mean diameter(μm)	6.2	10.3	10.9	10.7

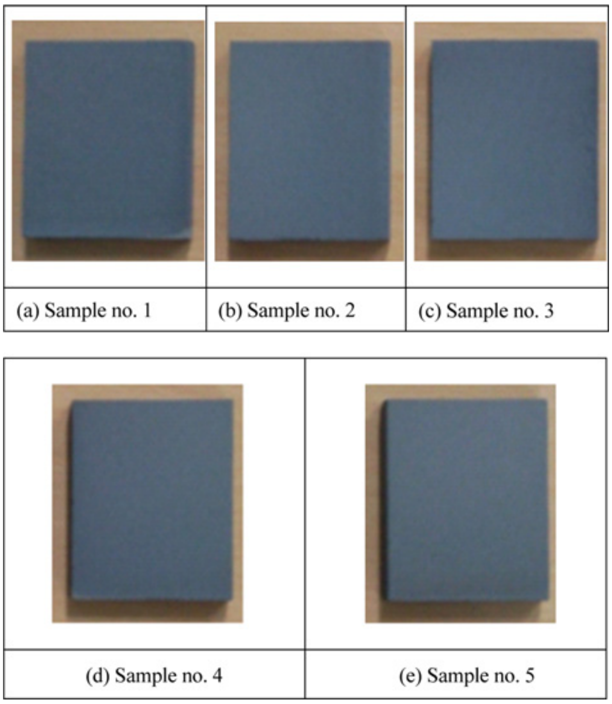
and, as a result, the mean diameter of particles is 6.2 μm.

The second powder originates from drying the sludge after the washing process. The second powder is found to be light brown in color as the Si fine powder adhering to SiC remains even after the washing process. Its SiC content amounts to approximately 97.1wt%, indicating that a considerable amount of Si fine powder can be removed after going through just the washing step. Therefore, the mean diameter of particles is measured to be 10.3 μm, thus coming significantly closer to that of fresh SiC.

Removal of a significant amount of Si fine powder that adhered to the surface of SiC by a reagent provides the main contribution for creating the light green color of the final drying powder, the original color of fresh SiC. The SiC content amounts to about 98.5wt% and its mean diameter is 10.9 μm, even greater than that of the reference fresh Sic, 10.7 μm.

3.5 Thermal Conductivity of SiC Heat Sink based on Multi-Modal Compositions

As seen in Fig. 9, five samples (40 mm × 40 mm × 2 mm) were produced by adjusting amount of coarse powder and fine powder among the recycled SiC particles. The detailed compositions are shown in Table 3. The coarse powder and fine powder can be separated based on the precipitation speed in the washing process. Sintering temperature was intended to be capable of low temperature co-firing while the sample is held for two hours at temperature of 900°C In addition, the previously used carbonate was replaced with Li_2CO_3 with the aim of achieving firing at much lower temperature. According to the results of measuring the thermal conductivity of the ceramic heat sink with a laser flashing method, Sample 4 was found to have the highest thermal conductivity, about 10.3 W/mK at room temperature, as seen in Table 4.



(a) Sample no. 1 (b) Sample no. 2 (c) Sample no. 3

(d) Sample no. 4 (e) Sample no. 5

Fig. 9 Plate-type heatsinks with various compositions

Table 3 Multimodal compositions of the SiC samples

Unit: wt%

Composition \ Sample No.	1	2	3	4	5
Recycled SiC powder (mean size:12.7 μm)	80	78	76	74	72
Recycled SiC finer powder (mean size:6.6 μm)	10	12	14	16	18
Li_2CO_3	5	5	5	5	5
Metal-Glazing	5	5	5	5	5

3.6 Thermal Performance Experiment of Porous SiC Heat Sink

A COB(chips on board) LED of approximately 1.5W was used as a heat source and the thermal performance of the SiC heat sink was compared with that of an aluminum heat sink of the same size through experiments. Experimental conditions include ambient temperature of 25°C, atmospheric pressure and natural convection without a cooling fan. According to Table 5, which shows the LED PCB temperatures at steady state, temperature of the porous SiC heat sink was 10°C lower than that of the same-sized aluminum heat sink, indicating better thermal performance. This is due to the fact that the heat transfer area of the porous SiC heat sink is much bigger than that of the aluminum heat sink. If micro pores can be modeled as a sphere with a diameter of 10 μm, the surface area of the SiC plate is larger than that of the aluminum plate about 300,000 times. Therefore, the porous SiC heat sink is better in terms of thermal performance and weight when natural convection cooling is necessary. On the other hand, under the condition of forced convection with a cooling fan, there is no difference between the porous SiC heat sink and the aluminum heat sink in terms of thermal performance, implying that the presence of numerous micro pores is effective only for natural convection.

4. Conclusions

In this study, a new process to get recycled pure SiC from solar sludge as well as porous SiC heat sinks as its application has been developed. Conclusions drawn from the study are as follows:

1) The solar sludge can efficiently remove Si particles adhering to SiC particles by going through the washing process alone, yielding

Table 4 Conductivity measurement of sample 4 with laser flash method

Shot number	Ambient temperature (°C)	Diffusivity (mm^2/s)	Conductivity (W/mK)	Density (g/cm^3)
1	25.0	7.007	10.263	1.917
2	25.1	7.020	10.282	
3	25.1	7.020	10.281	
Mean	25.1	7.016	10.275	

Table 5 Variation of LED PCB temperature with heat sinks

Flow type \ PCB temperature	Aluminum heatsink (°C)	Porous SiC heatsink (°C)
Natural convection	78	68
Forced convection	55	55

roughly 97% SiC powder. In particular, the addition of NaOH to the washing process contributes to obtaining recycled SiC powder with purity of 98.5 % and particle diameter of about 10.9 μm.

2) During the filtration process, friction with the filter caused by SiC particles may damage the filter, thus necessitating a cooling system that keeps the filter at 70°C or below.

3) With regard to the solar sludge drying methods, it is found that microwave drying is capable of drying both the inside and outside of the sludge simultaneously at a rapid speed.

4) A porous SiC heat sink manufactured with recycled SiC can be used efficiently for releasing heat of electronic goods owing to its high thermal conductivity of 10 W/mK and porosity of 30%.

In the future, additional studies on the thermal performance of various shapes of recycled micro-pore SiC should be carried out.

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