Recycling of silicon metal powder from industrial powder waste streams

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Most industries today have waste or side streams that are deposited or sold as bi-products. Industries that are cutting and grinding silicon metal, such as the photovoltaic and semi-conductor industry, are depositing valuable metal powder materials. ReSiTec has worked on research projects for several years and developed new technology for recycling and purification of valuable metal powders. The focus has been silicon metal powder from cutting and grinding production. The process has been developed to collect fine particles, with a size range of 0–150 μm, from highly diluted waste water. Furthermore, known separation and classification techniques for metal powder processing have been adapted with the purpose of purifying and upgrading silicon metal powder from waste to new products. The tests performed were successful and the results showed an increase in purity level from 50% to >99% metallic silicon and an acceptable yield. It is believed that this new technology can be suitable for similar types of industrial metal powder waste streams. Today, ReSiTec is supporting the process industry with R&D services and is producing more than 500 tons per year of recycled, high-purity silicon metal powder.

Introduction

Silicon metal is today one of the most important elements available to us and used in several applications such as ceramics, electronics, photovoltaics (PV), metallurgical industry (alloys of aluminum and iron) and chemical applications such as production of silicones. Several new applications using silicon metal powders are under development, like battery production and 3D printing.

Even though silicon is a semiconductor, pure silicon is referred to as silicon metal due to its electrical properties. Silicon metal is a gray, metallic and brittle material. In nature silicon is found as various forms of silicon dioxide (silica) or silicates and is the second most abundant element in the Earth’s crust (about 26% by mass) after oxygen. Depending on the application, silicon metal is used as lumps or powders [1] (Fig. 1).

In 2014, the world’s production of silicon metal was estimated to more than 2.5 million tons. The main consumption was used in foundry and chemical applications. Fig. 2 shows the areas of application for silicon metal. A rapid growth in the PV market has led to the consumption for solar cells to increase with about 30% per year. The demand and production of silicon metal is also predicted to increase the coming years [2].

Metallic silicon is produced by carbothermic reduction of silica to remove oxygen. Metallurgical grade silicon contains impurities such as iron, titanium, aluminum, boron and phosphorus, and has a purity level lower than 99.8 wt.%. Further refining is required to produce solar grade silicon and the ultra-high purity semiconductor/electronic grade silicon metal. Different applications have different purity requirements depending on the final product. The main grades of silicon metal are presented in Table 1 [1].

Manufacturing of silicon metal is a very energy consuming process, which means that recycling of silicon metal powder should be an important strategy for improving future energy utilization and reducing the CO₂ footprint of the silicon metal industry.

The energy consumption for production of silicon metal is depending on the purity level and can vary for different producers. Typical values are shown below [3,4].
Metallurgical silicon (98 wt.%) for use in alloys, 11–15 kWh/kg.
- Silicon (99.8 wt.%) for manufacturing of ceramics, electronics, silicones, etc., ~20 kWh/kg.
- Solar and electronic grade silicon (>99.999 wt.%), 50–100 kWh/kg.

In all production processes for manufacturing silicon metal there is a material loss of different degree and quality. These waste streams are collected as wet or dry powders, and due to the impurities from the production process, these streams are deposited as waste. It is estimated to be more than 100 000 tons of silicon metal waste generated yearly in the production of silicon metal. Waste generated in the value chain for the PV industry is shown in Fig. 3. The largest sources of silicon metal waste are from silicon ingot crystallization and wafer manufacturing [5,6].

There have been several R&D projects on recycling of silicon metal waste to solar grade quality. Today, we are not aware of any other commercially available plants for recycling of this type of silicon metal waste. ReSiTec has through several years worked on research projects for recycling of silicon metal waste from cutting and grinding processes. This extensive work has resulted in a new process for recycling waste streams that are generated in the high technology process for manufacturing of solar grade silicon metal. These streams have until now been deposited as waste. The energy consumption for the recycling process (<1 kWh/kg) is considerably reduced compared to conventional silicon metal production.

The R&D work has included mapping and characterization of each of the different silicon metal waste streams. ReSiTec has worked on a number of existing unit operations which have been further developed and adapted to the application. There are a number of safety issues related to handling and processing of silicon metal powders, such as reactivity in wet state, hydrogen evolution, the risk of exothermic reaction during drying and dust explosion.

Important parameters for recycling and upgrading of silicon metal powders are:
- Chemical purity (wt.% metallic silicon)
- Chemical composition of impurities
- Particle size distribution

As a part of the ongoing R&D work, ReSiTec is participating to CABRISS [7], a Horizon 2020 EU project, to establish a new concept for low-cost solar cells based on recycled silicon metal powder. The aim is a low environmental impact by the implementation of low carbon footprint technologies using recycled materials, resulting in a low energy payback (about 1 year). The main vision of the project is to develop a circular economy for the photovoltaic, but also electronic and glass industry.

Industrializing the recycling process has been very positive for both the manufacturer and the environment through reduced
volumes for deposit and energy consumption, and for ReSiTec through new salable products. In 2014 ReSiTec established a regular production of recycled silicon metal powder and is today producing about 500 tons of silicon metal powder, which is sold in the market.

Experimental work
In 2012 ReSiTec identified a number of different producers which deposited silicon metal generated in different parts of the manufacturing chain for photovoltaic materials. The first step was to characterize the materials by investigating the physical and chemical properties of the silicon metal powder. The characterization was important in order to select the proper method for recycling and upgrading. For some materials the impurities were present as separate particles. In other cases impurities needed to be chemically removed. The unit operations used for separation and treatment can be categorized as follows:

- Chemical treatment: Some elements can easily be removed by chemical treatment, especially when the impurities are not separate particles (e.g. removal of iron by acid leaching). Silicon metal powder can be oxidized when it gets in contact with air and water and this layer can be removed using hydrofluoric acid.

- Mechanical wet: Wet separation methods are developed to achieve a purity level of >98 wt.% silicon metal. Analysis shows that impurities in these materials are mainly found in the fines fraction. Due to safety issues concerning dry and fine powders, such as dust explosions and dust exposure, it is desirable to upgrade the material mainly in wet phase. The challenges are to develop and adapt suitable wet separation techniques, control oxidation, handle hydrogen evolution, purity level and material loss in these process steps.

  - Water classification gives a good separation based on particle size and/or difference in particle density.

  - Hydrocyclones separate particles based on size and density. Using a multi-step hydrocyclone setup, the separation can be as good as with water classification. The advantage is the capacity and low space requirements.

  - Filtration is performed using a filterpress to separate silicon metal powder from the liquid phase. The filtration process is challenging due to very fine particles and wide particle size distributions.

  - Powder cleaning inside the filterpress follows the filtration step. The filterpress has been used to remove chemicals and impurities in the silicon metal powder.

- Mechanical dry: To achieve a purity >99.5 wt.% silicon metal, dry separation methods were developed. Dry separation methods which are based on other physical properties than particle size and density were investigated. The main challenge was related to safety and to further develop known separation techniques, which had not before been used on silicon metal powders.

  - Drying of fine silicon metal powder is challenging. Experience with drying of fine silicon powders is limited as these materials are usually produced as coarse material and dried prior to milling. Due to the small particle size of the silicon metal powders important factors to consider were dust explosion properties and gas evolution (hydrogen). Exothermic reactions have been experienced during the drying process.

  - Electrostatic separation is based on the difference in conductivity between product and impurities. Very often impurities, such as oxidized silicon and iron, have lower conductivity than pure silicon metal and can be removed. The principle of electrostatic separation is shown in Fig. 4 [8].

  - Jetmilling and classification can be used to de-agglomerate dry silicon metal powder and produce specific particle size distributions. This is performed in an inert atmosphere.
presented in this chapter. For particle size distributions the median is called the D50. The D50 is the size in microns that splits the size distribution with half above and half below this diameter. In the following, D50 is referring to the particle size distribution for the silicon metal powder.

Silicon metal powder D50 = 25 μm
Silicon metal powder was collected from highly diluted water based slurries with solid content of 1 wt.%. The recycled silicon metal powder had D50 ~ 25 μm. The particle size distribution of the waste material (red) is presented in Fig. 5, together with the particle size distribution of the recycled silicon metal powder (green). The water slurry contained powder with a wide particle size distribution from 0 to 300 μm. To collect the desired product, the first step was to recover the coarser fraction. Recovery of the fines fraction is presented in Silicon metal powder D50 = 5 μm section.

The material was recovered using chemical treatment and mechanical separation steps. In Table 2 the chemical analysis are presented for both the waste and the recycled 25 μm silicon metal powder. The product is a recycled silicon metal powder with a purity of 99.5 wt.%.

Silicon metal powder D50 = 5 μm
To achieve an even higher yield, the fines fraction that was removed during processing of the coarser material, D50 ~ 25 μm, was collected in the next step. Due to the very fine particles, D50 ~ 5 μm, with a large surface area, the material was originally highly oxidized and agglomerated. In Fig. 6 the particle size distribution of the waste material (red) is presented together with the particle size of the recycled D50 = 5 μm silicon metal powder (green).

After processing the water slurry through a two-step process more than 95 wt.% of the particles had been collected. In Table 3 the chemical analysis before and after processing are presented.

![Image](Image1.png)

**FIGURE 5**
Particle size distribution of silicon metal waste and recycled silicon metal powder.

**TABLE 2**
Chemical analysis of silicon metal powder before and after recycling.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Appearance</th>
<th>Metal impurities (wt.%)</th>
<th>Oxygen content (wt.%)</th>
<th>Metallic silicon (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon metal waste</td>
<td>Agglomerated, oxidized</td>
<td>1.0</td>
<td>10.0</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Silicon metal powder 25 μm</td>
<td>Free-flowing powder</td>
<td>0.5</td>
<td>1.5</td>
<td>99.5</td>
</tr>
</tbody>
</table>

The product is a recycled silicon metal powder with \(D_{50} \sim 5 \text{ \mu m}\) with an even higher purity level of 99.9 wt.%. 

Silicon metal powder \(D_{50} = 50 \text{ \mu m}\)

Silicon metal powder \(D \sim 50 \text{ \mu m}\) was extracted from a waste filtercake containing only 50 wt.% metallic silicon. The material was recovered using both wet and dry mechanical separation. The particle size distribution of the waste filtercake (red), together with the recovered material (green), are presented in Fig. 7.

By characterizing the material, it was found that the non-metallic impurities were mainly present in the fines fraction of the powder. The first process step was wet mechanical separation where the smallest particles were removed. By doing this, the metallic silicon content increased from 50 wt.% to 85 wt.%. By analyzing the material it became clear that the remaining impurities were distributed throughout the particle sizes. To achieve an even higher purity, a dry mechanical separation step was applied. The chemical analysis before and after recycling is presented in Table 4. The final product has a purity level of 99.6 wt.%. The dry separation step in this case is electrostatic separation where particles are separated based on the difference in conductivity. To apply this method for fine silicon metal powder the equipment had to be modified to avoid the risk of dust explosion. The separation process was performed in an inert atmosphere giving a yield of approximately 90% for this process step.

Scanning electron microscope (SEM) analysis was performed to study impurities in the silicon metal powder. Fig. 8 shows impurities found as separate particles.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Appearance</th>
<th>Metal impurities (wt.%)</th>
<th>Oxygen content (wt.%)</th>
<th>Metallic silicon (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon metal waste</td>
<td>Agglomerate, oxidized</td>
<td>1.5</td>
<td>16.0</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Silicon metal powder 5 (\mu m)</td>
<td>Free-flowing powder</td>
<td>0.1</td>
<td>1.4</td>
<td>99.9</td>
</tr>
</tbody>
</table>
TABLE 4

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Appearance</th>
<th>Metal impurities (wt.%)</th>
<th>Non-metallic impurities (wt.%)</th>
<th>Metallic silicon (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon metal waste</td>
<td>Moist filtercake</td>
<td>1.5</td>
<td>48.0</td>
<td>50.0</td>
</tr>
<tr>
<td>Silicon metal wet separation</td>
<td>Moist filtercake</td>
<td>1.4</td>
<td>13.0</td>
<td>85.0</td>
</tr>
<tr>
<td>Silicon metal powder dry separation</td>
<td>Free-flowing powder</td>
<td>0.5</td>
<td>0.5</td>
<td>99.6</td>
</tr>
</tbody>
</table>

(a)

FIGURE 8
SEM analysis of impurities in silicon metal powder.

Conclusions

Today, large quantities (>100 000 tons) of silicon metal powder are deposited as waste. ReSiTec has worked on research projects for several years and developed new technology for recycling and purification of valuable silicon metal powders from manufacturing of solar grade silicon. The energy consumption for the recycling process (<1 kWh/kg) is considerably reduced compared to conventional silicon metal production. This means that recycling of silicon metal powder should be an important strategy for improving future energy utilization and reducing the CO₂ footprint of the silicon metal industry.

The process has been developed to collect fine particles, with size range of 0–150 μm, from highly diluted waste water. Furthermore, known separation and classification techniques for metal powder processing have been adapted with the purpose of purifying and upgrading silicon metal powder from waste to new products. The tests performed were successful and the results showed an increase in purity level from 50% to >99% metallic silicon and an acceptable yield. It is believed that this new technology can be suitable for similar types of industrial metal powder waste streams. Today ReSiTec is producing more than 500 tons per year of recycled, high-purity silicon metal powder.

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References