SOLAR SILICON

PART I

Part I this month shows how induction furnaces can significantly increase the volume of production. Part II next month will discuss furnace types and thermochemical refining.

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The earlier generation of furnaces and silicon processing techniques, designed for small volume semiconductor devices, cannot satisfy the growing demand for solar grade silicon. The semiconductor furnace industry is trying to scale up equipment, but the resistive radiant heating elements and construction materials in these furnaces can deliver a power density of about 4 to 7 W/cm^2 of surface area, limiting the heating/melting rate of silicon.

However, induction furnaces can deliver heat directly or indirectly into a mass of liquid silicon metal with power densities up to 30 W/cm^2, with controlled stirring of the liquid metal, allowing faster silicon production on a much larger scale. This makes induction furnaces a preferred choice for the next generation of thermal equipment for solar-grade silicon production.

This article describes the various silicon grades, discusses the chemical reactions that take place during processing, and shows how induction furnaces remove impurities.

Silicon grades

Measured by mass, silicon makes up 25.7% of the Earth's crust and is the second most abundant element on Earth, after oxygen. Pure silicon crystals are only occasionally found in nature; they can be found as inclusions with gold, and in volcanic exhalations. Silicon is usually found in the form of silicon dioxide (also known as silica), and silicate. Widely available silica sand has too many impurities and is not suitable for silicon production. Instead, pure lumpy quartz is primarily supplied for this purpose.

Before solar panel wafers can be made, silicon must be purified to 99.9999% (six nines) purity, usually referred as solar-grade silicon (SG-Si). To be designated as electronic grade (EG-Si), silicon must be purified to a much higher degree, 99.99999999% or eight nines, or higher.

Metallurgical grade

Metallurgical grade silicon (MG-Si) is the precursor for solar-grade and electronic-grade silicon. Silicon is commercially prepared by the reaction of high-purity silica with wood, charcoal, and coal, in an electric arc furnace with graphite electrodes, Fig 1. At temperatures over 1900°C, the carbon reduces the silica to silicon according to the chemical equation:

$$SiO_2 + 2C \rightarrow Si + 2CO$$

Molten silicon collects in the bottom of the furnace, and is then drained and cooled. An optional flat induction coil placed under the molten bath helps to stir the molten silicon, accelerating the chemical reaction. The MG silicon produced via this process is at least 98% to 99% pure. By this method, silicon carbide can form. However, provided the amount of SiO_2 is kept high, silicon carbide may be eliminated, as explained by this equation:

$$2\,SiC + SiO_2 \rightarrow 3\,Si + 2\,CO$$

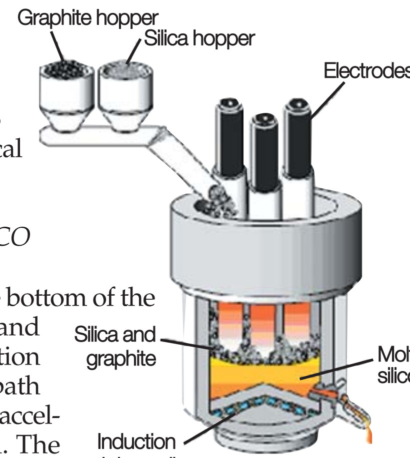

Fig. 1 — Production of metallurgical grade silicon (MG-Si).

MG-Si is contaminated with trace elements of metals such as iron, aluminum, titanium, vanadium, boron, and phosphorus, as well as inclusions of silicon carbide, silicon nitride, and silicon dioxide, and others. All of these would degrade the efficiency of solar cells.

In 2005, metallurgical grade silicon cost about $0.77 per pound ($1.70/kg). The industry produced 900,000 tons of MG-Si, of which about 50% was for the production of aluminum, steel, and titanium. About 45% was for the production of silicones for construction and households. Only about 5% was used for the production of semiconductor devices and solar cells.

Production of MG-Si does not represent a bottleneck, and can be easily increased with existing capacities. However, the pure solar grade silicon is currently in short supply and being sold for as much as $400/kg in the spot market.

To be suitable for the solar industry, the impurities must be removed from the silicon. Additionally, solar-grade silicon should have either a mono-crystalline or a very coarse multi-crystalline structure.

Induction furnace

In the induction furnace, elements less noble than silicon such as aluminum, calcium, and magnesium are oxidized in a reaction with silica. The SG silicon producers purify silicon by adding proprietary slags on the molten silicon surface. Liquid silicon is commonly treated with oxidative additives, mainly silica sand (SiO_2) and lime/limestone ($CaO/CaCO_3$). Other chemicals such as dolomite (CaO-MgO), calcium fluoride (CaF_2), and others are added, de-

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Element	Concentration, ppma
Al	1200 - 4000
B	37 - 45
P	27 - 30
Ca	590
Cr	50 - 140
Cu	24 - 90
Fe	1600 - 3000
Mn	70 - 80
Mo	<10
Ni	40 - 80
Ti	150 - 200
V	100 - 200
Zr	30

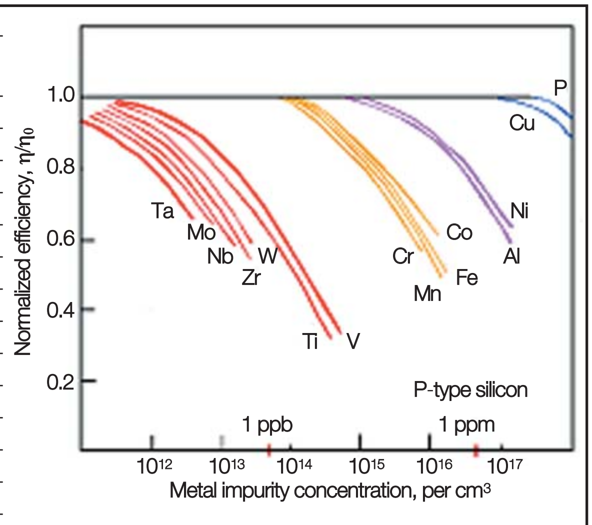

Fig. 2 — Impurities and their effects on solar cell efficiency.

pending on plant practices and customer requirements. The oxidation reactions are:

$$Al + SiO_2 \rightarrow Si + Al_2O_3$$
$$Ca + SiO_2 \rightarrow Si + CaO$$
$$Mg + SiO_2 \rightarrow Si + MgO$$

It is possible to reduce aluminum and calcium to very low levels via ladle metallurgy, but in practice this is prevented by the large heat losses during this operation. Therefore, an additional source of energy is required. This energy can be supplied by an induction coil.

In an induction furnace, MG-Si is first re-melted, and then may be vigorously mixed and stirred with oxidizing slag. After completion of oxidative refining, the slag, which contains part of the impurities, is removed mechanically or by gravity, and liquid silicon is poured into a casting mold.

It is well known that solid silicon does not conduct electricity and, therefore, does not absorb electromagnetic energy in an electromagnetic field. However, liquid silicon is highly conductive, and electric current can be easily induced into the molten bath. Therefore, when melting from a solid state, a conductive material (susceptor) must initially carry the current.

The induction furnace is almost perfectly suited for the slag metallurgy of liquid silicon. With slight modifications of construction, the induction coil may be split in two or three sections, as shown in Fig. 3. The AC current to each section may be applied with the proper phase shift, forming a "running" electromagnetic wave that causes vigorous stirring of the molten bath. Such stirring is beneficial, first for melting of liquid silicon, and then for mixing the slag with the molten silicon.

The stirring pattern in silicon refining furnaces is designed to flow up the walls of the induction furnace, and down in the furnace center. In this way, the solid chunks of silicon added to the molten bath are carried to the bottom of the furnace and quickly dissolved. Any other flow pattern may cause the silicon lumps to float on the bath surface and form a solid crust that prevents additional silicon from melting. Such lumps must be broken down by mechanical means.

Induction furnaces for melting and slag refining of silicon are being built with crucible capacity from one to seven tons of silicon. When a conductive crucible acts as a susceptor, the operating frequency may be changed in the process. First, while silicon is cold, the high frequency coil current heats only the crucible, and silicon melts by thermal conduction. Then, after the silicon begins to melt, the frequency is lowered and the induction current couples with the molten silicon bath directly.

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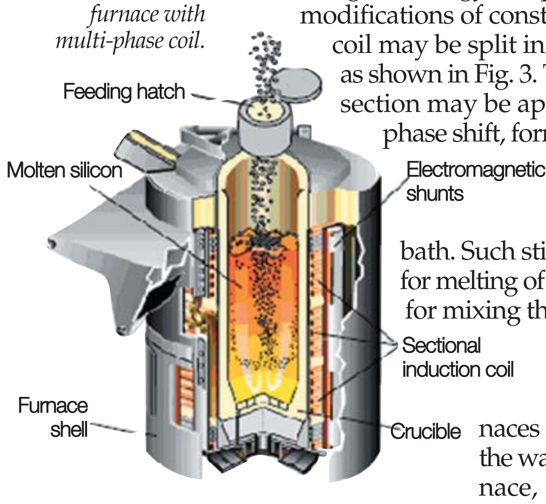
Fig. 3 — Stirring pattern in an induction furnace with multi-phase coil.



Removal of inclusions

The densities of SiC and Si_3N_4 particles are higher than the Si-melt:

- $SiC = 3.2\ gm/cm^3$
- $Si_3N_4 = 3.4\ gm/cm^3$
- $SiO_2 = 2.6\ gm/cm^3$
- $Si = 2.3\ gm/cm^3$

These heavier particles can be removed by settling in a quiet bath. The refining efficiency depends on the settling times and the SiC particle size. Theoretical calculations have shown that after one hour, 10 μm particles are removed down to 15% of the initial concentration, while almost all 20 μm particles are removed. These calculations were used to design a pilot scale reactor.

Induction furnaces may remove dense particles by taking advantage of settling. After vigorous stirring in slag metallurgy, the molten silicon bath may be left in a quiescent state to allow heavy undissolved particles to settle to the bottom of the bath. The partially purified silicon may be poured out, leaving the impurities in the bottom of the furnace.

Gas purging

The elements boron and phosphorus stay in the bulk silicon because their segregation ratio is poor: 0.3 for phosphorus and 0.8 for boron. Both boron and phosphorus act as dopant elements, and therefore must be strictly controlled in SG-Si feedstock.

Boron can be removed by bubbling argon or water (steam) through the bath of molten silicon. An effective way to remove phosphorus from silicon is to evaporate it in a vacuum. Gas purging and vacuum evaporation can be carried out in an induction furnace placed in a vacuum chamber. The gas may be introduced into the bottom by means of a porous plug.

To reduce remaining impurities, a molten bath of silicon is slowly solidified from the bottom to the top. The impurities migrate with the phase transition from solid state to liquid, and thus are removed to the surface in the process of solidification.