

METALLURGICAL SILICON FROM HIGH PURITY SAND CRITICAL ISSUES AND POTENTIAL DEVELOPMENT

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ABSTRACT

Silicon is one of the most important raw materials used in the Solar Cell production. The Photovoltaic Industry has been using existing supplies of mgSil in its polysilicon production steps and, given the robust nature of that chemical process, there has been little need or incentive to seek other forms of mgSil or to explore the use of alternative raw materials. As it stands, few industrial producers of mgSil have any serious plans for more efficient technologies and/or alternative process techniques outside of the traditional methods. However, two recent events may lead the industry to a different direction. The, up to now, failed development of UMG or upgraded metallurgical silicon in the mid-2000s served as a testing ground for using higher purity quartz (usually of smaller grain size resulting from chemical cleaning) for mgSil production as a way to bypass or circumvent the traditional polysilicon process. Many experiments were performed and some quasi industrial production was achieved using higher purity raw materials, some of which was high purity quartz. Secondly, the ongoing and aggressive development of the Photovoltaic industry in the MENA region where enormous quantities of high grade quartz sand is available has led to intense interest in exploiting this normally unusable but abundantly available material for production of mgSil in the region. Finding a technically and commercially viable solution for the Sand to Silicon problem has huge potential to opening up niche mgSil operations in these areas with an added benefit of increased quality and lower cost. Lastly, looking for the technical and commercial aspects is possible to see a lot of difficulties to use sand in the mgSil production, at the same time, is possible to find a huge amount of good chemical quality sand available to be used for example in this metallurgical industry. All these aspects together press this subject for a very good opportunity to invest in Research and Development of the sand usage for mgSil production.

KEYWORDS: Metallurgical silicon (mgSil), quartz sand, smelting, UMG, efficient technology, Photovoltaic Industry.

1. INTRODUCTION

The traditional metallurgical silicon or „mgSil“ process has not changed much in over 100 years and remains limited by certain physical and chemical boundary conditions related to the initial raw materials, quartz (SiO_2), carbon, wood, electrodes and energy [1]. The production process of mgSilicon is commonly known and is not the subject of this paper, rather the focus is on the critical mechanism that seems to be the limiting agent in the use of fine grain sand in mgSilicon production, i.e. the conversion of $\text{SiO}_{2(s)}$ to $\text{SiO}_{(g)}$ and the reduction of $\text{SiO}_{(g)}$ to $\text{SiC}_{(s)}$ and $\text{Si}_{(s)}$ in the furnace [1].

The importance of the Silicon source (SiO_2) for the process start in the top of the furnace, in the Upper Zone where this raw material is pre-heated up to 500°C to 600°C approximately. In the Middle zone the main reaction that occurs is the reduction of SiO in the gas state producing SiC in the solid state (α -SiC and β -SiC, both in solid state).

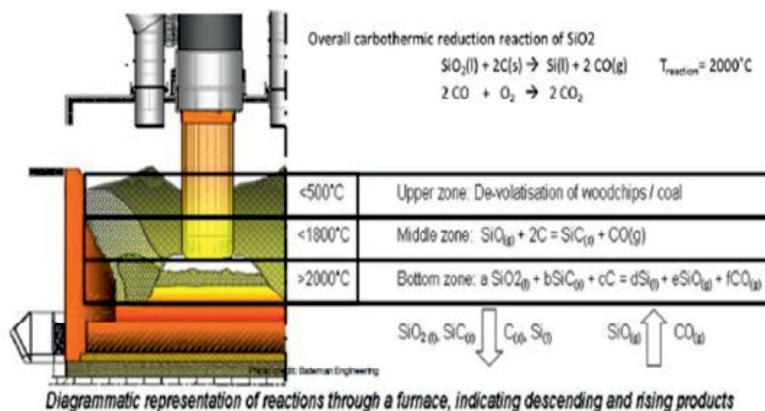


Figure 1: Diagrammatic Representation for mgSil Process (from Bateman Engineering)

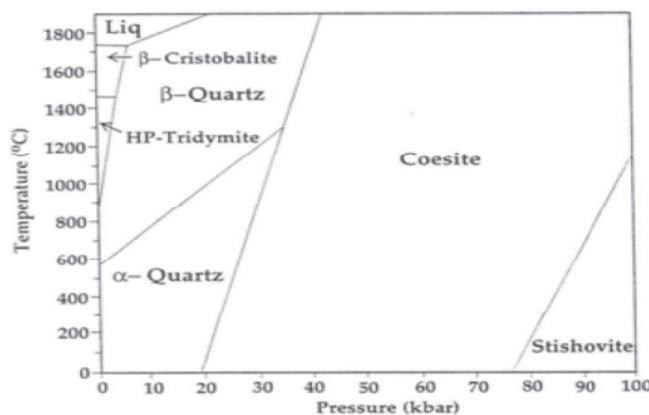


Figure 2: Phase Diagram for Silica System (from Klein and Hurlbut, 1993)

At this point, the contact surfaces of the Si (SiO or SiO_2) are fundamental for the reactions kinetics. In the Bottom reaction zone is the part of the Electrical Arc Furnace (EAF) where the liquid Silicon is produced in a high temperature approximately 2000°C – 2200°C [2].

The packaging effect that the raw material needs to have for a good gas distribution and the ideal thermodynamics, mass and energy balance in the EAF during the mgSil production process is very important in this point. Exactly because the packaging effect is very important keep under control the size distribution of all the raw material and the size distribution of the mixture of the charging (quartz, reductant and gas distributor).

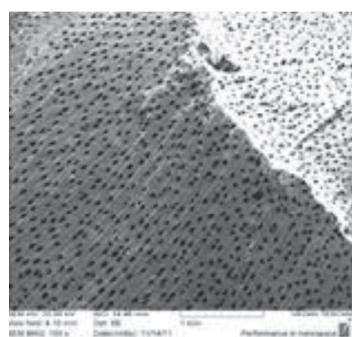


Figure 3: SEM of Reductant, Viridis.iQ GmbH

Typically, quartz in the size range of 25 mm to 75 mm is combined in the smelting furnace with a carbon reductant and a porosity agent (usually wood) to promote the reaction of:



The actual process is quite more complex and involved many different phases and conditions but this equation commonly represents the reaction. However, our first interest at present is the formation of $\text{SiO}_{(\text{g})}$ from SiO_2 . In the standard process, quartz lumps are added to the furnace and experience a thermal gradient up to 3000°C [3]. Depending on the location of the quartz in the furnace various phases of quartz occur based on the phase diagram for the Silica system. It is known that quartz undergoes a transition to cristobalite in the furnace and this, along with fluid inclusions and other impurities (mica), causes dis-integration of the material in the furnace. The main problem with this disintegration is that as the quartz fines increase in volume, a detrimental effect is seen on the porosity of the charge volume and results in lost potential conversion of SiO to SiC , and later to Si . Therefore, under normal conditions, quartz lumps are used from known sources with high or proven thermal stability. The process can be described as follows with each reaction providing chemical components for subsequent reactions.

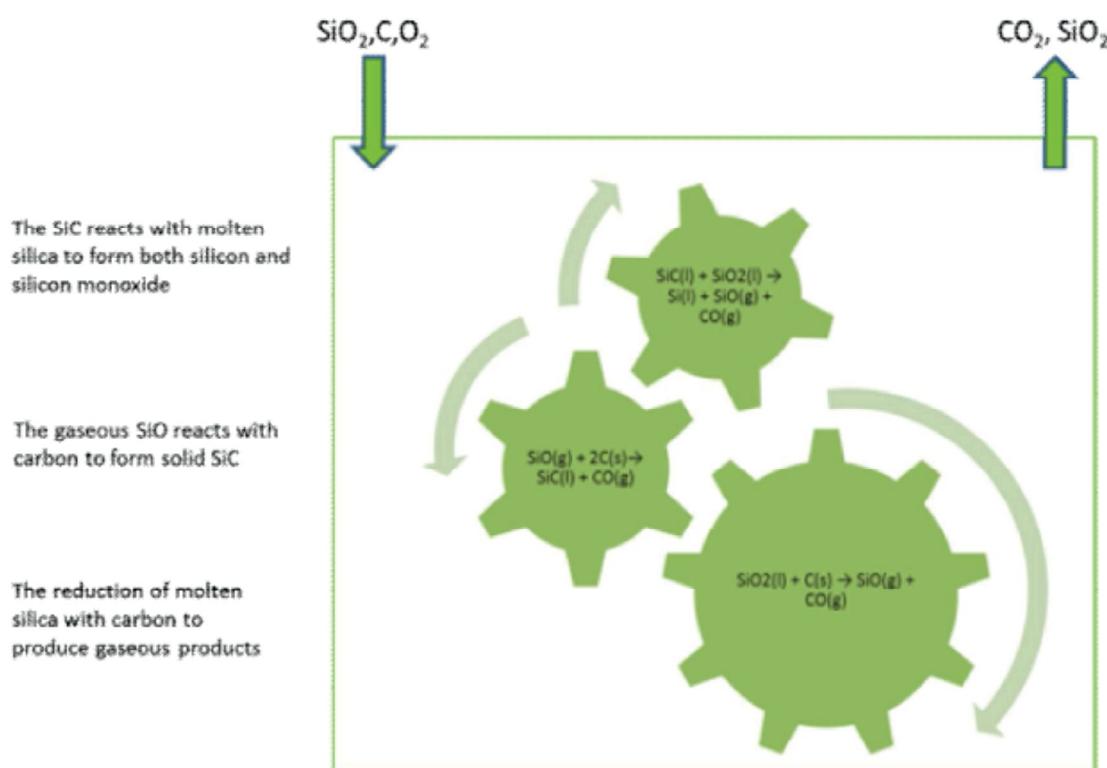


Figure 4: Silicon Reactions, Viridis.iQ GmbH

As the quartz phases are formed and fall into the highest temperature zone of the furnace, they become molten and react with carbon units in the furnace [3].

SiO(g) is then filtered via the porous carbon units in the furnace and converted to SiC(s) . This reaction occurs as the gaseous SiO enters the pores of the carbon unit and converts the carbon

into SiC (s). In this part of the process, high porosity is important but also critical is the reactivity of the carbon to SiO.

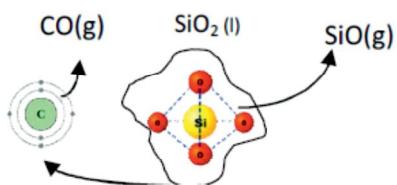


Figure 5: Reduction of SiO₂, Viridis.iQ GmbH

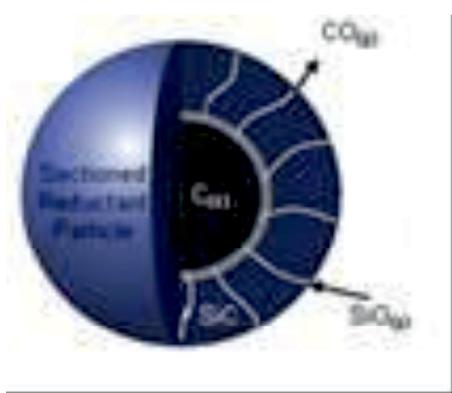


Figure 6: Carbon particle, (source: Bateman Engineering)

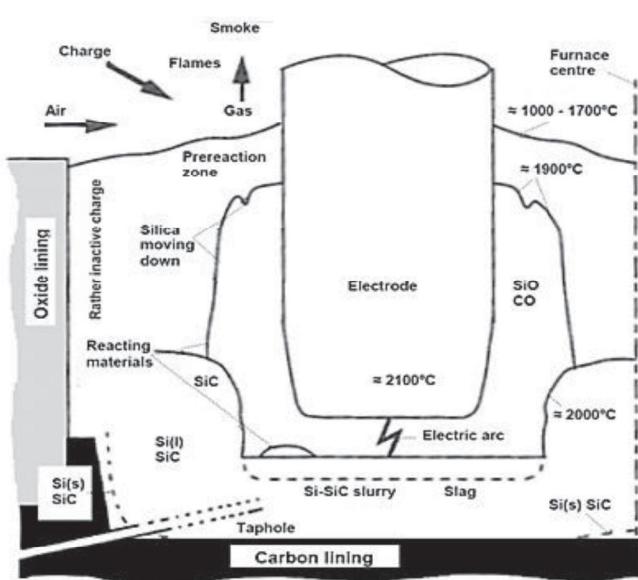


Figure 7: Silicon Furnace Schematic, Schei et al (1998)

The last step inside the furnace is the reaction between SiC(s) and SiO₂(l) to form Si(l), SiO(g) and CO(g), the later products are used to fuel the continuous reactions mentioned earlier. This reaction takes place near the bottom of the furnace as mixtures of sticky intermediate phases form and separate into Silicon and gas species [2].

The liquid silicon is then removed via channels and tap holes in the furnace.

2. THE USE OF SAND AS A SOURCE OF SiO₂

The use of fine grain quartz materials such as high purity quartz sand is generally seen as not viable for the industrial process for various reasons. The main ones being:

- Fines of any type (quartz or carbon) can reduce the porosity of the furnace and prevent the useful recovery of SiO.
- The much higher surface area of quartz fines can impart additional contamination into the furnace (although this may be compensated for with cleaning).
- High levels of quartz fines may interfere with the cavity formation around the electrodes which plays an important role in the process.

- Quartz sand can have different energy demands than lump quartz.
- Sand can sinter and interfere with the process dynamics.



Figure 8: Quartz Sand, internet search

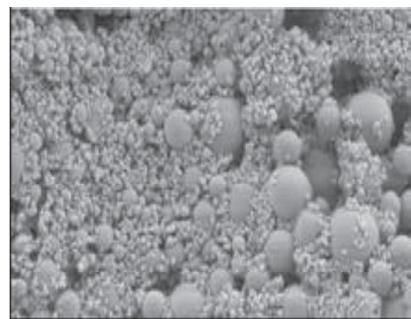


Figure 9: Quartz Powder, Dorfner Anzoplan GmbH

However, there are also some gains that might be realized with the use of the right form of quartz fines.

- Cristobalite formation may be faster and may accelerate the reduction process in certain zones of the furnace.
- Quartz sand has more open grains and may lead to less fracturing inside the furnace.
- Quartz sand is much more resistant to handling than lump quartz and may be more thermal resistant, thus preventing further crepitation.
- Quartz may react directly with carbon temperatures above approximately 1500°C when quartz and carbon have a high surface contact [4]. This could lead to a faster reaction, in principle.

3. PAST WORK ON UMG

In the mid-2000s, a consortium was funded by an EU Funding project to develop a cheaper alternative to polysilicon. This was one of many attempts to solve the issue of a viable “metallurgical route” as a substitute for high cost polysilicon. The idea was that if high purity quartz and carbon were used in a high purity furnace, the output should also be of high purity. The implementation of the work was the use of a two staged process and the modification of the relative size of the principle raw materials in the mgSilicon process.

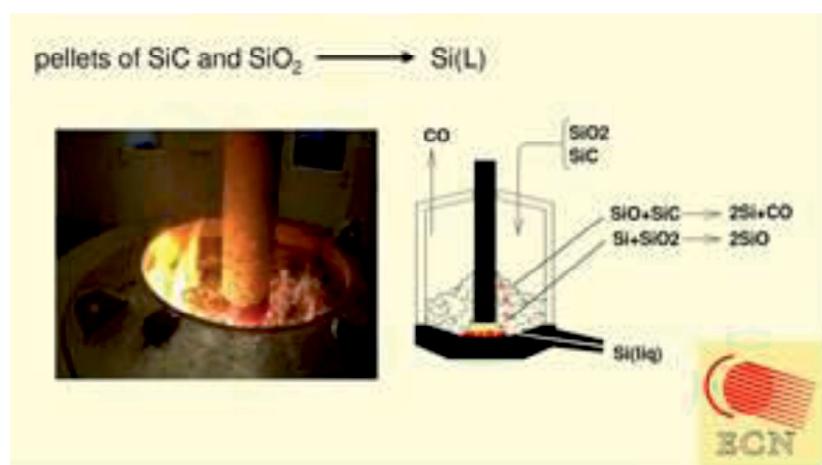


Figure 10: SOLSILC Process, ECN

The normal size requirements for quartz and carbon in the traditional process is 25 mm-75 mm for quartz and 15 mm – 90 mm for carbon or an average ratio of in practice of around 1.25. For quartz sand that has been chemically cleaned, with average sizes of 1mm, the use of a fine grain carbon source was also needed. Carbon black has been used in this context by the cracking of natural gas and special furnaces were built that used plasma burners and high purity electrodes. A special binder was used to bind carbon black to quartz fines.



Figure 11: SOLSILC Process, ECN

This intimate contact promoted the rapid formation of SiC, but further reactions required processing in a separate furnace environment, thus making the process unviable. The main problems with the process were:

- Contamination from the furnace lining and also possible from the handling of the material from one furnace to another.
- Poor recovery due to a need for high recycling rates.
- An aversion to use wood or other porosity agents for fear of further contamination.
- Additional steps were needed for filtering to meet the required quality.
- Costly modifications were needed in post smelting steps.
- The resulting solar cell efficiencies were well below industry standards.

While the relative size issue can be easily resolved with existing materials (carbon black), the porosity requirements of the process create a more complex problem. Wood fines, in principle, can also be used of the correct relative ratio, in practice this cannot be managed due to the high gas flow volumes inside the furnace environment and the tendency of the fines to burn [5]. This also will negatively affect the finer grain quartz and carbon fines.

4. PLANS FOR DEVELOPMENT

In the traditional process environment, quartz sand as a direct substitute for lump quartz will likely not perform satisfactorily [7]. Some modifications need to be considered to facilitate the physical form factor of sand in the modern silicon smelting furnace. The SOLSILC process shows

that a modification of the raw materials is theoretically possible but maybe not economically viable. Nevertheless, lessons can be learned from the effort.

However in the scope of this paper, a high purity substitute for polysilicon is not what is required. The question remains if high purity quartz can be used to make cheaper mgSilicon on a comparable quality scale.

➤ One option may be to use a different geometric shape of the inside of the furnace to facilitate mixing of the charge materials as well as high gas porosity.

➤ Another option may be to use positive pressure to keep the gases inside the furnace and promote gas flow as well as to promote the process kinetics.

➤ Lastly, internal structures can be considered to allow for gas flows that might be constructed of consumable materials.

It is highly unlikely that existing large scale producers of mgSilicon will invest in innovation for the use of high purity sand for many obvious reasons. New developments on mgSilicon smelting with sand will occur in regions with high incentives for such development and with proper funding and motivation. New furnace designs and new material configurations can be used to find optimal combinations of furnace performance and costs [6]. Small pilot furnaces can be designed for proof of concept and would be more tailored to smaller individual consumers of mgSilicon, such as the polysilicon industry. Smaller furnaces also are more forgiving in practice and can be modified quickly for test iterations.

5. CONCLUSIONS

Considering all the technical aspects mentioned above, we can summarize in the table below, some important characteristics for the Silicon Source in the mgSil production standard process in Electrical Submerged Furnace actually used for this metallurgical field.

Table 1: Summary of the Silicon source comparison

Silicon Source	Chemical Contents	Size distribution	Packaging Effect	Treatment	Thermo stability
QUARTZ	4-5	5	5	5	4-5
SAND	4-5	1	1	1	1
QUARTZITE	1-2	4	3	1	1

*1 – very bad 2 – bad 3 – average 4 – good 5 – very good

Considering the aspects above, is possible to see clearly that Quartzite and Sand are bad Silicon sources for the standard mgSil production process, but for both silicon sources there are a huge field of development to find a possible route to use this abundant raw material for mgSil production, considering the equipment and process parameters as well. The use of quartz sand as a substitute for lump quartz in the production of mgSilicon is not a traditional processing method, however, there has been work done using this material that shows a modified smelting process is possible. Further development work must be carried out to determine the optimal furnace design and process parameters.

6. REFERENCES

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