

SMALL SCALE LABORATORY EXPERIMENTS SIMULATING AN INDUSTRIAL SILICON FURNACE

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ABSTRACT

To simulate parts of the industrial Si process, SiC and SiO₂ is added on top of a Si+SiO₂ layer and heated. These experiments are performed in a graphite crucible which is heated in a small scale induction furnace (15 kVA). A temperature profile from 1900 to 1400 °C has been achieved in the crucible. With this technique it is shown how SiO gas condensate into layers of Si and SiO₂, how cavities in the low temperature area (~ 1700 °C) is formed due to condensation reactions and how Si metal may be formed in the SiC particles.

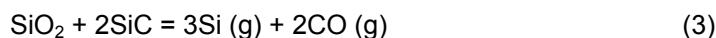
1 INTRODUCTION

The Si process is a high temperature process. On top of the industrial furnace the gas will leave with a temperature between 1000 and 1700°C and the highest temperatures in the furnace will be in the area of 2000°C. The high temperature is developed by an electric arc from the electrodes. From this it is evident that the difference between the highest and lowest temperature in the furnace may not be very high, only a few hundred degrees. But this gradient, between a high temperature zone and a low temperature zone, is a vital feature to obtain a high Si-yield in the production.

The Si process may be divided in 2 distinct zones according to theory [1]. First a lower temperature zone where the most important reactions are gas-solid reaction and condensation reaction according to the following:



In the high temperature zone the SiC produced in the upper part of the furnace will react with the melted quartz added, and Si will be produced. This Si will again react with SiO₂ to SiO gas.



The equilibrium conditions for these reactions are shown in Figure 1. According to the figure, the SiO pressure will not be high enough or CO pressure low enough, to produce silicon until a temperature above about 1800°C is reached. At this temperature the SiO pressure is about 0.7 atm. As the SiO and CO gases are ascending in the furnace, the gas temperature decreases and the SiO gas will, if any carbon is present, react to SiC. The rest of the SiO gas will condensate to Si and SiO₂. At 1400°C the SiO pressure in the off-gas will according to equilibrium conditions be about 1%. As equilibrium is not obtained at all levels in industrial furnaces, the industrial Si yield will be in the area of 80 to 90%.

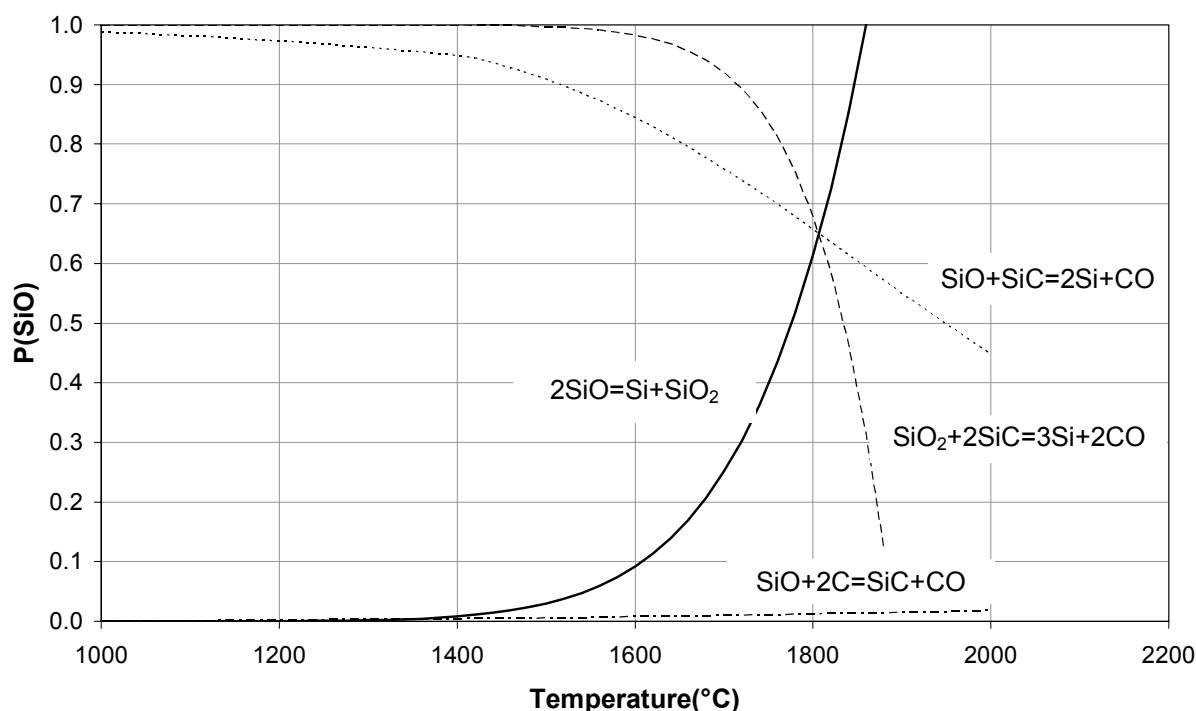


Figure 1: Pressure of SiO gas in equilibrium with SiO₂, SiC and C. (Total pressure of SiO and CO gas are 1 atm (HSC database)).

Table 1: Experimental conditions.

		Exp. 1	Exp. 2	Exp. 3	Exp. 4
SiO ₂	Type	C	C	A	B
	Particle size	3-10 mm	3-10 mm	7-30 mm	7-30 mm
SiC	Type	α-SiC	α-SiC	α-SiC	α-SiC
	Particle size	2-15 mm	2-15 mm	2-15 mm	2-15 mm
Si	Type	MG-Si	MG-Si	MG-Si	MG-Si
Bottom temp.		~1900 °C	~1870 °C	~1920 °C	~1890 °C
Holding time		~40 min	~80 min	~70 min	~70 min
Quartz layer above metal		no	yes	yes	yes

To study the reaction mechanisms in the Si process, one may excavate industrial- or pilot scale-furnaces. However, these types of investigations are relatively rare, as the cost of the method is high. If parts of the silicon process are to be investigated in laboratory scale furnaces, some challenges must be addressed. First, the high temperature of the process are close to 2000°C, which means that materials used in the furnace apparatus has to be carefully chosen. Next, as the reactions are involving a SiO gas, which is of major importance in both the high and low temperature zone, the reactor may either consist of 2 chambers or one chamber with a temperature gradient. An example of the two chamber setup, is SINTEF's SiO reactivity test, where SiO is produced in one chamber and then introduced in the chamber where it reacts with the carbon materials present. This paper presents introductory experiments in an induction furnace where the temperature gradient is one of the main features. As the SiC production was not an essential part of the experiments, SiO₂ and SiC was used as raw materials. In the bottom of the crucible the temperature is above 1900°C and at the top, the temperature may be 1400°C or lower. Hence, important parts of the Si production may be investigated in a cheap and time effective manner. The purpose of these experiments was to investigate the SiO condensation, reaction (1) and (2), as well as melting behaviour of various SiO₂ sources.

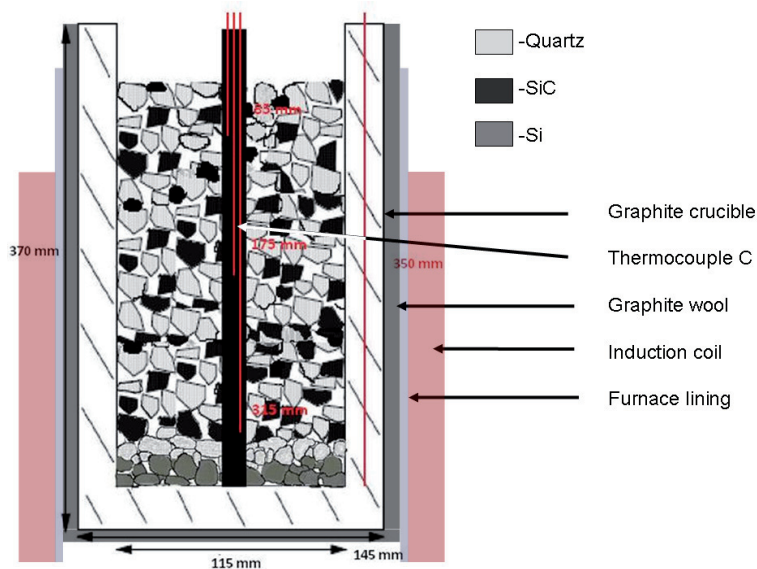


Figure 2: Experimental setup of furnace, thermocouples and charge.

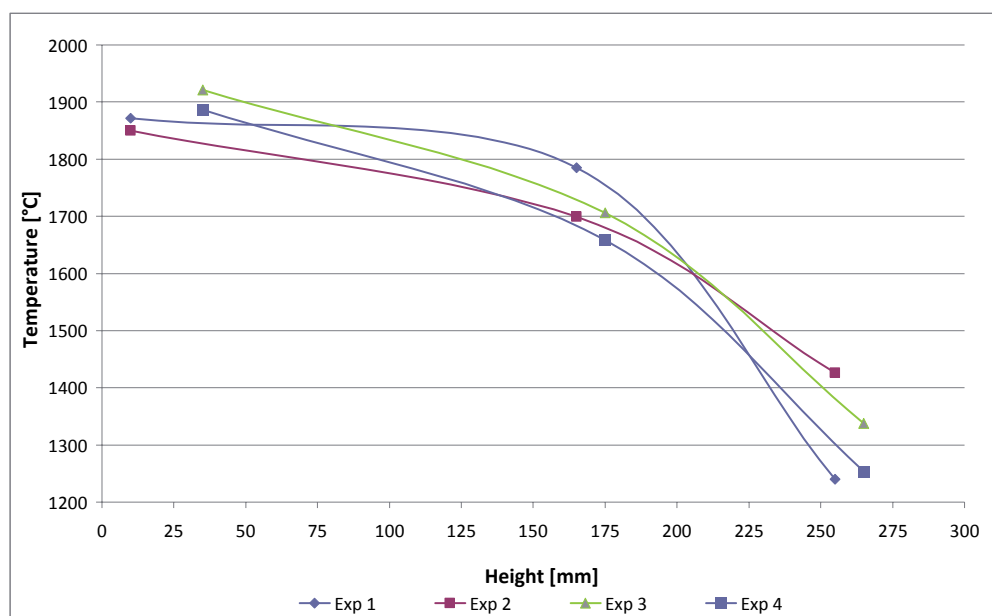


Figure 3: Temperature gradient in the crucible.

2 EXPERIMENTAL

The experiments were performed in a 115mm inner diameter, graphite, crucible as shown in Figure 2. The advantage about using a relatively large crucible is that industrial sized particles may be used. The molten quartz will descend in the crucible, and when flow mechanisms may affect the result, industrial sized materials should be used. To produce SiO gas in the bottom of the crucible, a layer of metallurgical grade silicon was added to the bottom of the crucible. In Table 1, the experimental conditions for the 4 experiments are shown. To increase the rate of SiO production in experiment 2, 3 and 4, the bottom metal layer was mixed with a quartz layer. On top of this bottom layer, a mix of SiO₂ and SiC was added. The temperature was measured with a C-thermocouple at 4 different positions, as shown in the figure. Based on the temperature measurements and the height of the crucible, the temperature gradient of the 4 experiments is shown in Figure 3. The temperature in the

lower part of the crucible was in the area of 1850 to 1920°C and the top temperature was below 1200-1400°C in the four experiments. As the top thermocouple was a bit below the charge surface, it means that the top charge temperature will be even lower. As the furnace is open, the off gas can be visually observed. No white smoke, from the oxidation of SiO gas, was observed.

After the experiments were terminated, the crucible was cooled and a two-component epoxy was added. The charge was now fixed. The crucible was cut in half and photographed. Samples were taken from different positions of the crucible and investigated in the EPMA.

3 RESULTS AND DISCUSSION

Pictures of the crucibles of the two first experiments are shown in Figure 4 and Figure 5. Experiment 3 and 4 shows in principle the same features, and are hence not included here. In the higher parts of the furnace the raw materials have their original shape and no condensate is found as shown in Figure 6. At higher temperatures the particles will be covered by condensate, and shortly thereafter, the quartz starts to melt. The condensation glues the particle together and prevents the charge from descending, in such a manner that a cavity will be formed underneath. The quartz may be melted in the same area as the condensate forms, as shown in Experiment 2, or at higher temperatures as seen in Experiment 1. In the last case there will not be much softened quartz above the cavity. Below the cavity the quartz is softened and envelopes the SiC particles. At the highest temperature, a mixture of Si, SiO₂ and SiC is present.

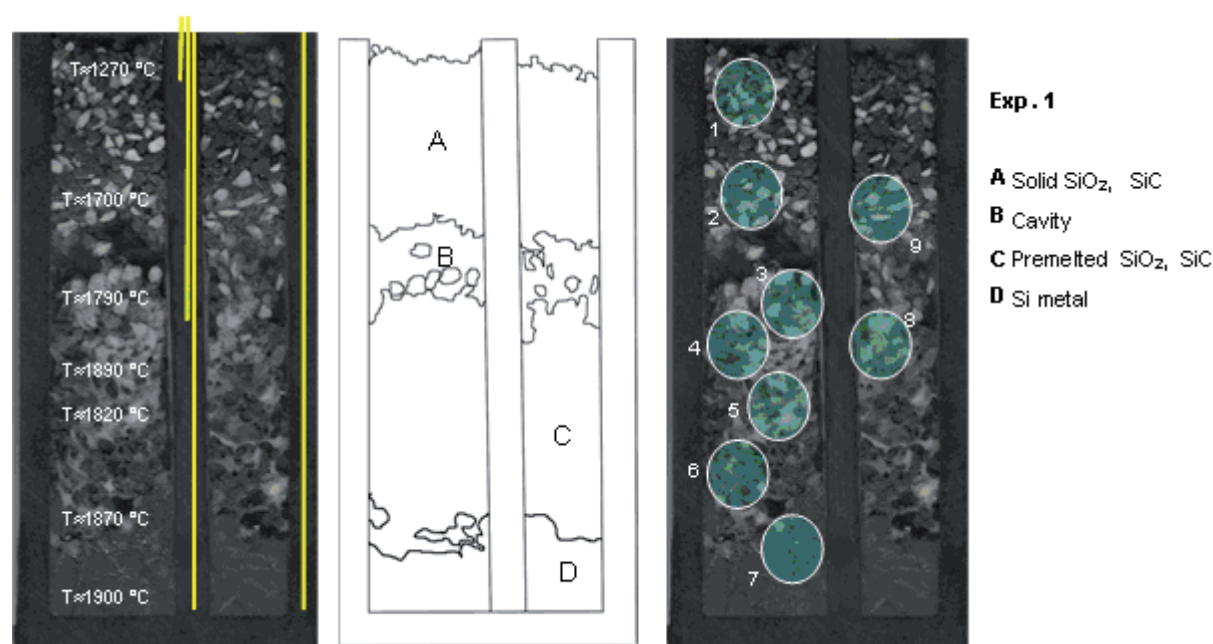


Figure 4: Pictures of the crucible interior of Experiment 1. Temperatures, zones and sample positions are shown.

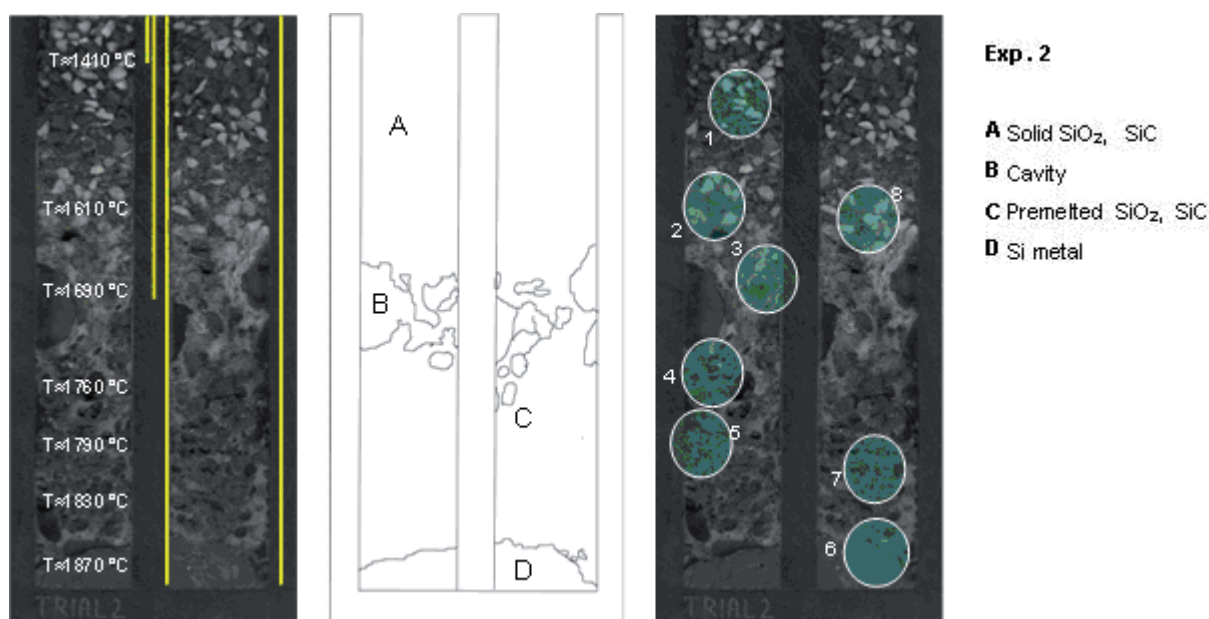


Figure 5: Pictures of the crucible interior of Experiment 2. Temperatures, zones and sample positions are shown.

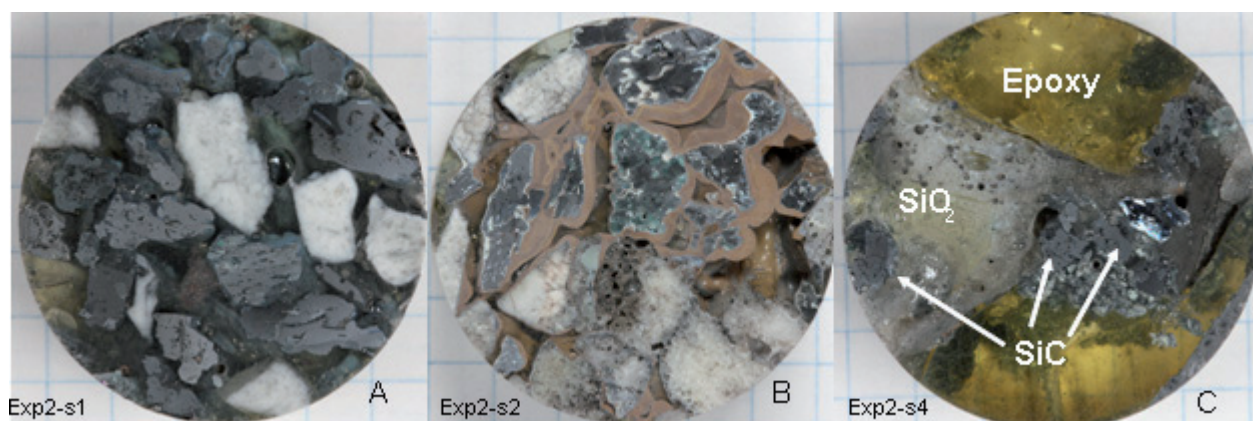


Figure 6: Samples from experiment 2. A) Before the condensation at about 1450°C, B) where there is condensation and softening of the quartz at about 1600°C, C) in the temperature at about 1760°C where the melted quartz surrounds the SiC particles.

The condensate was in Experiment 1 to 3 found between 1600 to about 1700°C, while in Exp. 4 the condensate was found between 1435 to 1600°C. A good explanation for this difference has not yet been found, as both the temperatures and the quartz type are different. Two kinds of condensates were found. One of them has a brownish colour and occurs in range around 1600-1700 °C just above the cavity. It typically surrounds the SiC particles. It is characterized as mixture of silicon and oxygen, where it seems as the oxygen content is varying. This situation is shown Figure 7. These layers contain very small metal particles, less than 1 µm as seen in Figure 8. The seemingly difference in oxygen/silicon ratios at the condensate layers, may be due to the varying sizes of the metal particles in the condensate.

The white condensate appears as a thin coating on the particles and also inside the cracks and pores. Silicon droplets were found in the white condensates layer which is presented at Figure 9. This size metal droplet was not found in the brownish layer.

The condensation reaction, reaction (2) will condensate above 1600°C when the SiO pressure is above 0.1 atm as seen in Figure 1. If in equilibrium, the SiO pressure in the lowest part of the crucible will be above 0.7 atm above 1800°C. The reason for not finding the condensate between 1700 and 1800°C is either because the driving force of the real SiO pressure versus the equilibrium pressure at 1700°C ($P(\text{SiO})=0.25$) is too low, or because the condensate is more difficult to observe, due to the white color of the condensate. The most probable is maybe a mixture of these two mechanisms.

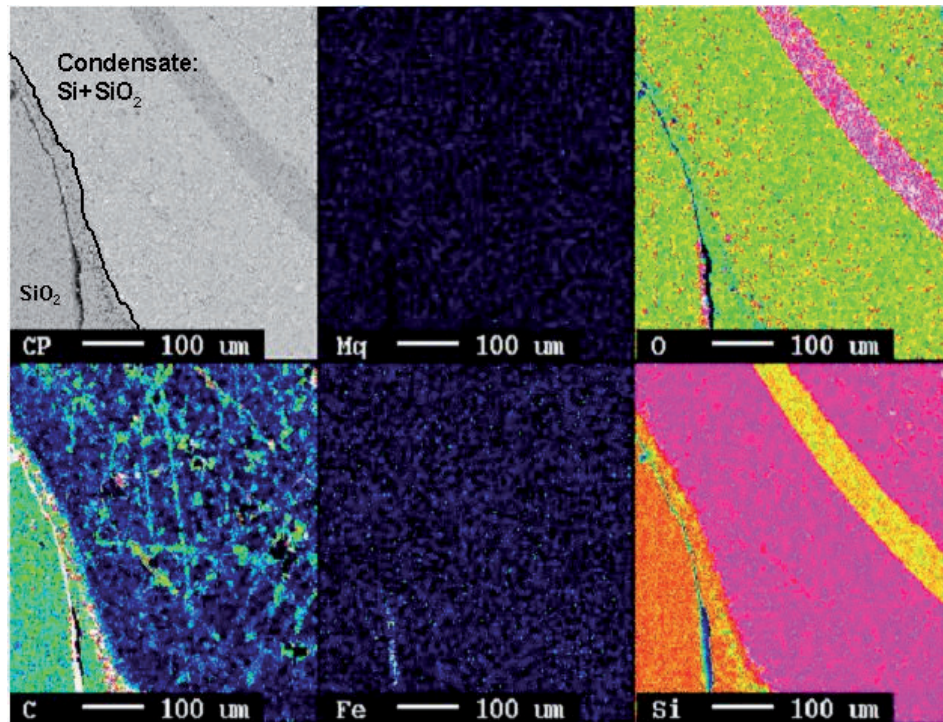


Figure 7: Mapping of brownish condensate layer (Exp.2 S2)

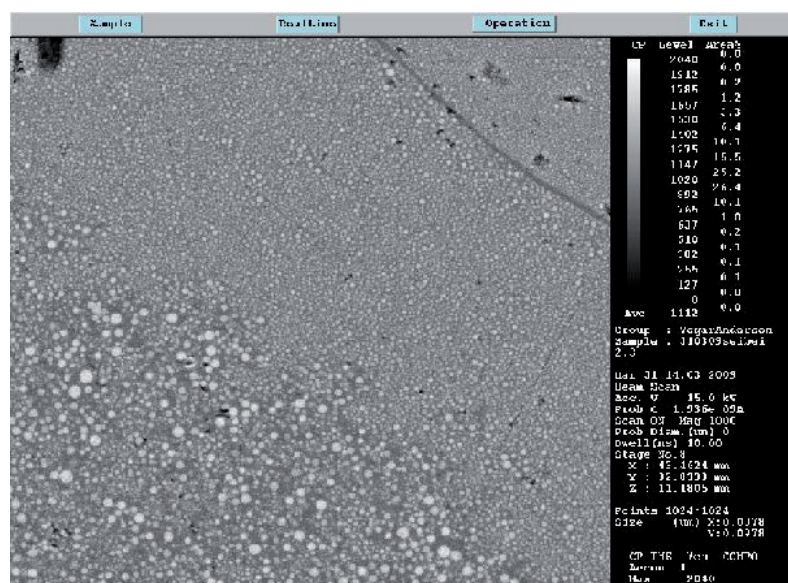


Figure 8: Enlarged picture of brownish condensate layer (Exp.3 S2)

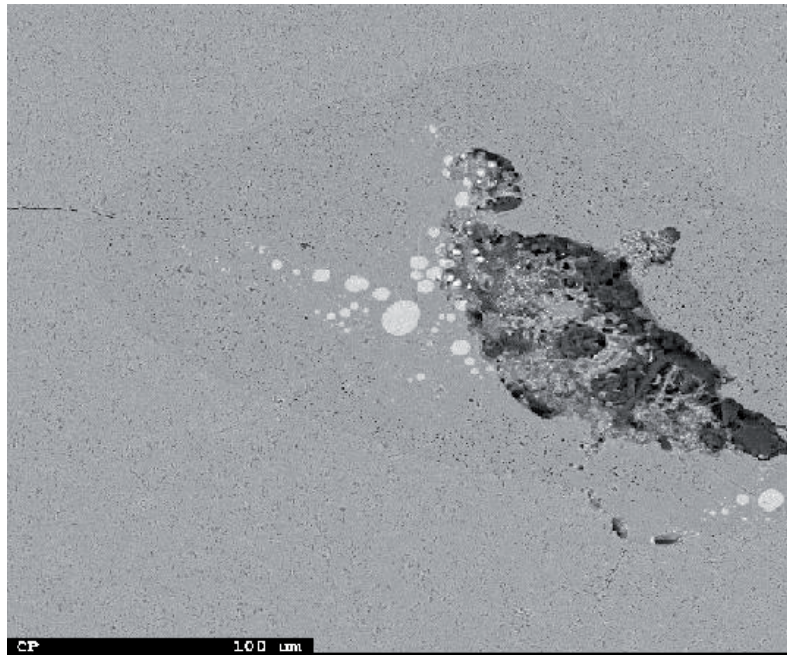
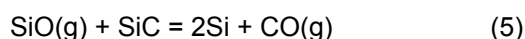


Figure 9: Picture of white condensate layer consisting of SiO₂ and Si. (Exp.2 S8)

In this series, various quartz' has been used. In Exp. 1 and 2, Quartz A had a softening point of about 1700°C. This softening point was also found for Quartz B, while in Experiment 4 Quartz C had a lower softening point of about 1600°C. The melting point of the quartz is very dependent on the transition from quartz, tridymite and cristobalite. As these phase transformations are very dependent on the temperature-time experience, these softening temperatures may be different in an industrial furnace. Åsly [4] showed that in laboratory experiments, hardly any of the quartz investigated, had changed to cristobalite. In the industrial excavation however, most of the quartz was found as cristobalite. Hence, when investigating industrial materials, they should beforehand be heat treated for hours at the given temperatures.

In these experiments it is shown that the cavity is formed due to condensate formation which will fixate the charge layer and prevent the charge descending in the furnace. In these experiments the cavity was in the temperature range from 1700 to a little less than 1800°C. According to literature the cavity in Si furnaces are as shown in Figure 10, which is one big cavity including both the crater zone and the cavity due to condensates. However, the present experiments suggest that there may be two cavities in the furnace; one condensate-cavity and one arc-cavity. This is also in accordance with the pilot-scale experiment in a 150 kW furnace done by Myrhaug[5], as shown in Figure 10. Here, two cavities are formed, one rather high up in the furnace, and one in the crater. If there is two cavities in the furnace, or if the two is collapsed to one, is probably very much dependent on how the furnace is operated.

The metal forming reactions are reaction (3) which occurs above 1800°C, and the formation of metal droplets in the SiO₂ matrix, that is condensate (2), at lower temperatures. The metal particles in the condensates are usually below 20 μm and in intimate contact with SiO₂. In these experiments also metal has been found in the SiC particles, as shown in Figure 12. This metal could have been produced according to the following equation.



However, at 1500°C, the SiO pressure must be higher than 0.9 for this reaction to occur. Although this is not observed in all the particles, it shows that metal may be formed at lower temperatures. This is in accordance with Myrhaug [5], who also describes charcoal with metallic Si in the low temperature zone, zone 7 in Figure 11.

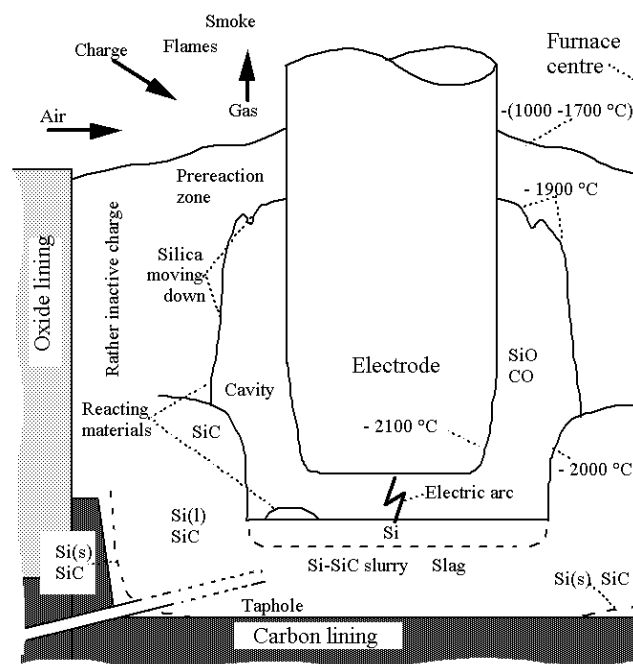


Figure 10: Schematic figure showing zones and temperatures in furnace from Schei et al. [1]

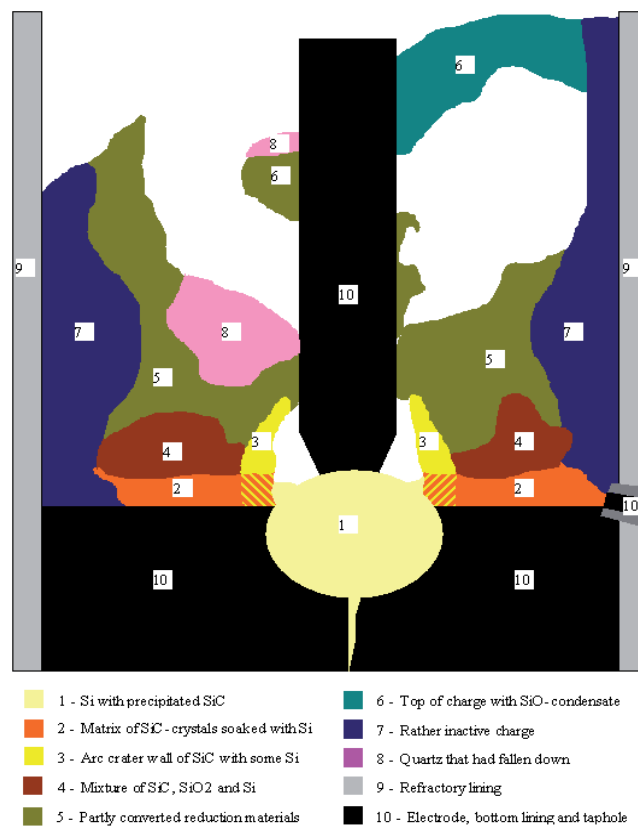


Figure 11: Sketch of zones found in pilot scale experiment from Myrhaug [5]

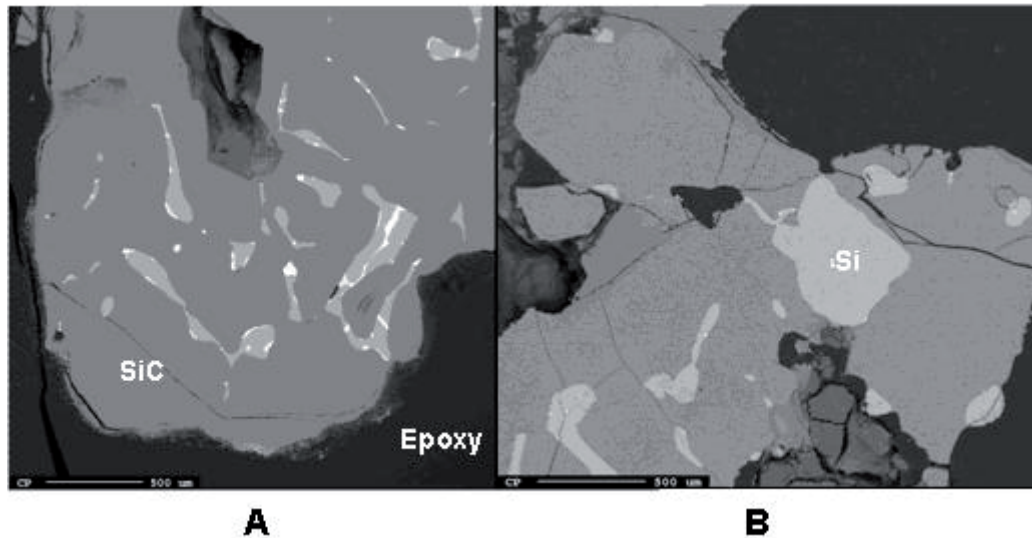


Figure 12: SiC particles (dark grey) with Si (light grey) from A) Exp.3 Sample 3 at around 1500°C and B) Exp.2 Sample 4 at about 1760°C. The white phase in the Si metal is metallic minor elements like Fe.

4 CONCLUSIONS

It is shown that parts of the Si process may be simulated in a small scale induction furnace. If a temperature gradient from 1400 to 1900°C is established, the production and condensation of SiO gas will occur. A brownish condensate layer, with Si particles less than 1 µm size, and a white condensate, with Si particles larger than 10 µm, is found in the temperature area between 1600 and 1700°C. This condensate fixes the charge, and a cavity will be formed below this temperature. This indicates that in industrial Si furnaces 2 cavities may be present, both the condensation cavity and the arc-crater.

The melting point of the quartz may also be investigated, however, this may done with some consideration, as the melting temperature is very dependent on the temperature-time run.

In addition to the metal formation in the condensate reaction, metal was also formed at lower temperatures inside of the SiC particles. No SiO₂ was spotted close to this metal as was expected. The mechanism is not yet determined for this reaction.

5 REFERENCES

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