CONDENSATE IN THE METALLURGICAL SILICON PROCESS – REACTION MECHANISMS

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ABSTRACT

The mechanisms in the metallurgical production of silicon have been examined in this paper. Through the investigation of several small scale induction experiments (~25 kW) a better understanding of this complex process has been obtained. Raw materials were mainly quartz (SiO_2) and SiC, to imitate the industrial carbothermic silicon process. Especially the silicon producing reactions and mechanisms as well as the condensate properties have been studied.

The material consumption (SiO_2 + SiC) was very low at temperatures below 1820°C as hardly any SiO gas was produced. Above 1900°C the reactions inside the furnace started to happen. Condensates of different colors were deposited in the upper and cooler parts of the crucibles used in the experiments. The most important type was the brown colored kind and was the product of the following reaction: $2SiO(g) = SiO_2(s) + Si(s)$. Brown condensate was deposited in the charge mix at temperatures below ~1680°C. This condensate glued the material in the upper part of the charge together. This agglomerate was thermally and mechanically durable and created a solid roof over the cavity left behind by the consumption of charge.

Mechanical tests were performed on the agglomerate created by the condensate. Agglomerate exposed to temperatures above 1670°C was weaker compared to the agglomerate exposed to lower temperatures. Typical compressive strength recorded for agglomerate exposed to 1670°C was 221 MPa at 25°C, significantly higher than Portland cement (40 MPa).

At temperatures around 1700°C, the silicon in the condensate (SiO_2 + Si) separated from the SiO_2 matrix leaving the rest of the SiO_2 intact. Perspiration of silicon is an important metal producing mechanism, especially when using SiO_2 and SiC as raw materials, since the SiO recovery mechanism with free carbon is disabled.

KEYWORDS: *Silicon production, condensate production.*

INTRODUCTION

The metallurgical production of silicon is a high temperature process where quartz (SiO_2) is reduced with carbon (C) to silicon (Si) and carbon monoxide gas (CO(g)). Typical consumption of electrical energy is 11-13 MWh per ton silicon metal produced. The overall reaction of the process can be written as [1, 2]:

$$SiO_2(s) + 2C(s) = 2Si(l) + 2CO(g) \qquad \Delta H_{2000°C} = 687 \text{ kJ/mol} \qquad (1)$$

The total description of the process involves many intermediate reactions and complicates the situation vastly from what reaction (1) describes. The internals of a submerged arc furnace can be divided into a high temperature ($T \approx 2000°C$) and lower temperature ($T \leqslant 1811°C$) zone, where different reactions dominate. In the high temperature zone around the electrode tip, the following reactions (2,3,4) occur:

$$2SiO_2(s,l) + SiC(s) = 3SiO(g) + CO(g) \qquad \Delta H_{2000°C} = 1364 \text{ kJ/mol} \qquad (2)$$

$$SiO_2(s,l) + Si(l) = 2SiO(g) \qquad \Delta H_{2000°C} = 599 \text{ kJ/mol} \qquad (3)$$

$$SiO(g) + SiC(s) = Si(l) + CO(g) \qquad \Delta H_{2000°C} = 167 \text{ kJ/mol} \qquad (4)$$

The slowest of these three are probably the SiO(g) producing reactions (2) and (3) which consumes a major part of the electrical energy developed. Silicon can be produced through reaction (4) at temperatures above 1811°C. The SiO-gas travels upwards in the furnace and is recovered either by reaction C-material (reaction 5) or by condensation where the temperature is sufficiently low (T<1800°C) (reaction 2rev and 3rev).

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \qquad \Delta H_{1800°C} = -78 \text{ kJ/mol} \qquad (5)$$

$$3SiO(g) + CO(g) = 2SiO_2(s,l) + SiC(s) \qquad \Delta H_{1800°C} = -1380 \text{ kJ/mol} \qquad (2rev)$$

$$2SiO(g) = SiO_2(s,l) + Si(l) \qquad \Delta H_{1800°C} = -606 \text{ kJ/mol} \qquad (3rev)$$

The condensate producing reactions (2rev) and (3rev) are strongly exothermic and are the main factor how heat is transported upwards in the furnace. The equilibrium conditions for the reactions (2), (3), (4) and (5) are shown in figure 1.

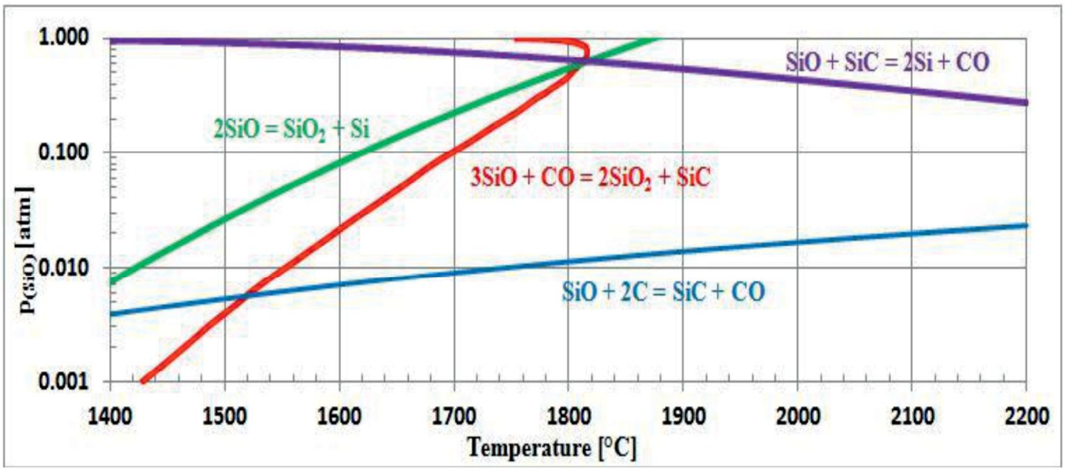

Figure 1: Partial pressure of SiO(g) in equilibrium with SiO_2, SiC and C. Total pressure of SiO(g) and CO are 1 atm. [2]

At the top of the furnace charge, the temperature can vary between 1000 to 1700 °C [1]. Typical industrial silicon yield is around 85% in a well operated furnace. Reaction (5) is the preferred SiO-recovery reaction above 1512°C. Below this temperature, SiO gas will only be captured by reaction (2rev) and (3rev). The temperature has a great effect on the equilibrium conditions for reactions (2rev) and (3rev). If the temperature at the top is ~1620°C (p_{SiO}=0.1 atm) and the main SiO recovery goes through condensation, then the Si-yield will be around 80%.

Much work has been done the recent years to define the reaction zones inside the silicon furnace. The doctoral thesis by Myrhaug [3], Infacon 12 paper by Tangstad et.al [4], the TMS 2012 paper by Ringdalen and Tangstad [5] and the master thesis of Vangskåsen [6] are good examples of recent publications on this subject.

In this work the condensing species will be investigated through small scale experiments, both when the condensation occurs, the structure of the condensate and the behavior during heating.

EXPERIMENTAL

A total of 13 different small-scale induction furnace experiments has been conducted. Two induction furnaces have been used and were operated between 20 and 25 kW. To simulate the Si process, the set up was arranged to give a high temperature at the bottom of the crucible, and a decreasing temperature towards the top of the crucible. Typically the temperature in the bottom was between 1800 and 2000 °C, and the temperature on top of the charge was about 1000°C.

The graphite crucibles (figure 2) used in the induction furnace were filled with quartz and SiC up to the rim in a molar fraction of $\frac{SiC}{SiO_2} = 2$. Both the quartz and the SiC material were sized 5 to 10 mm. In three experiments the charge composition were modified with addition of carbon materials as coke, coal and woodchips. The temperature was measured near the bottom in the crucible as well as just below the charge surface as seen in figure 2. The crucible was heated inside the induction furnace, the temperature was held at temperatures between 1800°C and 2000°C for 10 to 60 minutes.

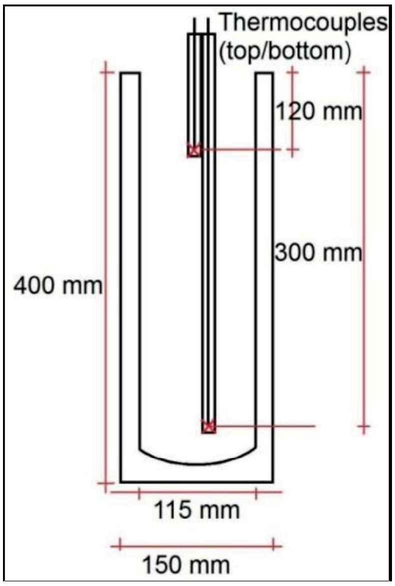

Figure 2: Setup in the induction furnace

After the crucibles had cooled, they were cut longitudinally with a circular saw so that the internals were exposed. Some were filled with epoxy to keep the remaining material together, but this was not necessary with most crucibles. Samples were drilled out from the cross-section and investigated using scanning electron microscope (SEM) as well as other tools.

Samples taken from the material inside the crucibles were also tested in a compression machine. As the pressure increased, the compressive strength of the different samples could be recorded.

RESULTS AND DISCUSSION

The cross-sections of four selected experiments are shown in figure 3. These crucibles were filled with SiO_2 and SiC and heated to temperatures around 2000°C in an induction furnace. As the material reacted in the bottom, SiO gas travelled upwards and reacted with SiC to produce Si metal if the temperature was sufficiently high. Deposits of brown condensate (Si + SiO_2) were created higher up in the crucibles, where the temperature was below 1700 °C. The condensate glued the material in the top together, creating a “cavity roof”, while the material beneath was consumed.

In figure 4, the temperature history graph for the experiment held for 60 minutes is displayed. In addition, the furnace load was monitored and the interaction between temperature and furnace load gave a hint of where the most endothermic reactions occurred.

Since several experiments with identical charge mixture were held at ~1980 °C at different durations, it became possible to make an assumption of how the cavity inside the crucible was created. A description of this is shown in figure 5. The cavity roof was established about the melting temperature of quartz (~1720 °C), so the temperature limit of condensation through reaction (3rev) was probably around the same temperature. At 1680 °C, the increase in temperature stagnated in the experiment displayed in figure 4. Indications are pointing strongly towards that the condensate production was constrained below ~1680°C. Above this temperature the reaction is unable to get rid of the excess heat and therefore shifted to the left.

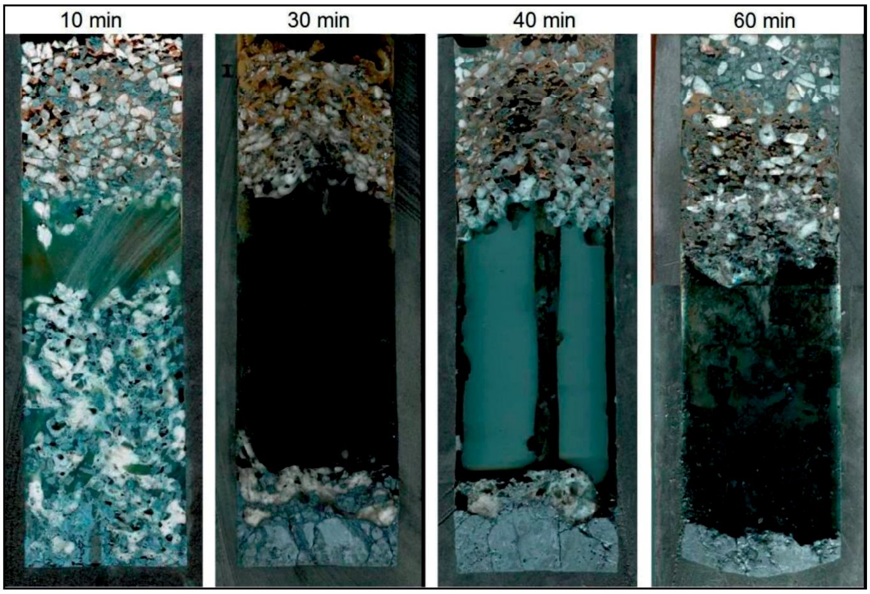

Figure 3: Cross-section of crucibles held between 1920 to 1980 °C for different durations. Temperature was measured in the bottom of the charge

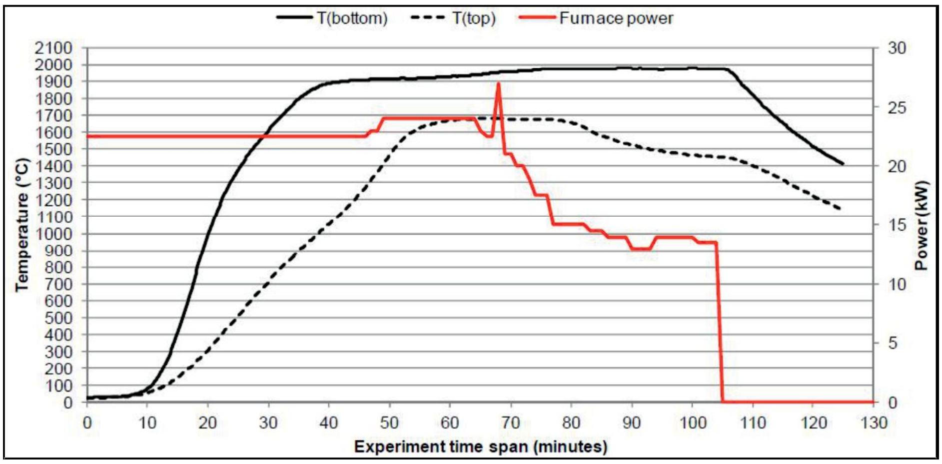

Figure 4: Time-temperature graph for the experiment held between 1920 and 1980 °C for 60 min

The brown condensate was also studied using the electron probe micro analyzer (EPMA). A line scan in figure 6 showed that the molar ration of Si/O was very close to 1. The stoichiometry of reaction (3rev) fitted very well with this product, and this was a good confirmation that the brown condensate was a result from the reaction: $2SiO(g)=SiO_2(s,l)+Si(l)$.

Between the brown condensate and the substrate, another condensate layer could be seen with the bare eye. The layer which could be less than one mm thick was called the white condensate due to its color. In the SEM, the layer was investigated, and it was assumed that it consisted of SiO_2 and SiC. The white condensate was possibly a product of the reaction 2rev: $3SiO(g)+CO(g)=2\ SiO_2(s,l)+SiC(s)$. A picture of the layer between the SiC-substrate and the brown condensate as well as a high magnification image of the white condensate is displayed in figure 7. In the high resolution image, bright particles can be seen in a grey matrix. Mean atomic number of SiO_2 and SiC is correspondingly 7.5 and 10, thus will SiC appear as the brighter phase in the backscatter detector.

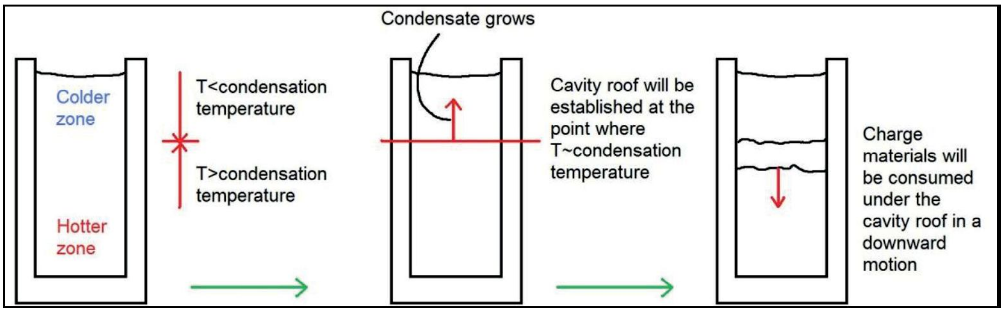

Figure 5: Description of the dynamics in the cavity formation

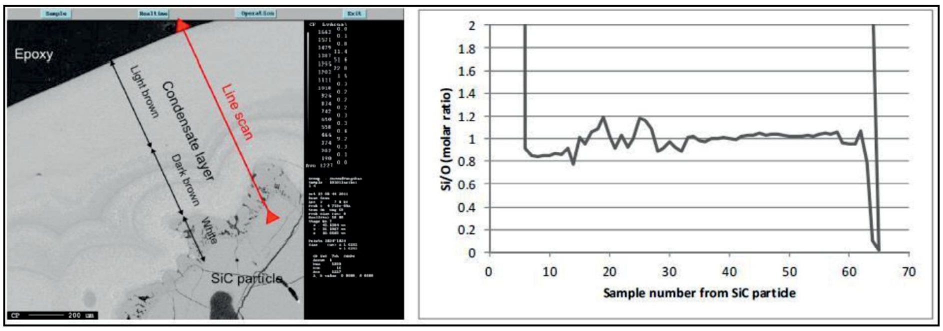

Figure 6: EPMA-image and line-scan over the brown condensate area

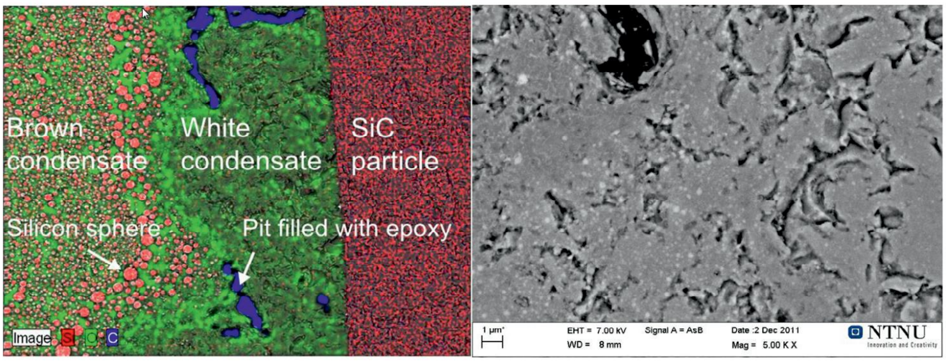

Figure 7: SEM-image of the white and brown condensate layers outside a SiC-particle, and a high resolution image of the white condensate

Small pieces (~3 mm) of brown condensate were collected and heated in a sessile drop furnace. In this furnace it was possible to take picture of the silhouette of the samples as the temperature was raised. The heating of brown condensate is visualized in figure 8. At temperatures above 1700 °C, the silicon phase seems to sweat out from the SiO_2 matrix. It would make sense if the condensation reaction reversed and produced SiO-gas when a mix of Si and SiO_2 was heated, but this did not happen. This behavior during heating is an indicator that the separation of silicon from the condensate can be a substantial contributor to the overall silicon production in an industrial furnace.

Tangstad [7] has in a case study found that the silicon production from the low temperature zone through separation of the condensate is between 5 and 15 % of the total silicon production.

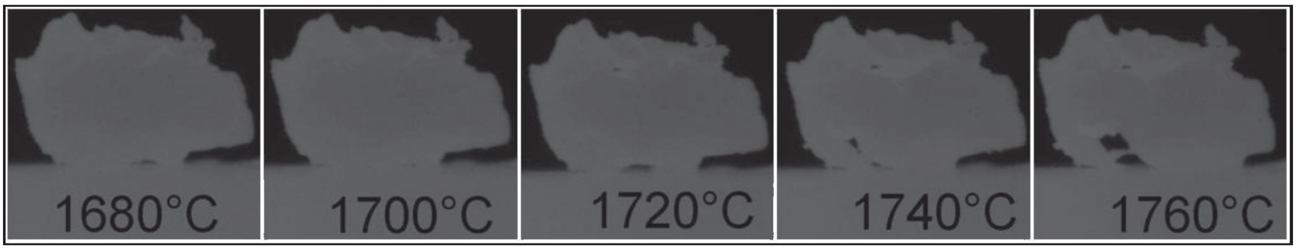

Figure 8: Heating of condensate ($Si + SiO_2$) in a sessile drop furnace

Schei et al [1] described the crust formation as a problem in the metallurgical silicon process. Condensate can grow if the furnace stoking is not performed correctly and thus create a sticky and sintered mix of materials. This will reduce the permeability of the charge closer to the furnace creating a passive volume. To indicate the strength of this crust, explosives are often necessary to break it down.

Compression tests were conducted on the material in the cavity roof. The samples did not consist of epoxy, but were only made up of the material exposed to the environment inside the crucible. The tests showed that the samples exposed to low temperatures ($T < 1670$ °C) had higher compression strength than those exposed to higher temperatures ($T > 1670$ °C) as shown in figure 9 and 10. The average compressive strength of the material exposed to $T < 1670$ °C was ~396 MPa while it was ~115 MPa for the material exposed to higher temperatures. To compare, regular Portland cement has a compressive strength of ~40 MPa. The quartz had begun to melt at the higher temperatures, as well as less condensate had been deposited. This may explain the difference of compressive strength between the two temperature regions.

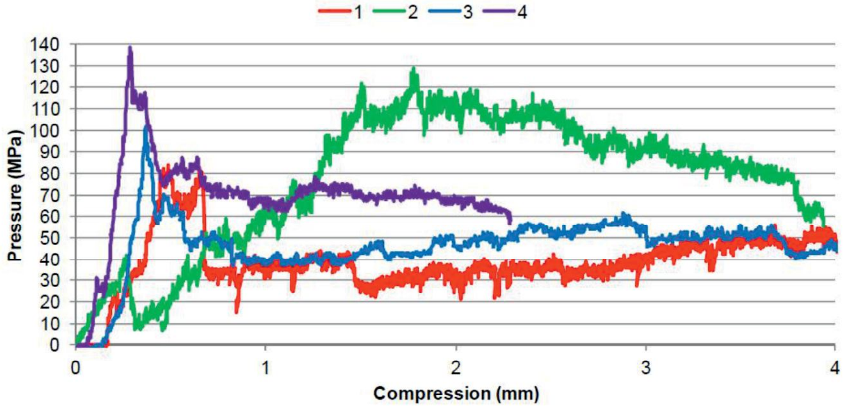

Figure 9: Compression tests of samples exposed to T>1670 °C

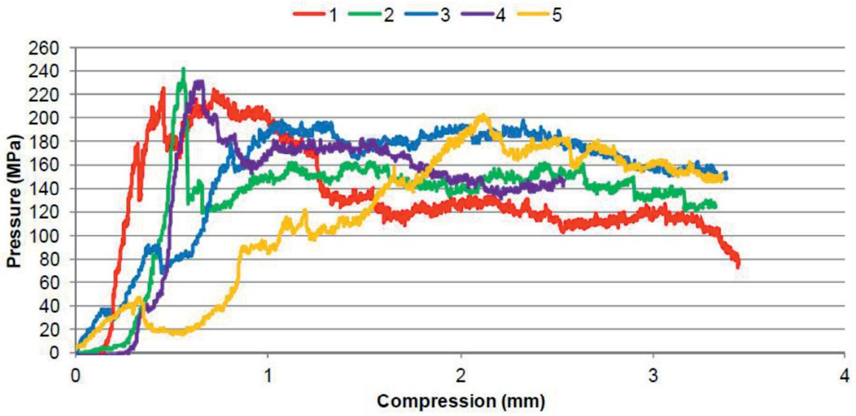

Figure 10: Compression tests of samples exposed to T<1670 °C

CONCLUSIONS

- The formation of brown condensate ($SiO_2 + Si$) occurred below ~1680 °C
- During heating of the brown condensate, the condensation reaction (3rev) did not go in the reverse direction. Instead the silicon metal separated from the SiO_2 matrix at temperatures around 1700 °C.
- The separation of silicon from the condensate during heating is probably an important silicon-producing mechanism.
- The compressive strength of the material glued together by the condensate can be as high as ~400 Mpa.

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