QUARTZ AND CARBON BLACK PELLETS FOR SILICON PRODUCTION

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ABSTRACT

In the commercial process of producing Si and Si alloys, carbon materials like charcoal, coal and wood chips are used as carbon material. Silicon is reduced by carbothermic reduction of SiO_2 following the ideal reaction of SiO_2 + 2C =Si + 2CO. Norway has huge reserves of natural gas. Natural gas also releases less CO_2 than traditional carbonaceous materials. In this project natural gas will be introduced to the Si production process as a raw material. Carbon black, obtained from natural gas cracking, will deposit on pelletized quartz and will be used as a substitute for quartz and carbon materials in the silicon furnace. The current work aims at describing the reaction mechanisms and kinetics occurring in the pellets during heating and reduction. Quartz powder is agglomerated (size, 1–3 mm) and then filled with carbon black from decomposition of methane. During the decomposition, the pellets expanded, and hence the porosity increased. Carbon black is decomposed as two types: (a) cover on the surface of quartz particle; (b) threads and clusters. During heating, the sessile drop test proved that gas generated according to reaction SiO_2 (s,l) + C (s) = SiO (g) + CO (g). Quartz transformed to the cristobalite phase and minor amounts of SiC was also produced after TGA experiments. The reaction during heating can be divided into three distinct temperature steps which are: a) Almost no reaction before 1500°C, b) A high weight loss from 1500 to 1600-1650°C, c) The reaction speed becomes slow again during the constant temperature stage. The value of the activation energy for reaction between SiO_2 and carbon black is found to be higher than the reaction between SiO_2 and SiC, whereas the activation energy at constant temperature is close to SiO_2 and SiC reaction.

1 INTRODUCTION

Industrial silicon is produced by the reduction reaction of quartzite or quartz with means of carbon materials in a submerged arc furnace (SAF) using carbon electrodes [1]. Generally, the carbothermic process could be described simply as follows.

$$SiO_2 + 2\,C = Si + 2\,CO \quad (1)$$

In the furnace [2], raw materials of silica and carbon materials react over the temperature range from 1300°C to over 2000°C. The furnace can be divided into two parts, the outer zone, which is the lower temperature part, and the inner zone, which refers to the hottest part. The silicon producing reaction appears around the electrodes with temperatures over 2000°C in the inner zone of the furnace according to reaction (2). Silicon monoxide and carbon monoxide are also produced in the inner zone according to reactions 3 and 4.

$$SiC(s) + SiO(g) = 2\,Si(l) + CO(g) \quad (2)$$

$$SiO_2(s, l) + Si\,(l) = 2\,SiO\,(g) \quad (3)$$

$$2SiO_2(s, l) + SiC(s) = 3\,SiO(g) + CO(g) \quad (4)$$

When SiO and CO gas flow upwards through the charge layer where the temperature is around 1500°C, SiO will reacts with carbon materials in charge according to reaction (5). In this reaction, free carbon in outer zone captures SiO gas from inner zone, transfers it to SiC and take the silicon back to the inner zone with charge materials. The SiO content of the gas and the ability of carbon to react with SiO-gas affect this process. At temperature below 1500°C, condensation happens according to reaction (6) and (8) (reversed reaction (3) and (4)). These reactions contribute to higher Si recovery even though these reactions are limited by the heat capacity and temperature of charge materials. When quartz powder and carbon materials is in intimate contact in an agglomerate, reaction (7) may happen at the temperature above 1500°C in outer zone.

$$SiO(g) + 2\,C(s) = SiC(s) + CO(g) \quad (5)$$

$$2\,SiO(g) = SiO_2(s,l) + Si(l) \quad (6)$$

$$SiO_2(s) + 3\,C(s) = SiC(s) + 2\,CO(g) \quad (7)$$

$$3\,SiO(s) + CO\,(g) = 2\,SiO_2(s,l) + SiC(s) \quad (8)$$

The main reductant materials in the silicon process are coal, coke/char, petrol coke, wood chips and charcoal [3, 4]. The first three listed above can be classified as fossil carbon materials and the rest are sorted as biological materials. The carbon materials mixed in the charge are determined by availability of materials, process parameters and the desired purity of produced metal. Coke/char, petrol coke and charcoal is produced at higher temperatures. The production

temperature is ranging from 300~1000°C and the production process will both consume energy and emit CO_2. Carbon black (CB) can hence substitute these materials. In this research, carbon black, obtained from natural gas cracking (according to reaction (9)), and pelletized quartz will be used as a substitute for quartz and carbon materials in the silicon furnace.

$$CH_4\,(g) = C(s) + 2\,H_2\,(g) \quad (9)$$

The reactions between SiO_2 and carbon black, and the reaction involving carbon black and SiO gas will be the main subject. Many studies have been conducted on the reactions SiO_2/C and C/SiO gas. Wiik [5] studied the reactions between solid silica and solid carbon at elevated temperature. He found that grain size, container design, carbon to SiO_2 ratio, temperature, quality of carbon material, gas pressure and total mass of charge affects the thermodynamics and the kinetics. The reaction step was believed to be as described in the following reactions:

$$SiO_2\,(s) + CO\,(g) = SiO\,(g) + CO_2\,(g) \quad (10)$$

$$CO_2\,(g) + C\,(s) = 2\,CO\,(g) \quad (11)$$

The overall reaction of reactions (10) and (11) is

$$SiO_2\,(s,l) + C\,(s) = SiO\,(g) + CO\,(g) \quad (12)$$

Ksiazek et al. [6] studied the reduction of silica by use of natural gas directly. Cracking of methane occurred and the solid carbon deposited on the edge and inside the quartz particles. Two different kinds of SiC were produced during the experiment at 1400°C and 1500°C. At 1400°C and 1500°C compacted-needle-shape SiC around SiO_2 particles was found. Another kind of SiC formation inside of the quartz particles was observed mostly at 1500°C . It occurs inside a quartz particle far from its edge with a different shape than SiC found outside of particles. Lee and Cutler [7] investigated the kinetics of reduction of silica present in the rice husks in different CO atmospheres. They also found that the reaction between silica and carbon proceeds *via* the gas phase. Agrarwal and Pal [8] studied the influence of pellet composition and structure on carbothermic reduction of silica. It was found that carbothermic reduction of silica at temperatures above 1773K is a composite reaction, and the possible mechanism involves the following three gas solid reactions (5), (11) and (12). The reaction rate is controlled by the combination of silica reduction reaction and the Boudouard reaction.

The aim of present investigation is:

(a) Characterization of the pellets through porosity measurements, XRD and SEM investigations. This also includes comparing the difference of pellets before and after carbon black deposition.

(b) Investigate the reaction kinetics occurring in the carbon black deposited pellets during heating and reduction. The mechanism of carbon black with quartz at high temperature will be evaluated using these pellets.

2 EXPERIMENTS AND METHODS

2.1 Work flow

Figure 1 shows the work flow of this paper. Quartz pellet was first prepared. Next, the carbon black (CB) deposited pellet (F1 and F2) were produced at different temperatures. In this paper the decomposition of carbon was done at 700 °C (F1) and 900 °C (F2). Behaviour of sample F1 and F2 at higher temperatures were studied by sessile drop and TGA. SEM, porosity test and XRD were used to investigate the properties of pellets from each step.

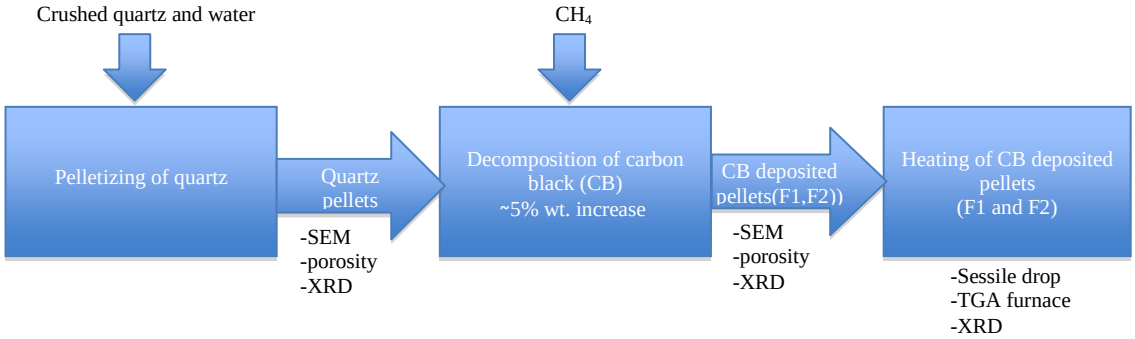


Figure 1: Overall work flow

2.2 Decomposition of carbon black

Agglomerated quartz pellet are used in this research. Figure 2 shows the crucible used for depositing the carbon black to the agglomerated quartz pellet. The process procedure was to charge the crucible with about 40g agglomerated quartz pellets, and then heat it to experimental temperature in inert atmosphere. It was applied 100% methane gas flow at 0.5 liters per minute (gas inlet in bottom of crucible). A stable temperature was maintained at fixed holding times. The crucible with pellets was cooled down in inert atmosphere. In the two experiments performed, the deposition tem-

perature was set to 700°C and 900°C. Samples of these two carbon black deposited pellets are named F1 and F2, respectively.

After the carbon black deposition, initial yellow-brown pellets became black, and the weight and volume of pellets increased. Weight increase of sample F1 and F2 is 5.48% and 4.89% respectively (Table 1). The volume expansion of F1 is three times of F2.

Table 1: Data of carbon black deposition process

Sample	Temp (°C)	Weight initial (g)	Weight increase (%)	Expansion (%)
F1	700	40	5.48	60
F2	900	39.45	4.89	20

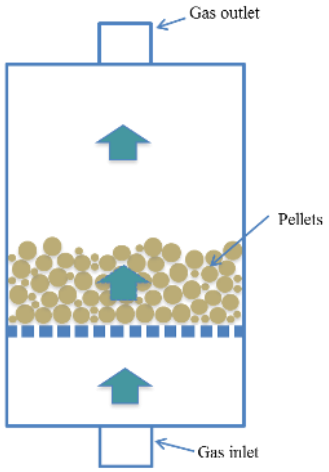


Figure 2: Schematic drawing of carbon black deposition process

According to table 1, the weight of the pellets increased about 5% during the decomposition step, that is, about 5% carbon black has been decomposed on the quartz pellets. This is confirmed by XRD, where carbon is found in F1 and F2 as shown in Figure 3.

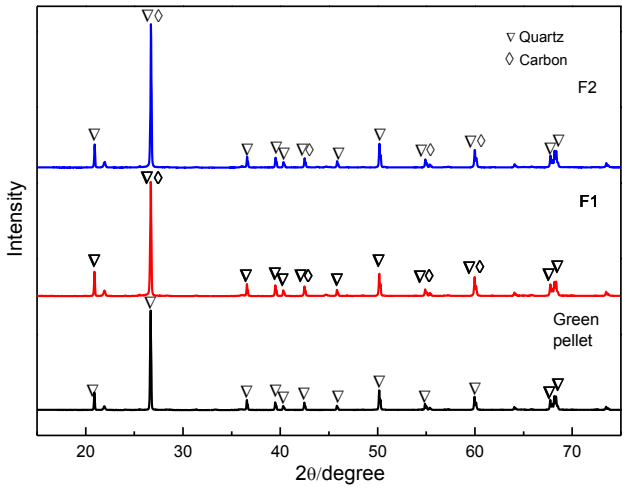


Figure 3: X-ray diffractometer pattern of quartz pellets, F1 and F2

The porosity of pellet is obtained by:

$$Porosity = \left[1 - \frac{apparent\ \ density}{absolute\ \ density}\right] \cdot 100\% \quad (13)$$

The apparent density of the particle is determined using a GeoPyc 1360 Pycnometer, which uses fine sand to determine the volume of the particle. The sand will encapsulate the particle but not penetrate it. The absolute density was determined using an AccuPyc 1330 Helium Pycnometer. The helium is able to penetrate the particle and fill the pores.

According to porosity test (table 2), the porosity of sample F1 and F2 is higher than that of the original quartz pellets, when no carbon black is deposited. The porosity increase in sample F1 is higher than that in sample F2. This explains why the sample F1 is fragile when a small external force is applied on it. The SiO_2 pellets need at least 36.3% porosity to fill up all the voids with carbon black, for a C/SiO_2 molar ratio of 2. Porosity of samples is all over 50%, which is larger than this theoretical calculation, which means more carbon black than needed can be filled in the pores of pellets. Even after the carbon black had filled the pores, the porosity did not decrease. This is due to a larger total volume as well as the fact that only about 5% of carbon was attached to the pellets.

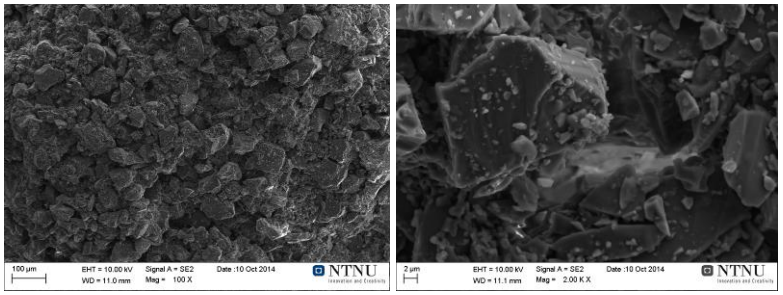
Table 2. Porosity of quartz pellets, F1 and F2

Sample	Preparation Temp(°C)	Porosity (%)
Quartz pellets	-	52.5
F1	700	60.5
F2	900	53.5

The surface and the interface when the particle was cut in half are investigated by SEM. Figure a) and b) in Figure group 4, 5 and 6 are the SEM picture of particle surface of the quartz pellets, F1 and F2. Figure b) and c) in Figure group 4, 5 and 6 show cut surfaces of the particles.

Figure 4 shows that the quartz particles are agglomerated together in the quartz pellets. We can also see the pores inside of quartz pellets, which coincide with the result from porosity test.

The surface and the edge of the quartz particles can't be seen in sample F1 and F2 under lower magnification (Figure 5 and 6). Under higher magnification, we can see that carbon black and carbon filaments growing from quartz surface covered the surface of quartz particle. These carbon filaments look similar to carbon nano-tubes. The carbon black does not cover the surface uniformly when Figure 4 b and Figure 6 b is compared. SEM images of sample F2 are quite similar with F1 under lower magnification. Carbon fiber of F2 is not as long as F1, which makes F1 looks more similar to threads and clusters. This further confirms why particles of F1 have higher porosity and are more fragile compared to F2.

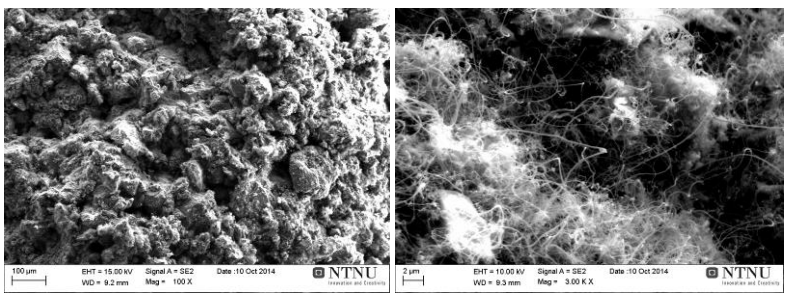


a)100x b)500x

c) 30x d)100x

Figure 4: SEM images of quartz pellets.

a) and b) are surface images and c) and d) through cut pellets.



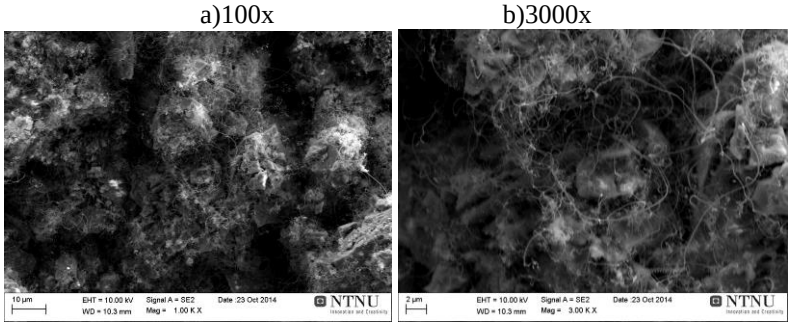


Figure 5: SEM images of sample F1.
a) and b) are surface images and c) and d) through cut pellets.

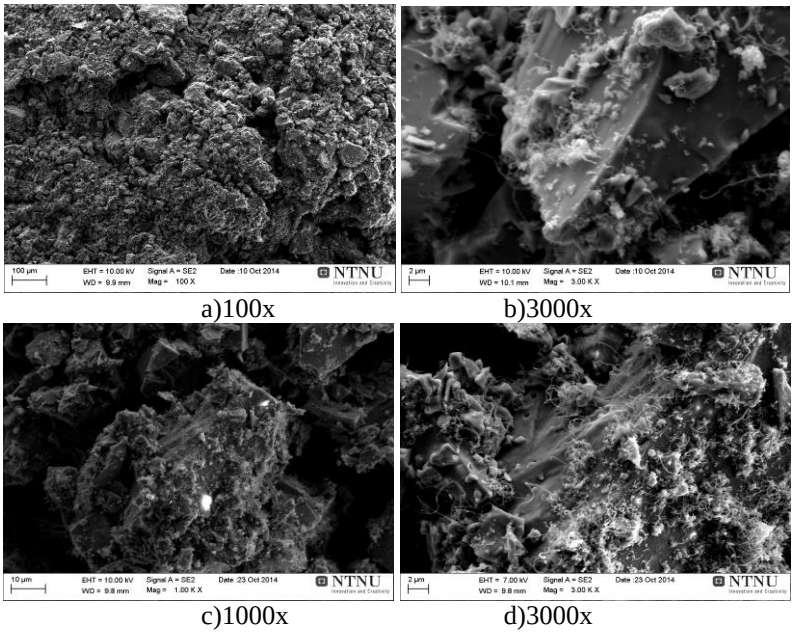


Figure 6: SEM images of sample F2.
a) and b) are surface images and c) and d) through cut pellets.

2.3 Experiments and methods during thermal behaviour of carbon black pellets

The quartz pellets, F1 and F2 was heated in two furnaces to investigate the behaviour during heating, the sessile drop test and the TGA apparatus (Figure 6).

The sessile drop furnace is designed to measure the contact angle of a liquid drop on a 10mm diameter substrate. It is possible to measure the wetting angle of a sessile drop, observe the melting point of substances and investigate the reactivity between different materials. A firewire digital video camera with a telecentric lens was used to record images from the furnace at a resolution of 1280 x 960 with a ½″CCD sensor. The telecentric lens is able to produce an image from 40 to 3.3mm across the frame, which at maximum magnification is equivalent to 2.5μm per pixel. During the experiments, furnace chamber was vacuumed at first, and then continuously purged with 0.5 Nl/min of argon. The quartz pellet was heated at 300°C/min to 950°C, then 50°C/min 1550°C and finally at 10°C/min until the pellet was melted. The samples F1 and F2 were heated at 300°C/min to 950°C, then 50°C/min 1750°C and finally at 10°C/min to 1830°C and held for 5 minutes.

All the TGA experiments were carried out using TF1 thermo-gravimetry furnace with 5 mL/min CO gas flow. High-purity α-Al_2O_3 crucible was used as inner crucibles. About 5g of pellets were used in each experiment. Two series of experiments were designed. We assumed that reaction: $SiO_2 + 2C = Si + 2CO$ occurs during the TGA experiments. This means that when weight loss is 10%, approximately 5% carbon black in sample F1 and F2 is consumed. The first experiments, a series of two experiments, were designed to investigate the pellets' behaviour at a weight loss of 10%. The pellets were heated to 1500°C with a rate of 25°C/min, and subsequently at 15°C/min to 1700°C, and the experiment was then stopped at 10% of weight loss. The second series of experiments was designed to investigate the pellets' behaviour when temperature was held at 1600°C and 1650°C. The heating rate was 25°C/min up to holding temperature. The cooling time of each experiment from highest temperature to 1000°C took about 6 minutes.

Phase structure of the pellets was determined by X-ray diffraction (XRD, Bruker AXS D8 Advance diffractometric with Cu Kα1 radiation). The morphology samples were investigated by field-emission scanning electron microscopy (LVFESEM, Zeiss Supra 55VP) with energy-dispersive X-ray spectrometers (EDX).

3 RESULTS AND DISCUSSION

3.1 Sessile drop test

In the sessile drop test the pellets were heated continuously while photographed on a graphite substrate. The area ratio (S/S_0) of pellets in photos is used to signify the volume changes when pellets were heated. Figure 7-10 shows the visual picture of quartz-pellets and quartz pellets with carbon black (F1 and F2) during heating. According to Figure 7 - 10, nearly no change occurs to the three pellets before 1575°C. For the quartz pellet, the volume of particle starts to expand (Figure 7) at increasing temperature. When the temperature is above approx. 1700°C, quartz started to melt. The melted quartz filled the pores inside the pellet, and then the volume of the pellet starts to shrink. After 1750°C, there was no significant change in volume, while more and more quartz melted. The pellet tends to be a standard sphere. At the temperature of 1810°C, the pellet became complete spherical in shape with smooth surface as shown in Figure 10 a.

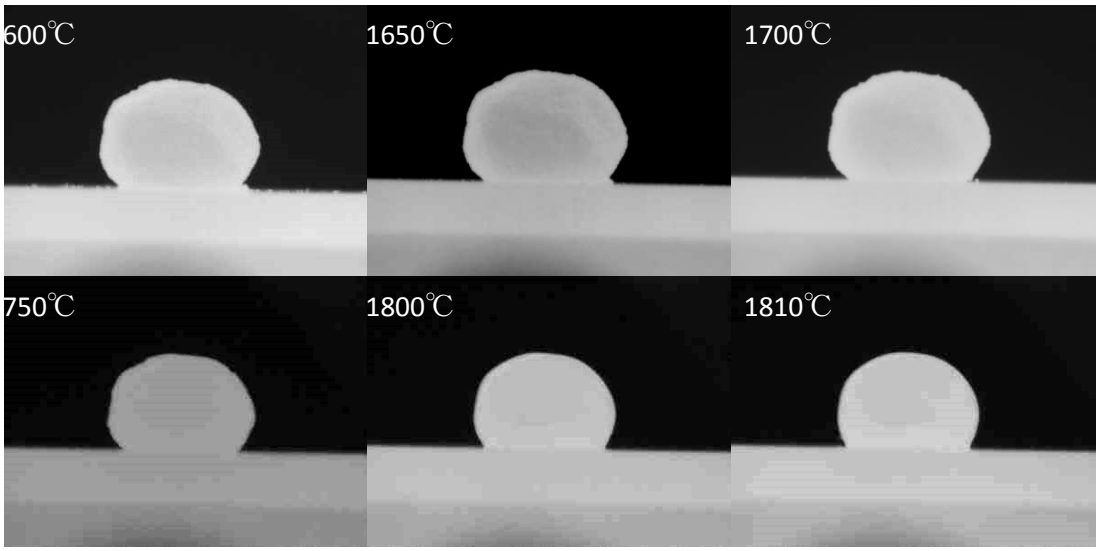


Figure 7: Quartz pellet heated from 1600°C to 1810°C

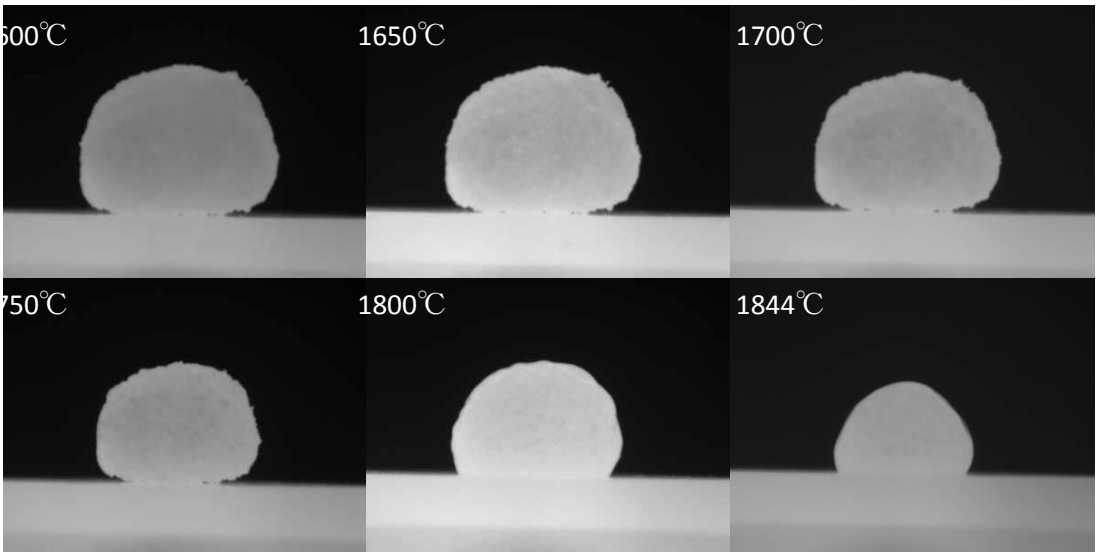


Figure 8: Pellet of Sample F1 heated from 1600°C to 1844°C

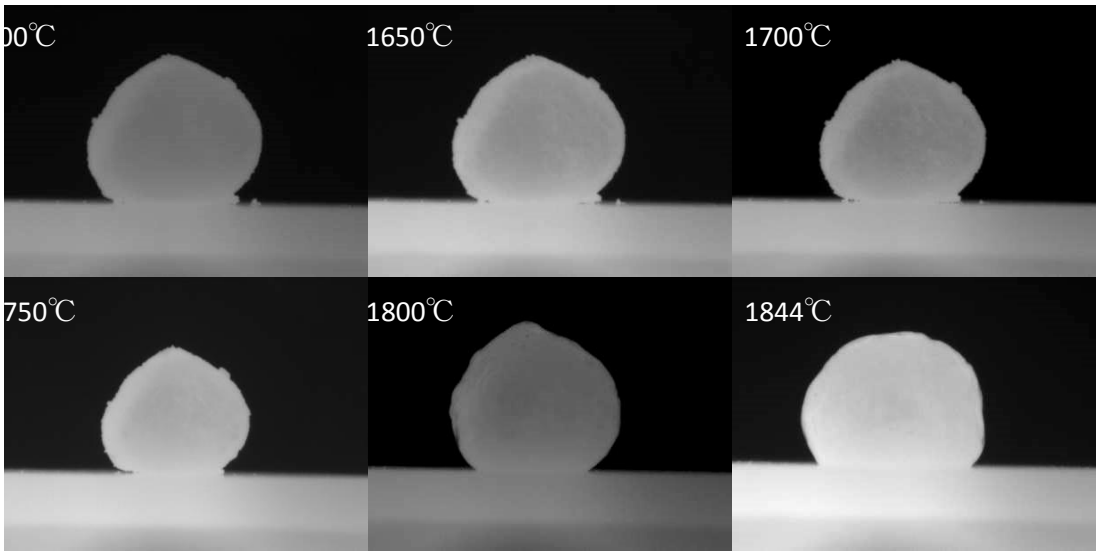
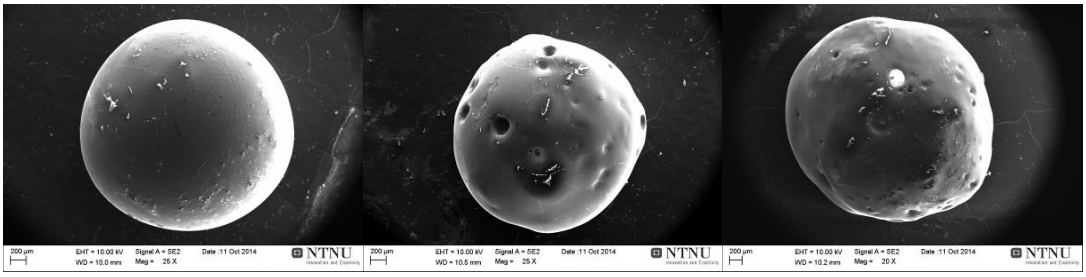


Figure 9: Pellet of Sample F2 heated from 1600°C to 1844°C



a) b) c)

Figure 10: Surface of sample quartz pellets, F1 and F2 after sessile drop test.
a), b) and c) are surface of quartz pellet, F1 and F2 respectively.

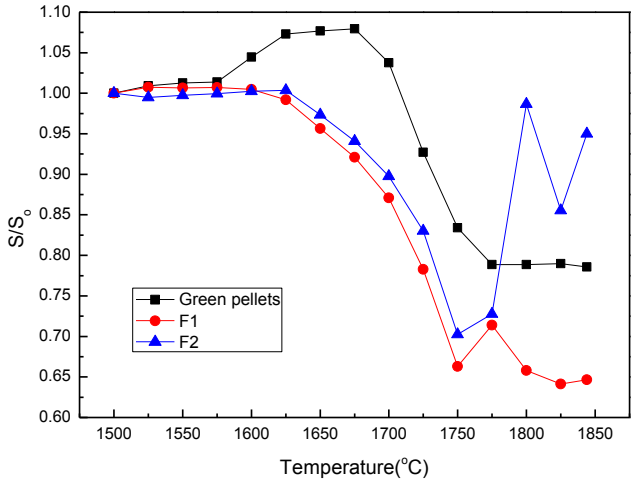


Figure 11: S/S_0 ratio change of pellets during sessile drop test

The sample F1 started to shrink when temperature was higher than approx.1650°C. When temperature is higher than 1700°C, the volume decreased dramatically. As the temperature was increased to 1750°C, the pellet expanded followed by shrinkage. The cavities on the pellets surface left by gas when the sample is cooled down is shown in Figure 10 b. Sample F2 behaves quite similar with temperature , but the volume of pellet didn't shrink in the same manner. The cavities of the cooled down sample is smaller than F1.

3.2 TGA Experiments

Experiments were performed in the TGA furnace. The first series was at increasing temperature and the second was at constant temperature. The first series of experiments was stopped when the weight loss of pellets reached about 10%. For sample F1, the temperature was 1646.7°C when the weight loss reached 10.75%. Sample F2 was heated to 1700°C and after 10.1 minutes the weight loss reached 10.12%. In the second series, samples F1 and F2 were heated to 1600°C and 1650°C, respectively, and held for a certain time to obtain about 10%. The weight loss of experiments for samples F1 and F2 were 11.56% and 10.34%, respectively, at 1600°C. The weight loss of experiments where samples F1 and F2 were heated to 1650°C was 15.57% and 11.61% respectively. This indicates that higher temperature provides favourable conditions for the reactions, as should be expected.

After cooling, the samples were studied by XRD. Two things took place during the TGA experiments according the X-ray diffraction analysis (Figure 12). The first is the phase transformation. After the experiments, quartz in the two samples was transformed from trigonal crystal system to its polymorph, cristobalite with tetragonal crystal system. No other quartz group structures are found. This transformation takes place when temperature is above 1400°C and the rates of quartz/cristobalite transformation and of amorphous silica formation vary with quartz source [9].

The possible reactions between SiO_2 and C are 1) $SiO_2+2C=Si+2CO$ (reaction 1), $SiO_2+3C=SiC+2CO$ (reaction 7) and $SiO_2+C=SiO+CO$ (reaction 12). Though reaction (7) is thermodynamically possible in CO gas, only minor quantities of SiC were found as seen in Figure 12, and hence it is believed that reaction (12) is the main reaction in both the TGA and the sessile drop tests.

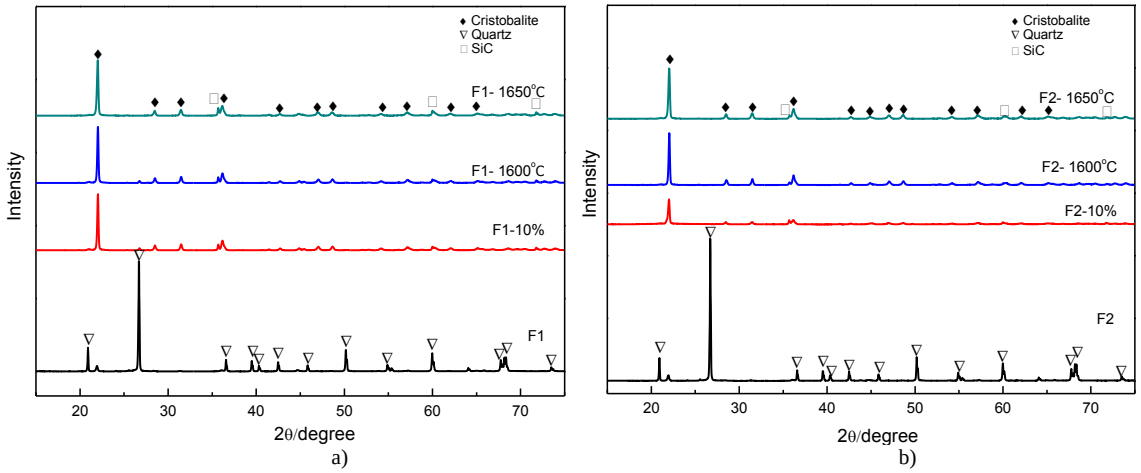


Figure 12: X-ray diffractometer patterns of F1 and F2 after TGA experiments compared with patterns before TGA experiments. a) samples of F1, b) samples of F2.

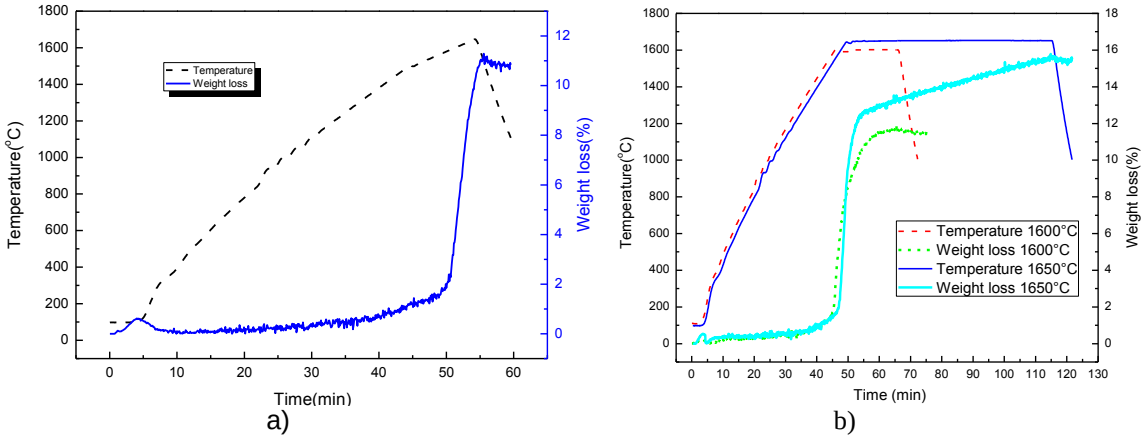


Figure 13: Weight loss and temperature profile for F1.
a) %weight loss and temperature for experiment at increasing temperature to 10% weight loss
b) %weight loss and temperature at constant temperature.

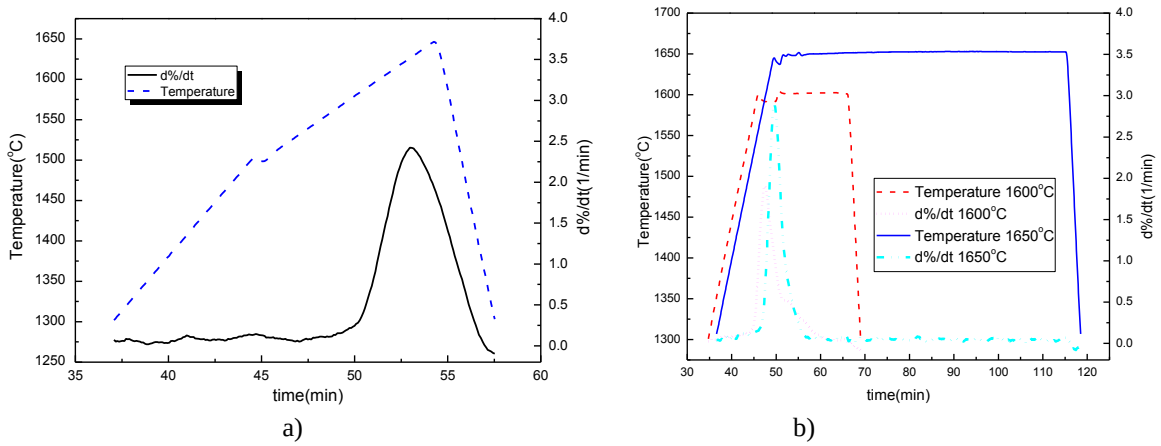


Figure 14: d%/dt and temperature profile for F1.
a) d%/dt and temperature for experiment at increasing temperature to 10% weight loss
b) d%/dt and temperature at constant temperature.

The TG and DTG curves of the experiments are shown in Figure 13-16. The reaction process can be divided into three different steps, as shown in the figures. When temperature was below 1500°C, almost no reaction took place. With the increasing temperature, weight loss of samples is increasing slowly to 1600°C. Weight loss of all six experiments before 1600°C was less than 5.1%. This may be caused by some slow solid-solid/gas-solid reactions. When the crucible was heated to approx.1600°C, the weight loss curves become much steeper and the d%/dt of each experiment increased.

In these 6 experiments, the second step lasts up to six minutes. The weight loss also increased 5-6 times of its value at the beginning of the first step. The reaction speed slows down after the second step, in the constant temperature area (Figure 14 and 16). This may attribute by either that the carbon present is consumed or a SiC layer formed on the surface of the pellets, which makes mass transfer slow.

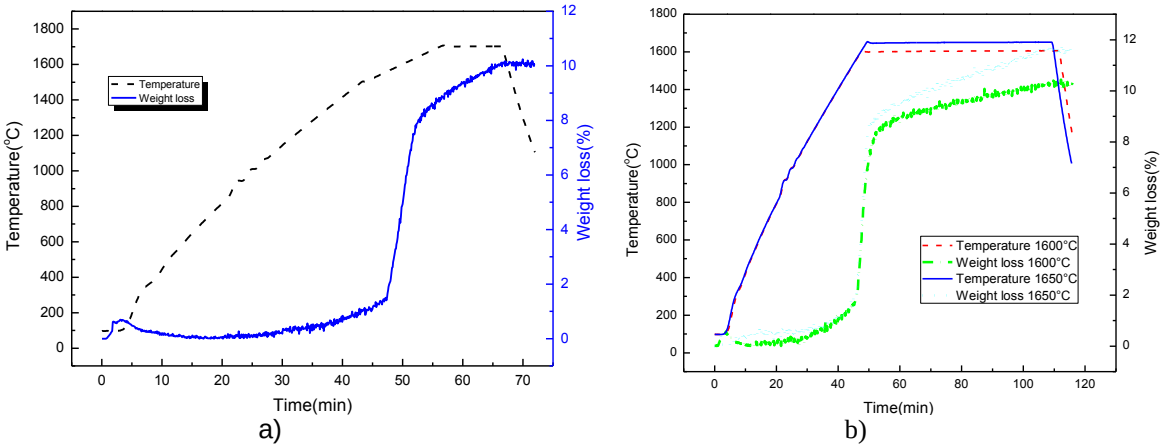


Figure 15: Weight loss and temperature profile for F2.
a) %weight loss and temperature for experiment at increasing temperature to 10% weight loss
b) %weight loss and temperature at constant temperature.

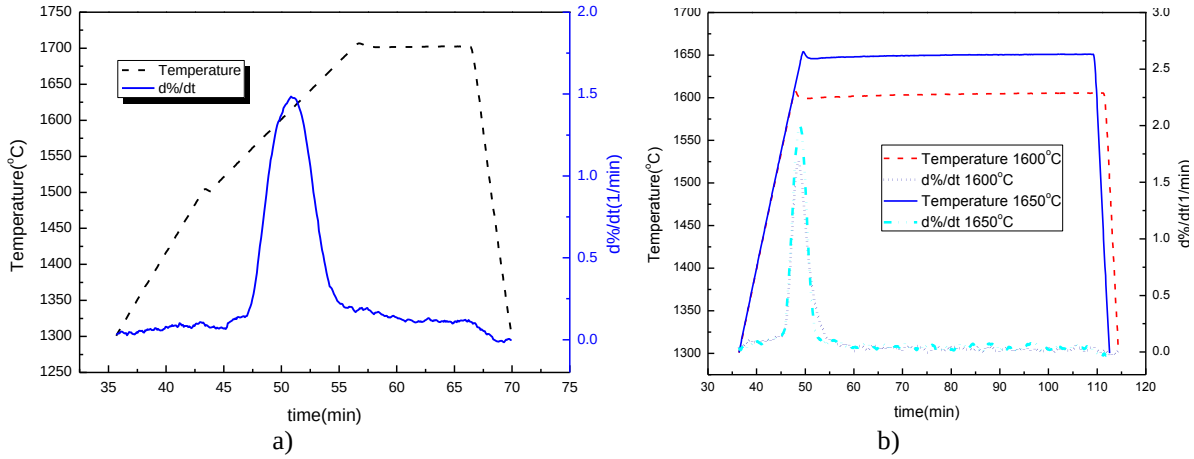


Figure 16: d%/dt and temperature profile for F2.
a) d%/dt and temperature for experiment at increasing temperature to 10% weight loss
b) d%/dt and temperature at constant temperature.

The rate of the reaction in a pellet may be expressed by reaction (13), consisting of a geometrical function f(%) and a temperature dependent term. The activation energy, E, of the second reaction step is calculated by the following kinetic equation [10] (R is the gas constant and the T is the temperature in Kelvin):

$$\frac{d\%}{dt} = f(\%) \cdot \exp\left(-\frac{E}{RT}\right) \tag{13}$$

By assuming that the f(%), the geometrical function, is constant in two consecutive time steps, the activation energy can be calculated:

$$E = -R\left[\frac{\ln\left[\frac{d\%}{dt}\right]_n - \ln\left[\frac{d\%}{dt}\right]_{n+1}}{\frac{1}{T_n} - \frac{1}{T_{n+1}}}\right] \tag{14}$$

The activation energy can be shown in Figure 17 versus temperature for the six TGA experiments using time steps of 120 s. With the increasing temperature, activation energy increased accordingly. This was not expected, as the activation energy is a constant term. For experiments stopped at the weight loss ratio 10%, the curves have two peaks, which may be caused by different heating rate. The peak value of each experiment is higher than 800kJ/mole. For experiments stopped at the weight loss ratio of 10%, the second peak value is higher than the first one. This indicates that

the slower heating rate may produce higher activation energy. The value of activation energy in this research are also higher than the activation energy of reaction between SiO_2 and SiC as it was reported to be less than 500 kJ/mole[11].

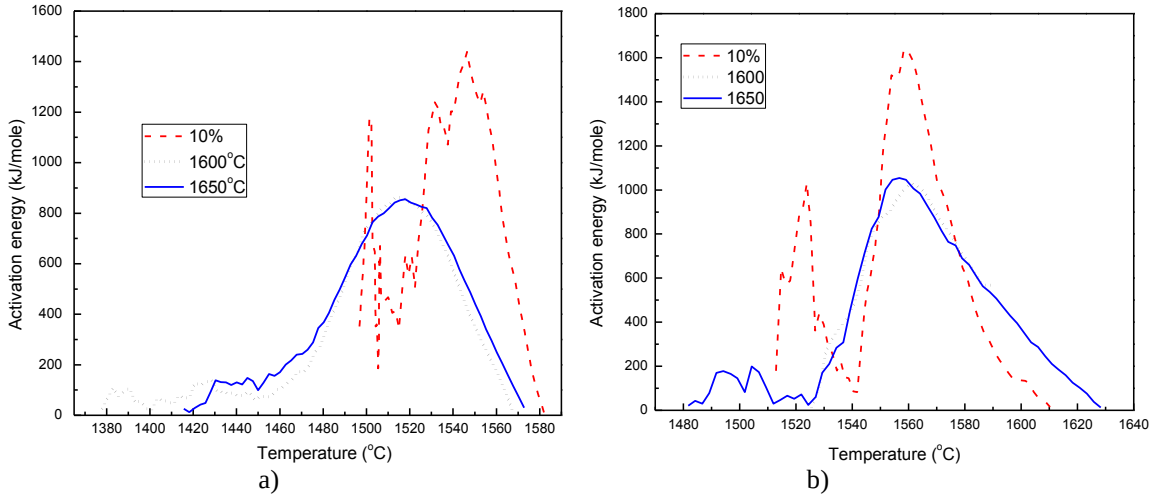


Figure 17: Activation energy versus temperature
a) F1, b) F2

Friedman method [12] was also used to calculate the activation energy of experiment F2-1600°C and F2-1650°C. The average activation energy of this stage is 346 kJ/mole, which is quite close to SiO_2 + SiC calculation by Andersen [11]. In the second step, the main reaction may be this solid-solid reaction.

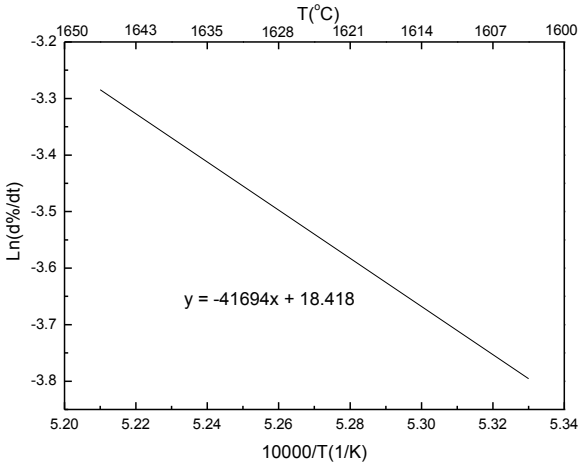


Figure 18: Logarithm of the reaction rate versus 1000/T at constant temperature of experiment F2-1600°C and F2-1650°C

4 CONCLUSIONS

Carbonaceous materials are one of the key input parameter in the silicon production process. The behaviour of pelletized quartz and carbon black in outer reaction zone of silicon furnace is the focus in this research. The main conclusions from the present work are as follows:

(1) The porosity of samples increased after deposited with carbon black. There is more than enough room to get enough carbon black in the pores of pellets for the reaction SiO_2+2C=Si+2CO.

(2) Carbon black in pellets is present as two types: a) cover on the surface of quartz particle; b) threads and clusters.

(3) Though minor amounts of SiC was found after heating, it is believed that the main reaction is SiO_2 (s,l) + C (s) = SiO (g) + CO (g).

(4) During the TGA experiments, quartz transformed to the cristobalite phase.

(5) When the pellets were heated, the reaction can be divided into three steps which are: a) Almost no reaction before 1500°C, b) A high weight loss from 1500 to 1600-1650°C, c) The reaction speed becomes slow again during the constant temperature stage. Activation energy of about 800 kJ/mole is found in the reaction during the fast reaction step. The activation energy for the reaction between SiO_2 and carbon black is found to be higher than the reaction between

SiO_2 and SiC. The activation energy in the following slow step is 346 kJ/mole, which is close to the activation energy for the SiO_2 and SiC reaction.

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