

Chemistry of the Si–O–C system

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The only abundant natural sources of silicon are silicon dioxide or silicates, which can be derivatives of silicon dioxide. This chapter considers the reactions that are important in the reduction of silicon dioxide to silicon by carbon. The chemical compounds and the phase relations are first outlined, followed by a discussion of equilibria and the reaction kinetics of the main reactions.

2.1 Species in the system

Figure 2.1 provides a graphical survey of the species in the ternary Si–O–C system. There are no commonly accepted ternary compounds in the system.

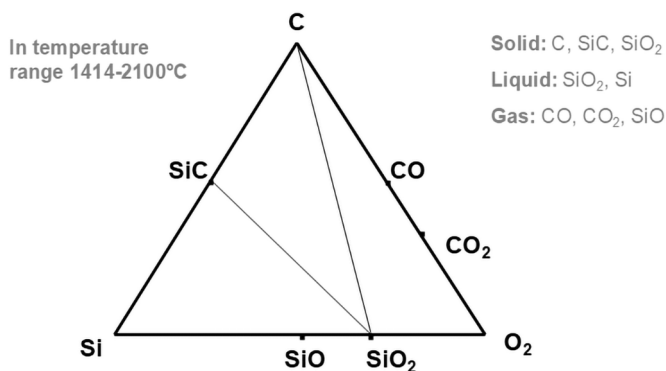


Figure 2.1 Schematic diagram of the phase relations in the Si–O–C system.

Silicon

The melting point of silicon is reported as $1412 \pm 2^\circ\text{C}$ (Yaws *et al.*, 1981), but several values in the range $1400\text{--}1420^\circ\text{C}$ have been suggested in various papers. Silicon is a semiconductor in the solid state, but in the liquid state it has the same electrical conductivity as a metal.

The content of Si(g) , $\text{Si}_2\text{(g)}$, $\text{Si}_3\text{(g)}$ and $\text{Si}_4\text{(g)}$ above liquid silicon is low. The vapour pressures are $5 \cdot 10^{-4}$, $1 \cdot 10^{-5}$, $2 \cdot 10^{-6}$, $9 \cdot 10^{-12}$ bar at 2000°C , respectively. These species are important in the evaporation of Si and SiC, but their contents are very low.

Carbon

The stable modification is graphite. It does not melt at 1 bar pressure, but sublimates at about 3500°C . Carbon materials used in the production of high silicon alloys consist of carbon-containing compounds such as coal, coke, charcoal and petroleum coke. Further details are given in the description of raw materials in Chapter 5. It is usually assumed that the thermodynamic properties of the fixed C in these materials are close to the thermodynamic properties of graphite. However, when it comes to the kinetics, that is, the rate of the reactions, this will of course not be the case.

Oxygen

Oxygen is a bimolecular gas, O_2 , that is partly dissociated into atoms at high temperatures. The vapour pressure of free oxygen is very low under the conditions required for SiO_2 reduction. Even so, this vapour pressure is sometimes convenient as a variable in equilibrium calculations.

The Si–C system

The Si–C phase diagram is shown in Figure 2.2. The only stable condensed compound in the Si–C system is SiC, which occurs in several hexagonal polytypes called $\alpha\text{-SiC}$ and one cubic modification called $\beta\text{-SiC}$. According to the JANAF Thermochemical Tables, the cubic $\beta\text{-SiC}$ is more stable than the hexagonal $\alpha\text{-SiC}$ at all temperatures, but the difference is so small that it is unimportant in the equilibrium evaluation of the system (Chase *et al.*, 1985).

According to Scace and Slack (1959), SiC decomposes peritectically at 2830°C, giving a liquid with 19 at % C, as seen in the phase diagram in Figure 2.2a. They investigated the system up to about 3000°C with an overpressure of about 20 bar of argon to suppress the vaporisation of the sample. The solubility was extended tentatively to the melting point of C at a pressure of about 100 bar.

The eutectic temperature is very close to the melting point of pure silicon, as seen in Figure 2.2b. Measured values of the content of carbon in silicon in equilibrium with SiC are shown in Figure 2.3, and the results scatter considerably. Analyses of samples of industrial silicon metal give 100–200 ppmw C after ladle treatment around 1450–1500°C. The solubility at the melting point may be lower than this, but reported values in excess of 200 ppmw must be deemed incorrect due to solid SiC particles being present.

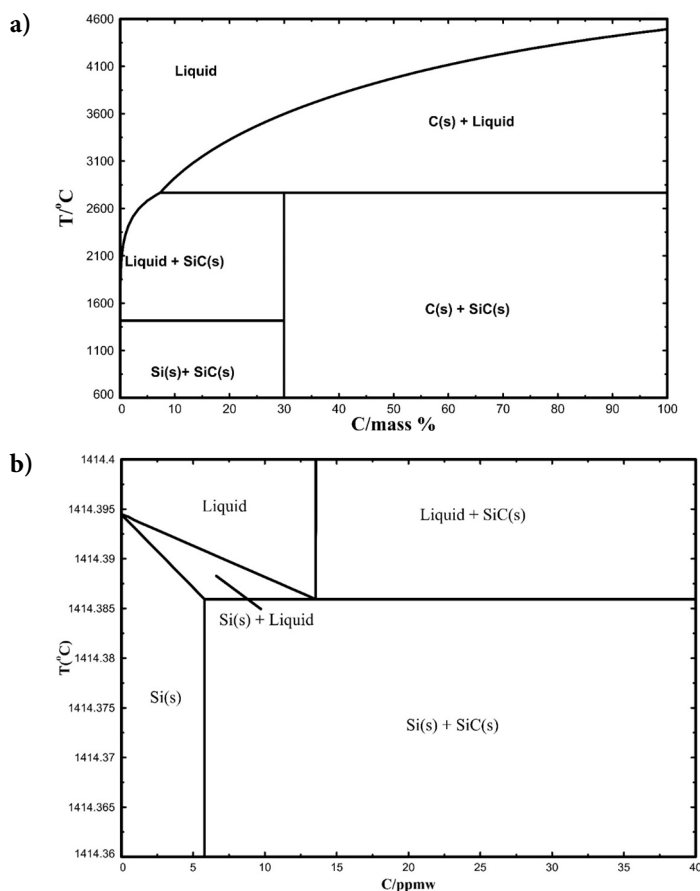


Figure 2.2 a) The Si–C binary phase diagram calculated by the use of FactSage using the FTlite database where b) shows the magnified area at low C levels.

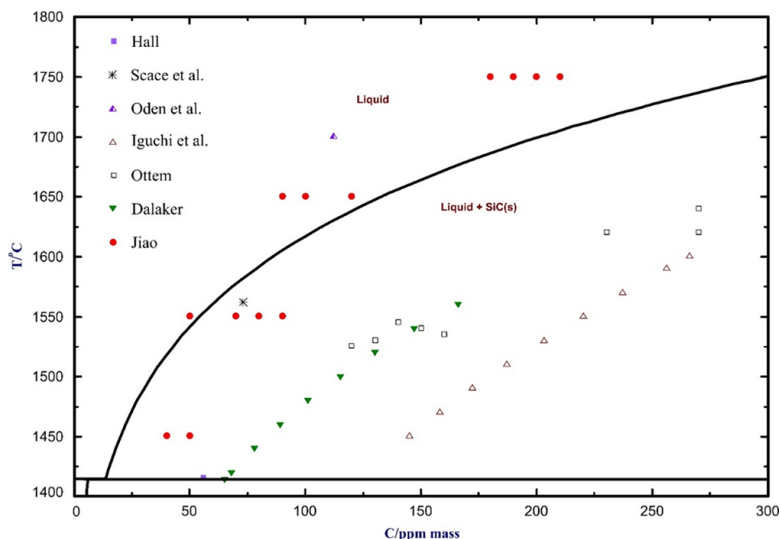


Figure 2.3 The content of C in liquid silicon in equilibrium with SiC summarized by Jiao (Hall, 1958; Scace and Slack, 1959; Oden and McCune, 1987; Iguchi and Narushima, 1993; Ottem, 1993; Dalaker and Tangstad, 2009; Jiao, 2020) [With permission from J.M. Jiao].

The gas species SiC_2 and Si_2C are the most stable binary gas species in this system, with a gas pressure of $2 \cdot 10^{-4}$ and $3 \cdot 10^{-4}$ bar, respectively, at 2000°C (HSC ver. 9.8.1.2).

The Si–O system

There are two stable compounds, SiO_2 and SiO , in the Si–O system. SiO_2 appears in the solid forms quartz, tridymite and cristobalite, all of which have high- and low-temperature modifications. High temperature cristobalite is said to melt at about 1725°C , but, as the heat of melting is low and the resulting melt is very viscous, it is easily undercooled to a glass. A tentative Si– SiO_2 phase diagram is shown in Figure 2.4a. It is correct in principle, but it should not be used quantitatively. It can also be mentioned that Stevens and Hand found that tridymite is not a stable phase in the pure Si–O system and is rarely found in SiO_2 samples excavated from industrial furnaces (Stevens and Hand, 1997). Figure 2.5 shows the oxygen solubility according to FactSage in the high silicon area. Since the ingoing data on oxygen solubility are rather uncertain, the result must be seen only as a tentative diagram (Tang, 2009; Mikkelsen, 1985).

SiO is a gas that is stable at high temperatures, and it is a very important participant in the reactions in the silicon process. It has been claimed that SiO also can exist as a thermodynamically stable solid, but no convincing evidence has been produced.

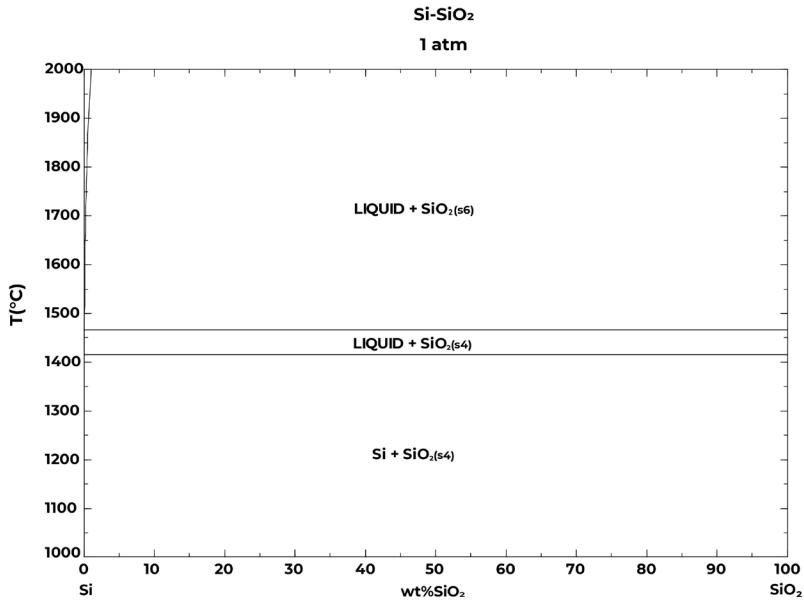


Figure 2.4 *The Si-O phase diagram calculated by FactSage.*

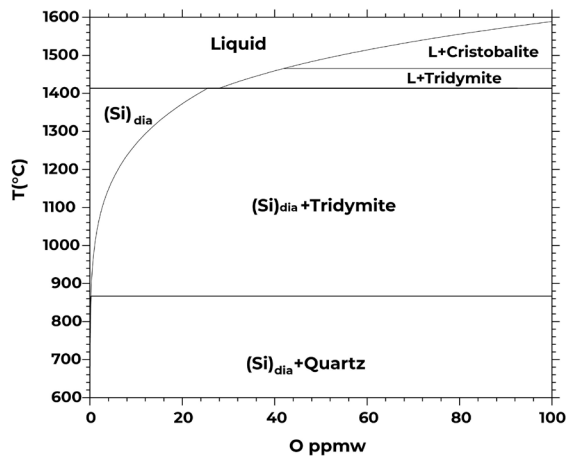


Figure 2.5 *The Si-O phase diagram at low oxygen contents calculated by FactSage.*

The C–O system

The two compounds CO and CO₂ in the system are both gases. In equilibrium with solid carbon, the CO pressure will be close to 1 bar, as shown in Figure 2.6 above 1000°C. In silicon production, one can hence assume a very low CO₂ pressure below the charge level. When FeSi is produced using iron oxides, CO₂ will, however, be produced.

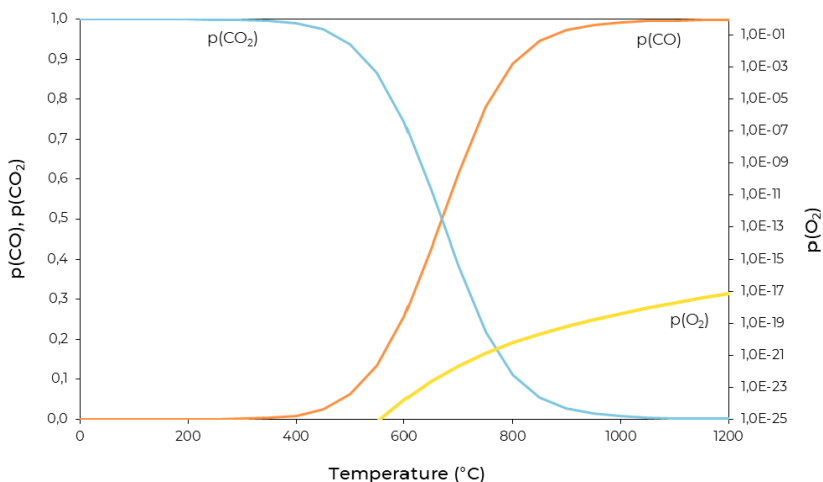


Figure 2.6 CO and CO₂ gas pressures [bar] in equilibrium with solid carbon, versus temperature. The respective oxygen pressure is shown in the secondary axes. (Calculated with HSC ver. 9.8.1.2).

2.2 Equilibria in the system

Equilibrium calculations give the final end-state of a reaction, but they do not indicate the time necessary to reach equilibrium. Some reactions are completed in less than a second, while others may take thousands of years. It is therefore not possible to predict the result of a reaction from equilibrium calculations with certainty. If the equilibrium calculations show that a reaction is possible at a given temperature, the rate may be increased by various means, and a process development may be justified. However,

if the calculation shows that the equilibrium is unfavorable, the reaction will not run even with very reactive reactants. Therefore, an estimation of the equilibria gives background understanding of the chemical behavior of the system.

In a reduction furnace there will always be several solid or liquid phases and one gas phase in a reaction zone. Rather than considering specific reactions in the zones, we may regard a zone as a chemical system consisting of a number of phases. The calculation of the equilibria for the interesting phase combinations is given in detail in Appendix A, and the main conclusions will be summarized here. The phase combinations will have a certain equilibrium gas pressure, and this pressure can be used to estimate the reactions of the reduction process. The phase rule for the system gives a relation between the number of phases Ph and the number of degrees of freedom F :

$$Ph + F = 5 \quad [2.1]$$

The number of degrees of freedom gives the number of thermodynamic variables that have to be fixed to determine the system completely. The gas phase is always present in the reduction process, and, for convenience, we can count the number of condensed phases Ph_{cond} , which is one less than Ph . The system has four species SiO_2 , C, SiC and Si that are condensed in the temperature range of the process. The combination $\text{SiO}_2(\text{s})$ – $\text{SiO}_2(\text{l})$ at the melting point of silicon is not of interest in the understanding of the process. The thermodynamic variables of this system are the temperature, the pressure and the composition of the phases. The number of condensed phases thus determines the variables that must be fixed to determine the system completely, as shown in Table 2.1. If we fix all the necessary properties except one, we have a system with one degree of freedom. In the system we can select one property as the free variable and draw graphs of any property as a function of this variable.

Table 2.1 *Thermodynamic variables necessary to determine the system Si–O–C completely.*

Phcond	F	Thermodynamic variables to be fixed to determine the system
1	3	Temperature, total pressure, partial pressure of one gas species
2	2	Temperature, total pressure or
		Temperature, partial pressure of one gas species or
		Pressure, partial pressure of one gas species or
3	1	Temperature or
		Total pressure or
		Partial pressure of one gas species
4	0	None

With the simultaneous presence of the four condensed phases SiO_2 , C, SiC and Si, the system is completely determined. This means that the total pressure, the gas composition and the temperature are all given. Extrapolating the thermochemical calculation with the species present around 2000°C shows that the coexistence temperature must be higher than 2700°C , and the pressure more than 2000 bar. At this temperature, the solubility of C in Si is very high, and the species SiC dissociates peritectically. Therefore, there is no justification for extending the extrapolation to higher temperatures. In any case, the temperature and pressure are far outside the range that is interesting in the study of the silicon production furnace.

For three condensed phases, the system is completely determined when the temperature, the pressure, or the content of one gas component is determined. For our purposes, the temperature is selected as the free variable. The system has four possible combinations of the condensed phases SiO_2 , C, SiC and Si, but two combinations are unstable because they contain C and Si, which will react to form SiC according to reaction [2.2].



This reaction is displaced to the right for all temperatures up to the peritectic point of Figure 2.2. The gas pressures for the remaining stable combinations are given as functions of the temperature in Figure 2.7 and Figure 2.8. The gas species CO_2 , Si, Si_2C and SiC_2 have been included in the calculation, but their partial pressures fall outside the graphs. The figures show fixed points where the total pressure of each combination is equal to an ambient atmosphere of 1 bar. These points are at about 1520°C and 1800°C for the $\text{C-SiO}_2\text{-SiC}$ and $\text{Si-SiO}_2\text{-SiC}$ systems, respectively, depending on the database used. These fixed points have also been determined experimentally.

System $\text{SiO}_2\text{-SiC-C}$ (Rein and Chipman, 1963) 1533°C

System $\text{SiO}_2\text{-SiC-Si}$ (Gjerstad, 1968) 1819°C

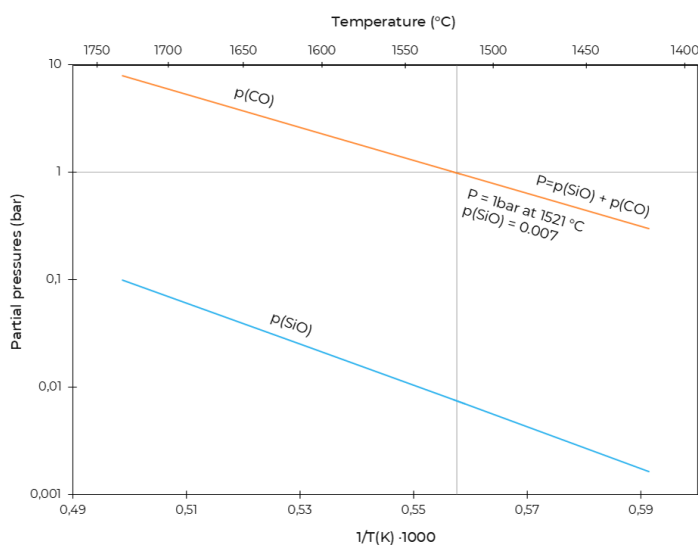


Figure 2.7 Equilibrium pressure above the condensed phase combination $\text{SiO}_2\text{-C-SiC}$ calculated in the temperature range $1400\text{--}1700^\circ\text{C}$ from HCS ver.9.8.1.2. The graphs for p_{CO} and P are superimposed.

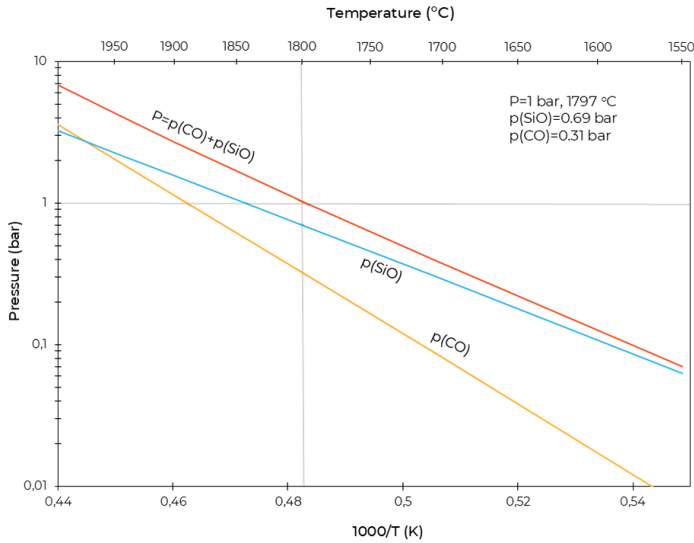


Figure 2.8 *Equilibrium pressure above the condensed phase combination SiO_2 - SiC-Si calculated from HCS ver.9.8.1.2.*

In the silicon furnace process, there are of course not only two fixed temperatures, but a gradual increase from the charge top to the high temperature zone. As such, the case where two condensed phases are in equilibrium with a gas phase better explains the gas pressure and the phases present in an industrial furnace. For two condensed phases, the system has six combinations of the four condensed phases. The system is determined if we fix the temperature and the total pressure, and the SiO partial pressure can be shown in a graph as a function of the temperature. Figure 2.9 shows the SiO pressure as a function of temperature at 1 bar for the five combinations that are interesting for a discussion of the silicon process.

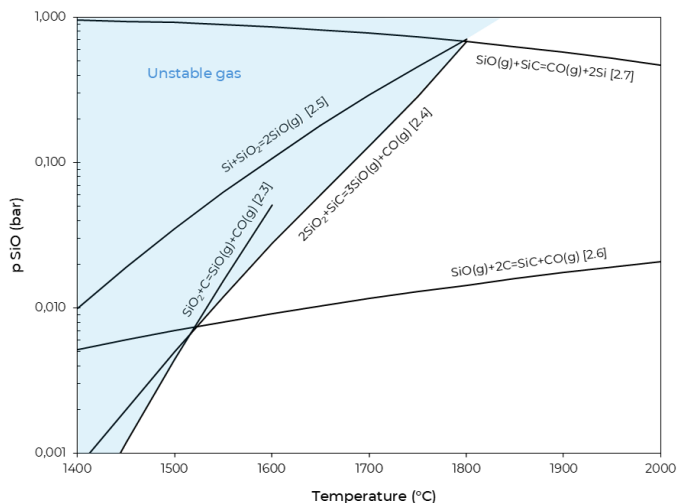
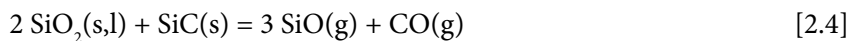
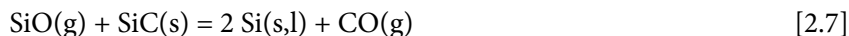


Figure 2.9 Equilibrium SiO pressures above the condensed phase combinations C–SiC, SiO₂–C, SiO₂–SiC, SiC–Si and SiO₂–Si calculated from the HSC ver. 9.8.1.2. Total pressure, P , is 1 bar, and $P = p(\text{SiO}) + p(\text{CO})$.

Three of the combinations have condensed species on the left-hand side and only gas on the right-hand side:



Each of these reactions splits the area of Figure 2.9 in two. The gas is unstable for gas compositions corresponding to points to the left of them. If such gas compositions appear, the reaction is reversed and results in condensation of the gas. The fourth and the fifth combinations correspond to reactions that consume SiO(g):



The sixth combination, reaction [2.8], is metastable, since Si and C will react to SiC according to Reaction [2.2]. This metastable equilibrium is not fulfilled in the reduction of SiO_2 , and it will not be discussed further.



Figure 2.9 can be used to illustrate the SiO pressure in an industrial FeSi/Si furnace, under the assumptions of chemical equilibrium, as shown in Figure 2.10. In the high temperature zone ($> 1800^\circ\text{C}$), the SiO pressure is given by equation [2.7]. It will hence range from 0.68 bar at 1800°C to 0.47 bar at 2000°C . When the gas rises in the furnace to lower temperatures, it will form condensed phases, either by reaction [2.4] and/or [2.5]. As [2.4] has the lowest SiO pressure, the gas would react until the SiO pressure was equal to that of reaction [2.4], illustrated by the red line. We can use Figure 2.10 to discuss the overall reactions in the industrial furnace. At less than 1400°C , the SiO leaving the charge should be less than 0.001 bar. With a typical industrial Si yield of 80–90%, the SiO pressure is closer to the area 0.01–0.1, showing that

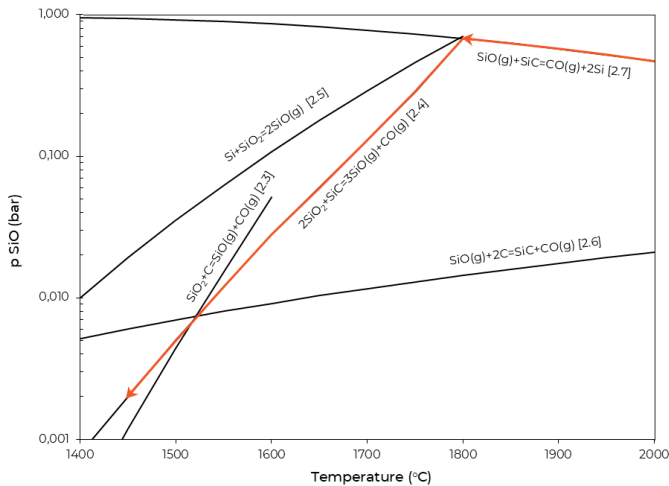


Figure 2.10 Equilibrium SiO pressures above the condensed phase combinations C–SiC, SiO_2 –C, SiO_2 –SiC, SiC–Si and SiO_2 –Si calculated from the HSC ver. 9.8.1.2. Red lines indicate the SiO pressure in an industrial furnace under the assumption of chemical equilibrium.

the gas has not reacted to the equilibrium state with SiO_2 and SiC as it should have, according to reaction [2.4]. As the SiO gas pressure is higher in industrial furnaces than in reaction [2.4], it also means that the SiC formation from carbon material, reaction [2.6], will occur at all temperatures above 1400°C .

2.3 Kinetics in the Si–O–C system

The equilibrium determines the final state of a system, but the establishment of equilibrium may take a long time. Therefore, knowledge of the kinetics is important in predicting the behavior of a system.

$\text{SiO} + 2\text{C} = \text{SiC} + \text{CO(g)}$ [2.6]

As shown by the equilibrium calculations in Chapter 2.2, the SiO pressure in the high temperature zone will vary from $\frac{1}{3}$ to about $\frac{1}{2}$ as the temperature varies from 1800 to 2000°C . As will be seen in Chapter 3, this will give a Si-yield between 33 and 50% if carbon is not capturing the ascending SiO gas according to reaction [2.6]. The capture of the SiO gas, reaction [2.6], will hence be one of the most important reactions in the high silicon furnace process. The reactivity of this reaction has been investigated in a number of studies. To mention just a few, the doctoral theses of Myrhaug, Myrvågnes, Ramos, and Jayakumari give a thorough summary of the literature, as well as new knowledge regarding this reaction (Jayakumari, 2020; Myrhaug, 2003; Myrvågnes, 2008; Ramos, 2018).

The topochemical model, also called the shrinking core model, can be used to explain the reaction mechanism. This model may be used if diffusion into the unreacted particle is slow, or if the chemical reaction is very fast. At the start of the reaction, the SiO gas will meet the surface of the carbon particle, and a SiC layer is formed. For the reaction to continue: a) the SiO gas must diffuse through the SiC layer; b) the chemical reaction must occur between C and SiO gas; and c) the CO gas must be able to diffuse through the SiC layer. This is illustrated in Figure 2.11. Charcoal particles are typically transformed according to a topochemical model, as seen in Figure 2.12 (Jayakumari, 2020; Myrhaug, 2003; Raaness and Gray, 1995; Videm, 2000, 1995). Although other carbon materials like coal and petroleum coke do not necessarily have the same

topochemical structure, as found by Jayakumari (2020), the topochemical model can still be used to model the rate of the reaction.

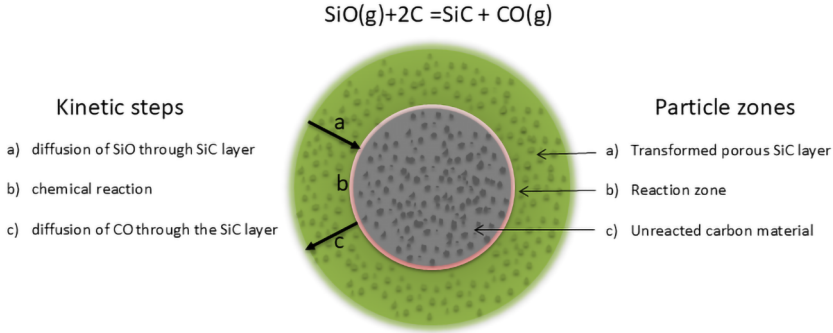


Figure 2.11 *Topochemical reaction of a carbon particle.*

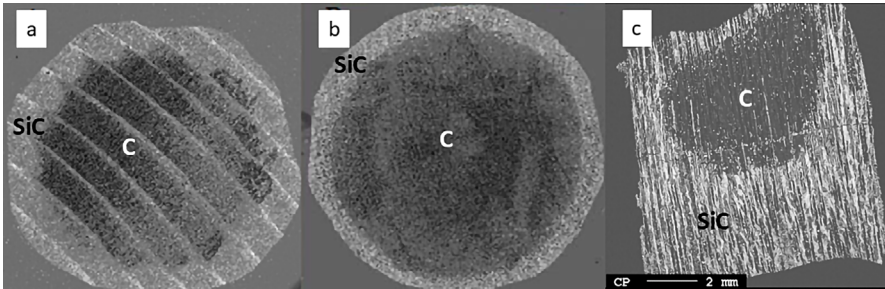


Figure 2.12 *Partly reacted charcoal particles (Myrhaug, 2003; Jayakumari, 2020) [With permission from L.V. Myrhaug].*

It has been found that diffusion of SiO gas into, and CO out from, the reaction zone affects the rate. When diffusion determines the rate, the rate can be expressed by

$$\frac{dX}{dt} = \frac{12 \cdot D_{\text{SiO}} \Delta C_{\text{SiO}} M_{\text{SiO}}}{\rho_{\text{SiO}} d_0^2 \left[(1-X)^{-1/3} - 1 \right]} \quad [2.9]$$

where X is the fraction reacted, t is the time (s), D_{SiO} is the diffusion coefficient of SiO gas in the SiC materials (cm^2/s), ΔC_{SiO} is the concentration gradient of

SiO gas, M_{SiO} is the molar weight (g/mol), ρ is the density (g/cm³), and d_0 is the diameter (cm) of the original particle. The following equation therefore expresses the total time it takes to convert the particle:

$$t_{\text{tot}} = \frac{\rho_{\text{SiO}} d_0^2}{24 \cdot D_{\text{SiO}} \Delta C_{\text{SiO}} M_{\text{SiO}}} \quad [2.10]$$

In these equations, the diffusion of SiO gas has been used, however, the diffusion of CO gas may of course be expressed in the same manner. A higher SiO pressure in the bulk phase, or a lower CO pressure in the bulk phase, will therefore increase the rate, as the concentration gradient ΔC_{SiO} , or ΔC_{CO} , increases.

It can also be noted that the time is proportional to the square of the particles' original diameter, d_0 . This means that if the particles double in size (i.e., in diameter), the rate will decrease by a factor of four, and the total time it takes to convert the particle will therefore increase by a factor of four. Small particles have a shorter diffusion path than larger particles.

The diffusion coefficient, D_{SiO} or D_{CO} , is determined by the structure of the transformed SiC materials, and especially by the porosity in the transformed SiC. When the porosity is higher, gas diffusion will increase. This is illustrated in Figure 2.13, which shows that, within a group of carbon materials (e.g. charcoal), the reactivity increases with porosity or, in other words, increases with lower density. However, the correlation between SiO reactivity and porosity within a carbon group can also be quite low. Jayakumari and Tuset stated that SiO reactivity correlated with the bulk weight, specific surface area and CO₂ reactivity (Jayakumari and Ringdalen, 2022; Tuset and Raaness, 1976). Such a correlation was, however, not found in the medium reactive carbons. It has also been discussed whether the main effect is not the porosity as such, but rather the cell wall thickness (Jayakumari, 2020), as the cell wall thickness is typically correlated with porosity and density. As SiC has a larger molar volume compared to carbon, it is expected that the porosity will decrease with the reaction, and the SiC layer may be denser. This means that it will be harder for SiO to diffuse into the cell wall, and the dependency on cell wall thickness may therefore be important.

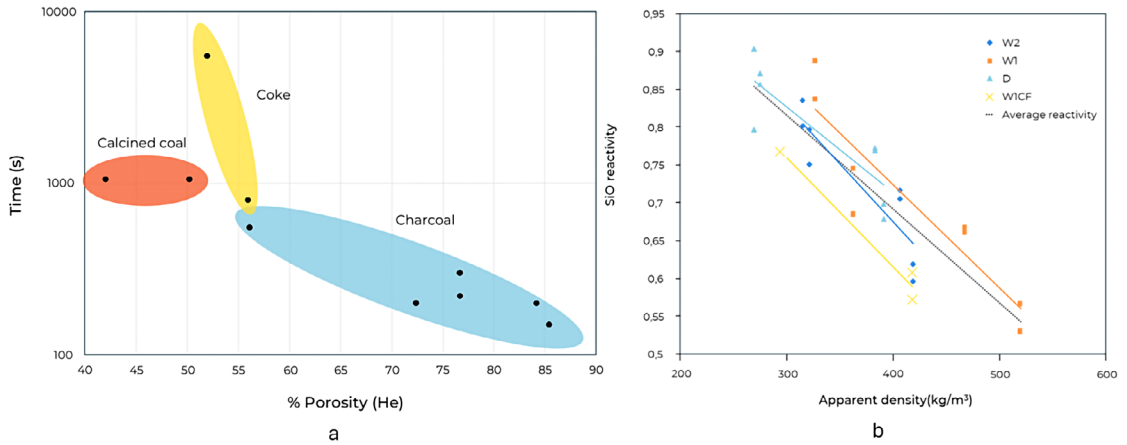


Figure 2.13 Increasing porosity generally increases the SiO reactivity as shown in a) where the total time of reaction decreases with increasing porosity (Myrhaug, 2003) and b) SiO reactivity for eucalyptus charcoal from varying clones and production methods where the main effect on SiO reactivity was found to be the density (Ramos, 2018) [Used with permission from L. V. Myrhaug and D. Ramos].

The SiO reactivity of coal has been investigated by a number of researchers, such as Raaness and Gray (1995), Narciso-Romero *et al.* (1999), Videm *et al.* (2000), and Myrvågnes (2008). In an effort to correlate the petrographic and anisotropic properties of the coals with SiO reactivity, it was seen that a higher rank will decrease the SiO reactivity, as shown in Figure 2.14. The figure shows the SiO reactivity of nine bituminous coals and their rank. Low-rank coals with low vitrinite reflectance are reported to show higher SiO reactivity (i.e., a lower amount of unreacted gas) than bituminous coals. The petrographic properties of the coal also influence the physical properties of the resultant coke and chars, such as porosity, pore size distribution and the type of porosity (Raaness and Gray, 1995).

Carbon reductants such as chars and coke derived from coal and petroleum exhibit a variety of microscopic textures that differ in the size and shape of their anisotropic units. Narciso-Romero *et al.* investigated several cokes derived from coal and petroleum (Narciso-Romero *et al.*, 1999). They found a high correlation between the size, shape and crystallographic order of the anisotropic carbon components (optical textures) and SiO reactivity. Other factors, such as porosity and the Fe, Ni and vanadium contents of the ashes,

also affect the formation of SiC. Videm *et al.* (2000) investigated cokes obtained from coals of different rank and type. The cokes consist of a binder carbon phase, produced from reactive macerals which soften during carbonisation (optical textural components), and a filler carbon phase, derived from inert macerals during carbonisation. They found that the SiO reactivity of metallurgical cokes was mainly determined by the content of the binder carbon phase within the cokes, as well as their volume weight and porosity.

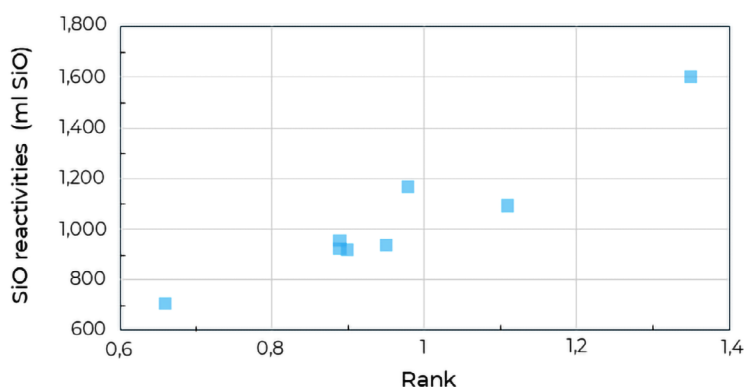


Figure 2.14 SiO reactivity for coals, showing that a higher rank will decrease the SiO reactivity (Raness and Gray, 1995) [With permission from M. Raness].

The most typical carbon materials used are coal, charcoal, char and petroleum coke, and, especially for FeSi, also metallurgical coke. Each material has quite a large SiO reactivity range, as also shown in Figure 2.15. The overall trend, however, is that charcoal and coal typically have a higher SiO reactivity compared to coke and petroleum coke. It can, however, be mentioned that SiO reactivity is usually measured at low SiO pressures, and one cannot rule out that the differences between the various carbons may be different at higher SiO pressures.

The formed SiC layer may spall off, or it may have very low strength and thus increase the amount of fines in the furnace. In some materials, the produced SiC layer will also be so dense that the reaction will stop before all carbon is transformed. These phenomena are not described thoroughly in the literature and will therefore not be discussed further here (Paull and See, 1978; Tuset and Raness, 1976).

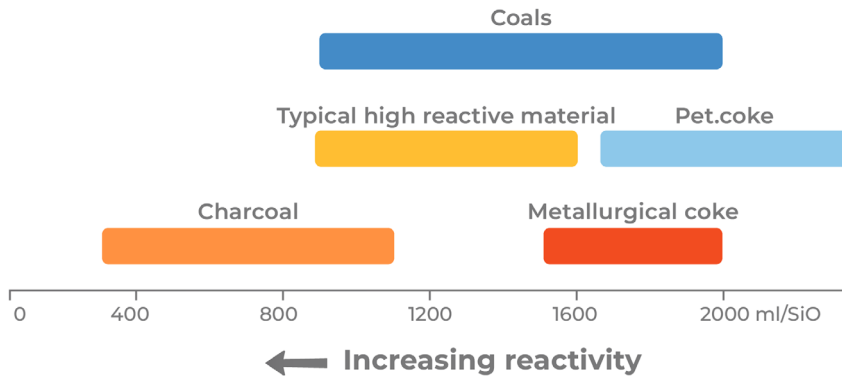


Figure 2.15 *SiO reactivity for various carbon materials, where a lower number of SiO gas not reacting signifies a high SiO reactivity (Raanes and Gray, 1995). [With permission from M. Raanes].*

$\text{SiO}_2 + \text{SiC} \rightarrow 3\text{SiO(g)} + \text{CO(g)}$ [2.4]

The reaction between SiO_2 and SiC is one of the two main reactions producing SiO gas in industrial furnaces and the other is the reaction between SiO_2 and Si . At temperatures lower than the melting temperature of SiO_2 , both reactant species are solid. For the reaction to occur directly, the particles must be in contact. However, first, the contact surface will be small and, second, as the reaction starts to occur, the particles will no longer be in contact. It is therefore believed that the overall reaction happens through the gas phase. At the SiO_2 surface, CO-gas will react according to the following reaction:



Thermodynamically, the CO_2 pressure is very low above 1500°C ($< 10^{-4}$), and the CO_2 will therefore react with the SiC particles according to Reaction [2.12].



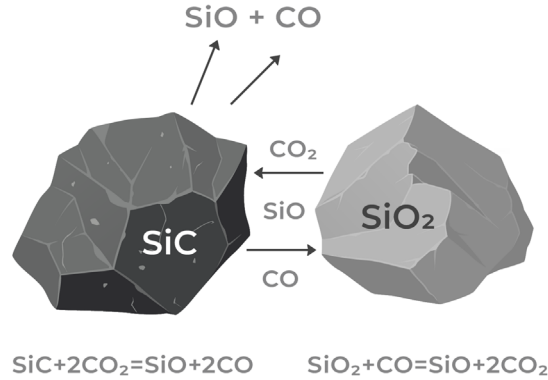


Figure 2.16 Illustration of the reaction $2\text{SiO}_2(s) + \text{SiC}(s) = 3\text{SiO}(g) + \text{CO}(g)$.

The overall rate of a reaction can be expressed as the general equation for all kinetic reactions:

$$\text{rate} = \frac{\text{driving_force}}{\text{resistivity}} \quad [2.13]$$

In this context, the rate can be expressed as weight change per time unit, $\frac{dw}{dt}$, or as the fraction of reactant reacted per time unit, $\frac{d\alpha}{dt}$, where α is the fraction of reactant reacted. α will then go from 0, when no reaction has occurred, to 1, when all the reactant is consumed. Typically, α can be given in % instead of as a fraction. The correlation between the two parameters describing the reaction rate is:

$$\frac{d\alpha}{dt} = -\frac{1}{w_0} \frac{dw}{dt} \quad [2.14]$$

The initial weight of the sample is w_0 .

When the reaction rate is kinetically controlled by the chemical reaction, the driving force is the distance from equilibrium. Typically, the distance from equilibrium can be expressed as the difference between the equilibrium constant K and the ratio of the real gas pressures Q , when SiO_2 and SiC are pure species and hence their activities are 1:

$$K - Q = K - \frac{p_{\text{SiO}}^3 p_{\text{CO}}}{a_{\text{SiO}_2} a_{\text{SiC}}} = K - p_{\text{SiO}}^3 p_{\text{CO}} \quad [2.15]$$

p_{SiO} is the partial pressure of SiO gas, p_{CO} is the partial pressure of CO gas, a_{SiO_2} is the activity of SiO_2 in quartz, and a_{SiC} is the activity of SiC. Based on this equation, it can be seen that when CO is added to the system, the reaction is expected to proceed more slowly. The resistivity is generally given as the inverse of the conductivity, where the conductivity is typically a function of temperature and of the geometrical relations between the reactants. This can mathematically be written:

$$\text{Resistance} = \frac{1}{A^* k} \quad [2.16]$$

where A^* is the geometrical factor and k is the rate constant.

- A^* is dependent on the shape and form of the raw materials, how they are mixed (sizing, pellets, particles etc.), and the total size of the raw materials, that is, the extent of the reaction, α . It is also expected that A^* will change dramatically when the quartz melts.
- k is a rate constant that depends on temperature according to the Arrhenius equation: $k = k^0 \exp\left(\frac{-E}{RT}\right)$, where E is the activation energy, R is the gas constant, and T is the temperature in Kelvin. The micro-structure and pollution elements in the SiO_2 and SiC may also affect the rate constant.

Based on the above discussion, the rate can be written as:

$$\frac{d\alpha}{dt} = A^* k (K - p_{\text{SiO}}^3 p_{\text{CO}}) \quad [2.17]$$

The real gas pressures of SiO and CO in the pellets are not known, and the rate equation can be simplified to reaction [2.18].

$$\frac{d\alpha}{dt} = f(\alpha) k(T) \quad [2.18]$$

The simplification is a product of one function that accounts for the geometrical relations, $f(\alpha)$, and one that accounts for the temperature, $k(T)$.

It must be emphasized that this temperature-dependent part also accounts for the temperature-dependent part of the equilibrium constant. This is also discussed previously by Filsinger and Bourrie (1990). Based on this, Tangstad derived the specific equation for SiO_2/SiC pellets, as shown in Reaction [2.20] (Tangstad *et al.*, 2019).

$$\frac{d\alpha}{dt} = k_0 A (1 - \alpha) \cdot \exp\left(\frac{-Q}{RT}\right) \quad [2.19]$$

$$\frac{d\alpha}{dt} = 1.9 \cdot 10^8 (1 - \alpha) \cdot \exp\left(\frac{-460 \cdot 10^3}{RT}\right) \quad [2.20]$$

The term $1.9 \cdot 10^8$ represents the reaction area times the reaction constant:

$$1.9 \cdot 10^8 = 1.9 \cdot 10^5 \cdot A_{\text{SiO}_2}^o \left(\frac{\text{cm}^2}{\text{g}} \text{SiO}_2 \right) \text{ if the area of SiO}_2 \text{ determines the reaction}$$

$$\text{rate, or } 1.9 \cdot 10^8 = 3.24 \cdot 10^5 \cdot A_{\text{SiC}}^o \left(\frac{\text{cm}^2}{\text{g}} \text{SiC} \right) \text{ if SiC determines the reaction area.}$$

This equation was valid for the reaction between 1600 and 2000°C. In some of the experiments, the $\text{SiO}_2:\text{SiC}$ ratio was measured after the experiment, and it was seen that some side reactions, such as elemental silicon formation, also took place.

Most of the published literature, except for Khrushchev (2000), reports the activation energy to be between 350 and 550 kJ/mol, as seen in Table 2.2. The reaction was studied from 1270 to 2033 °C, both below and above the melting temperature of SiO_2 . Khrushchev measured a higher activation energy than the others, of about 800 kJ/mol above the melting temperature. This can possibly be attributed to the larger particle size used (0.16–0.20 mm). The high activation energy was attributed to carbon diffusion in SiC being the rate-determining step, as the temperature dependency of C diffusion in SiC is in the same area.

Table 2.2 *Published data for the activation energy for the reaction*
 $\text{SiO}_2 + \text{SiC} = 3\text{SiO}(\text{g}) + \text{CO}(\text{g})$.

Author	Technique	Temperature (°C)	Activation energy (kJ/mol)
(Pultz and Hertl, 1966)	Isothermal weight loss in reduced pressures	1270–1430	406–548
(Filsinger and Bourrie, 1990)	Thermogravimetry	1833–2033	348
(Khrushchev, 2000)	Isothermal weight loss	1800–1900	794–823
(Andersen, 2010)	Thermogravimetry, non-isothermal	1450–2000	T < 1750°C 370–420 (avg. = 402)
(Bao <i>et al.</i> , 2013)	Isothermal	1550–1820	351
(Ni, 2015)	Isothermal	1650–1750	Dip at 1730°C
(Tangstad <i>et al.</i> , 2019)	Non-isothermal	1650–2000	424–464 kJ/mole

As will be discussed in Chapter 5, natural quartzes go through various phase transformations with increasing temperature. At low temperatures, α -quartz is the stable phase. At atmospheric pressure, a second-order phase transformation to β -quartz occurs at 573 °C (Stølen, 2004). Before entering the high-temperature phase cristobalite, it transforms to an amorphous phase. The extent of the amorphous phase varies between different natural quartzes, as described by Ringdalen (Ringdalen, 2014; Ringdalen and Tangstad, 2016). Pure SiO_2 melts at 1996 K (1719 °C). However, it may start to soften at temperatures between 1873–2073 K (1600 to 1800 °C). This indicates that the reaction between SiO_2 and SiC may occur with various polymorphs and at different stages of solid, softened, and melted SiO_2 . It should also be mentioned that the viscosity of liquid SiO_2 is very high. It is $2 \cdot 10^7$ Poise at the melting temperature and decreases to $5 \cdot 10^4$ Poise at 2000 °C. The reaction rate may therefore be affected by the polymorph, even in the solid state. Wiik suggested that cristobalite would give a higher reaction rate when SiO_2 reacted with carbon, compared to quartz (Wiik, 1990). This contradicts Tangstad, who observed the same reaction rate for quartz and cristobalite (Tangstad *et al.*, 2019). Hakamada suggested that amorphous silica would react faster than quartz, both with C and with SiC (Hakamada *et al.*, 2010).

Poch found that the reaction is rather slow in mixed powders [$\text{SiO}_2 + x \text{SiC}$] at 1 bar pressure in a stream of CO and Ar below 1550°C, but that the rate increases with rising temperature (Poch and Dietzel, 1962). Below about 1800°C, the stoichiometry of the reaction is close to Reaction [2.4], but at higher temperatures there is an additional weight loss that is thought to be due to evaporation of Si from Reaction [2.7]. In vacuum, the reaction rate is significant at lower temperatures (Wiik, 1990). According to Tuset (unpublished work quoted by Wiik, 1990), the reaction rate seems to be quite insensitive to the type of SiO_2 material. However, it increases strongly when crystalline industrial SiC is replaced by, for example, SiC made from charcoal.

$\text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO(g)}$ [2.5]

There are a few published projects regarding SiO formation from silica and silicon (Andersen, 2010; Bao *et al.*, 2013; Sindland, 2020). Using particles, Sindland observed an exponential increase in the reaction rate with temperatures from 1650 to 1950°C (Sindland, 2020). Andersen and Bao, who used pressed mixed powder, experienced a reduction in the rate between about 1720°C, the melting point of silica, and about 1860°C (Andersen, 2010; Bao *et al.*, 2013). Because silica is quite viscous at low temperatures, the gas may be trapped in the pellets and hence reduce the reaction rate. When particles are used, the gas can escape more easily. Accordingly, Sindland did not observe this reduction in reaction rate when using particles from 1 to 8 mm. This was also verified by Kyaw, who found that a mix of particles gave a higher reduction rate than mixed powders or granules (Kyaw and Tangstad, 2024).

The wettability between molten silica and silicon is not very high, as shown in Figure 2.17. Interaction of silicon with 4 natural quartz sources shows a wettability of about 90°C (Sindland, 2020), and this does not vary significantly between different quartzes. This means that, when the quartz particles and the silicon particles melt, the silicon will agglomerate into larger droplets in the melted silica, as shown in Figure 2.18.

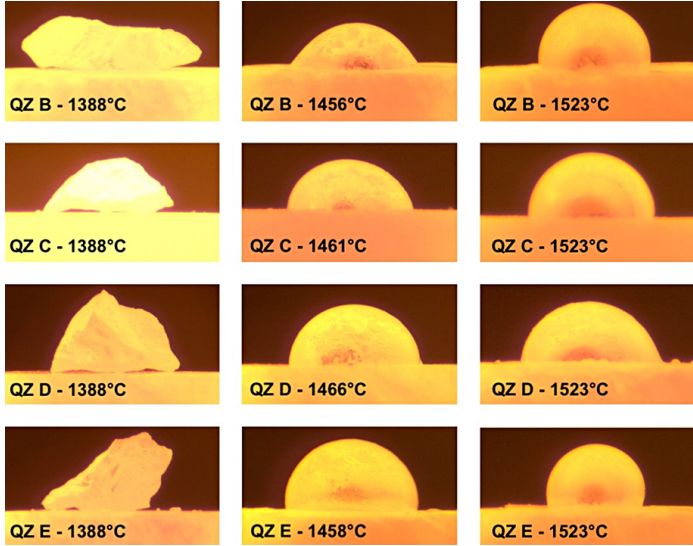


Figure 2.17 Interaction of silicon with 4 natural quartz sources showing a wettability of about 90°C (Sindland, 2020) [With permission from C. Sindland].

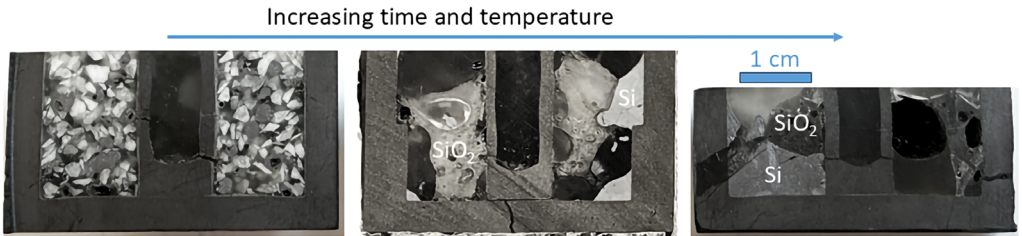


Figure 2.18 The silica and silicon behavior with increasing reaction. This figure shows that the silica will agglomerate, and the silicon will agglomerate, into larger particles during melting, lowering the reaction area between the two phases (Sindland, 2020) [With permission from C. Sindland].

The reaction rate between the silica and silicon particles can be expressed by the same simplified equation used for the $\text{SiO}_2 + \text{SiC}$ reaction shown in [2.19].

$$\frac{d\alpha}{dt} = 6.28 \cdot 10^9 A_{0,\text{Si}} F(1-\alpha) \cdot \exp\left(\frac{-557 \cdot 10^3}{RT}\right) \quad [2.21]$$

where $6.28 \cdot 10^9 \text{ g} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ is the frequency factor, $A_{0,\text{Si}}$ ($\text{cm}^2 \cdot \text{g}^{-1}$) is the original surface area of the Si particles, α is the degree of reaction varying from 0 to 1, and 557 kJ/mol is the apparent activation energy. This value is quite close to the activation energy found by Andersen (2010) below the melting point of quartz, which was between 438 kJ/mol and 528 kJ/mol for SiO_2/Si pellets. The factor F accounts for silica-particle agglomeration when both the silicon and silica are liquid. F equals 1 below the melting temperature of quartz and 0.5 above the melting temperature of quartz. This is a simplification of the true reaction area and how it changes with increasing temperature. However, it fits the experimental points quite well, as seen in Figure 2.19. In this figure, it can also be seen that the 5 different natural quartzes, with quite different properties in melting, pollution content and phase transformation degree, have quite similar reaction rates.

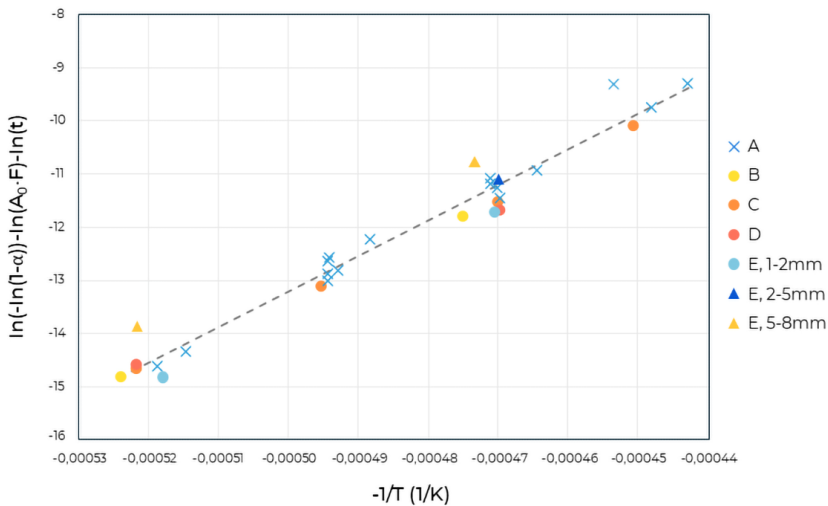


Figure 2.19 An Arrhenius plot showing the comparison of the experimental results and the reaction rate given by equation [2.20]. The experiments were performed at various holding times, particle sizes in the range 1 to 8 mm and for 5 different commercial natural quartz sources.

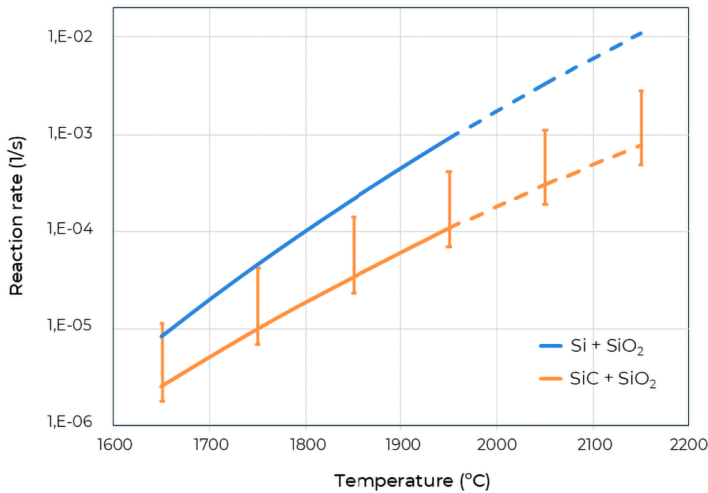


Figure 2.20 Comparison of reaction rate of the two SiO producing reactions given by [2.19] and [2.21] using 1–2 mm silica particles for the Si + SiO reaction and 1–2 mm silica particles for the SiO₂ + SiC reaction. The dotted part of the lines are extrapolated outside the temperature range of the models (Sindland, 2020). [With permission from C. Sindland].

In industrial furnaces, the SiO gas may be produced by both the SiO₂ + Si reaction [2.5] and the SiO₂ + SiC reaction [2.4]. A comparison of the rates given by the rate equations in [2.19] and [2.21] for particle sizes of 1–2 mm is shown in Figure 2.20. It shows that the rates of the two reactions are within a factor of 10. This means that the area between the reactants will be one of the main factors determining whether most of the SiO gas comes from reaction [2.4] or [2.5], because the area changes by a factor of 10 if the particle diameter is decreased by a factor of 3, assuming circular particles.

Condensation reactions

The ‘condensation reactions’ is an industrially common name for the reactions that occur from the gas phase to condensed phases, such as the reverse of reaction [2.4] and [2.5].



The $\text{SiO}_2 + \text{Si}$ condensate is typically recognized as a dense brown mass that glues the particles together, as shown in Figure 2.21. Microscopically, it consists of Si spheres in a matrix of SiO_2 . This has been recognized and studied by several researchers, including Tangstad, Vangskåsen, Ksiazek, and Broggi, to mention a few (Broggi *et al.*, 2021; Ksiazek *et al.*, 2015; Tangstad *et al.*, 2010; Vangskåsen, 2012, 2011). The spherical particles may vary in size and can therefore give different shades of brown, as seen in Figure 2.23. Solid substrates, such as charge materials in a furnace, will hence be covered with layers of condensed materials in various shades.

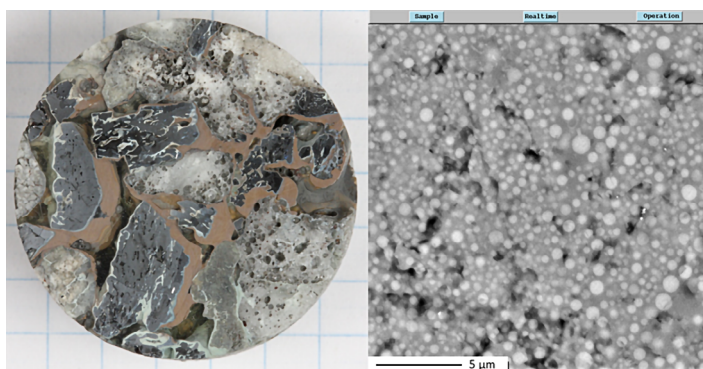


Figure 2.21 Brown condensate, consisting of Si spheres in a SiO_2 matrix, condensed on quartz and SiC particles. (Tangstad *et al.*, 2010).

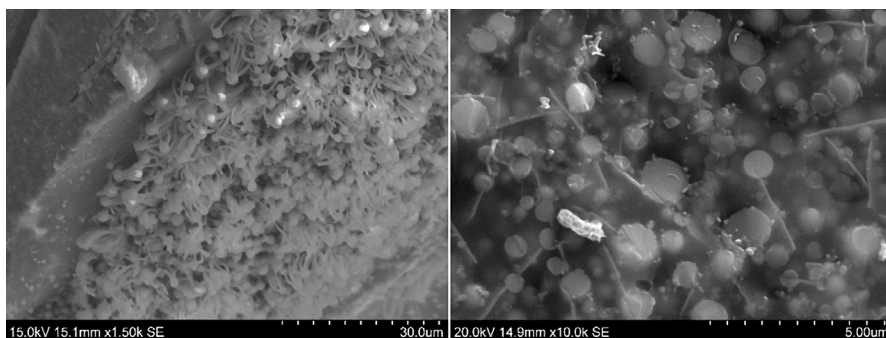


Figure 2.22 Brown condensate shown with two different magnifications: spherical silicon particles in a SiO_2 matrix. (Broggi *et al.*, 2021)[With permission from A. Broggi].

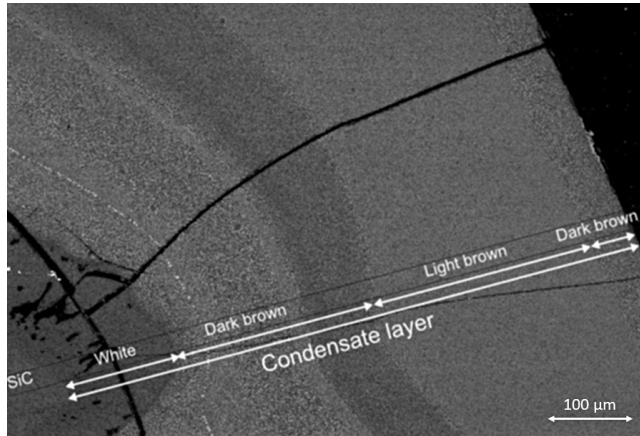


Figure 2.23 Layers of brown Si and SiO₂ condensate with various silicon sphere sizes giving various brownish colours, condensed on a SiC particle. Adapted from. (Vangskåsen, 2012) [With permission from J. Vangskåsen].

When investigating the SiO₂ + Si condensate more closely, additional features can be observed. First, there are cracks between the silicon spheres, as seen in Figure 2.24. Silicon can flow through these cracks in the silicon matrix and accumulate into larger silicon spheres, which may explain the variation in sphere size. As the condensate is heated while it descends with the charge materials in the furnace, the silicon spheres increase in size, as seen in Figure 2.25. It has also been observed that silicon separates from the condensate at temperatures above the melting point of silica, above 1720°C, as shown in Figure 2.26. The silicon produced as part of the condensates may therefore contribute to the silicon produced in the furnace, as the separation will be faster than the backreaction of $\text{Si} + \text{SiO}_2 = 2\text{SiO}(\text{g})$, reaction [2.5].

Although this condensate mainly consists of silicon and silica, microscopic investigations have also shown that some SiC forms on the surface of the silicon spheres, as shown in Figure 2.27. It is believed that SiC may form directly from the CO- and SiO-gas, as more SiC is present than could be precipitated from the dissolved carbon in the elemental silicon phase. This is of course due to the low carbon solubility, as shown in Figure 2.3.

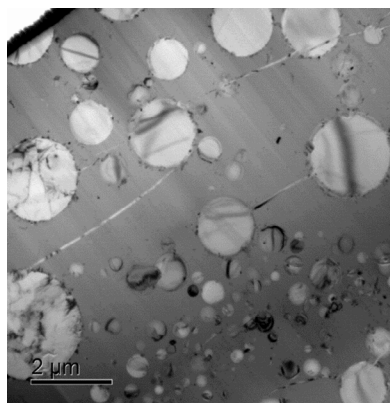


Figure 2.24 Silicon spheres in a SiO_2 matrix where the large Si spheres are connected by cracks (Broggi, 2021). [With permission from A. Broggi].

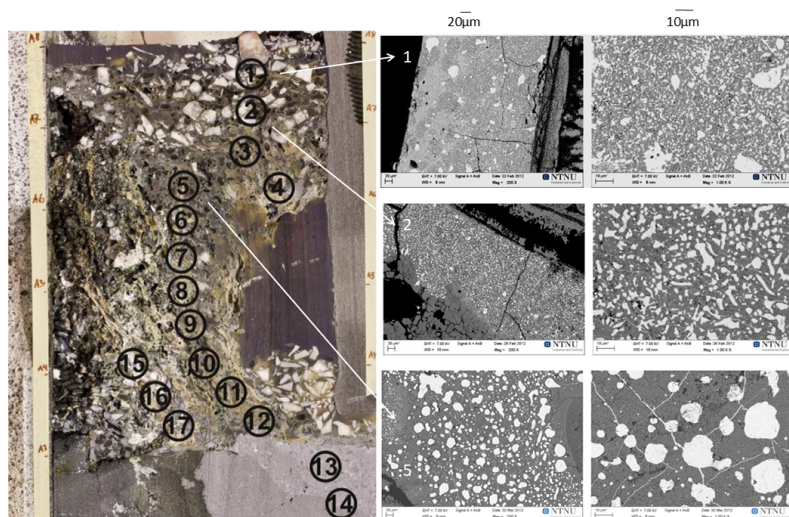


Figure 2.25 Condensates investigated from a pilot scale furnace that show how the silicon particles grow in size over time and temperature (Vangskåsen, 2012). [Permission from J. Vangskåsen].

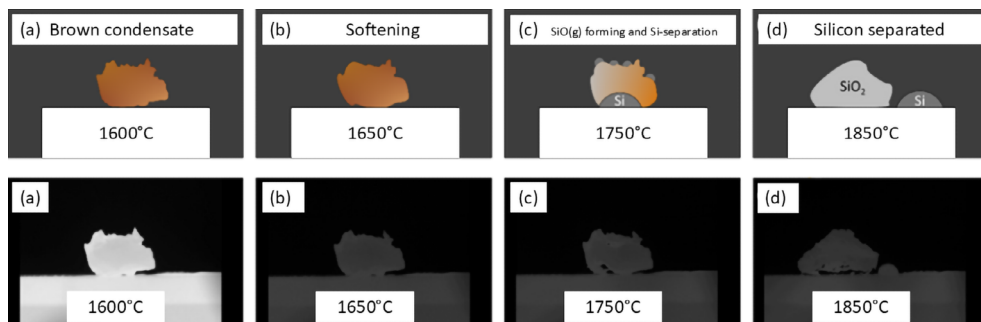


Figure 2.26 Separation of silicon from the $\text{SiO}_2 + \text{Si}$ condensate at high temperature (Broggi, 2021, Vangskåsen, 2012)[With permission A. Broggi and J. Vangskåsen].

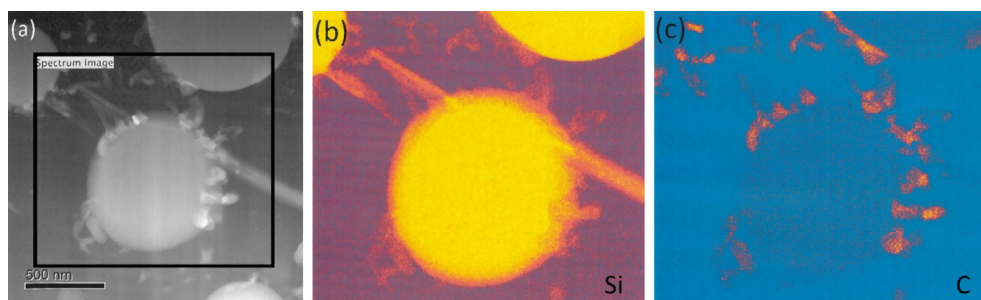


Figure 2.27 Silicon and carbon mapping of a Si sphere, signifying that there are some SiC particles on the surface of the larger Si spheres (Broggi, 2021). [With permission A. Broggi].

The $\text{SiO}_2 + \text{SiC}$ condensate from the reversed reaction [2.4], $3\text{SiO}(\text{g}) + \text{CO}(\text{g}) = 2\text{SiO}_2 + \text{SiC}$, has been found to be a white, blue or orange cottonlike structure. The condensates consist of nanowires with and without nodules, as seen in Figure 2.28. The colour mainly depends on the size and amount of nodules (Broggi, 2021). The nanowires form with a SiC-core surrounded by a SiO_2 layer, as seen in Figure 2.29. Both due to the melting point depression of nano-sized materials and the exothermic energy released by the condensation reaction, the SiO_2 is liquid over a large temperature range. When liquid, the SiO_2 layer

will try to lower its surface energy by contracting into spherical particles and hence, SiO_2 nodules form. The SiO_2 is amorphous silica, and the SiC core has a high density of stacking faults (Broggi, 2021).

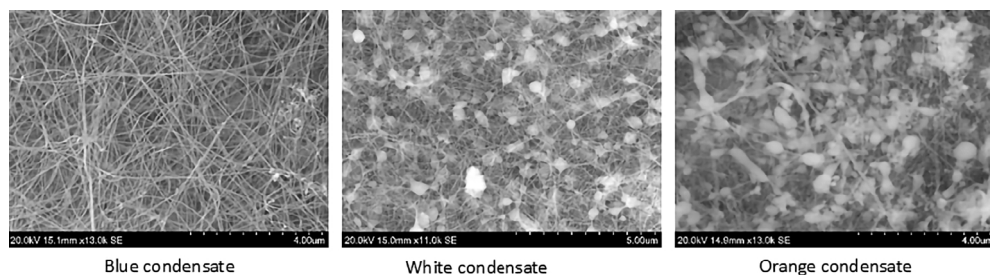


Figure 2.28 SiO_2 + SiC condensates as wires, with and without nodules. The various colours are reflecting the size and amount of nodules (Broggi, 2021). [With permission A. Broggi].

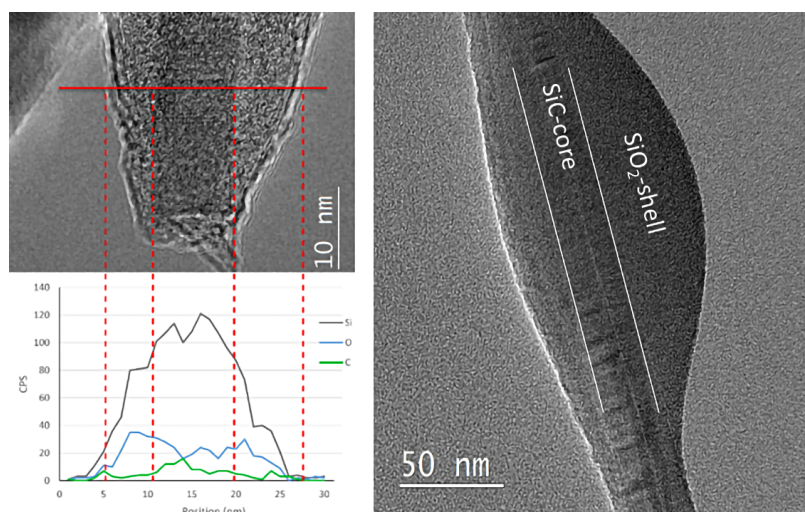


Figure 2.29 Example of nanowires in the SiO_2 + SiC condensate, where the nanowires contain a SiC core surrounded by a SiO_2 -shell. The right picture shows the SiO_2 -layer starting to form a nodule (Broggi, 2021) [With permission A. Broggi].

The condensate will typically form between 1000 and 1800°C. At higher temperatures, the driving force is low, and at lower temperatures the reaction rate is slow. It seems that the $\text{Si} + \text{SiO}_2$ condensate forms in a smaller temperature range between 1600–1750°C, while the $\text{SiO}_2 + \text{SiC}$ can form at both higher and lower temperatures. The presence of a substrate increases condensate formation, and according to Broggi (2021) it seems that there will be more condensation with smaller particle sizes, which equals a larger condensation area.

In small scale experiments, where the temperature gradient between 1900 and 1000°C in industrial furnaces has been simulated, it is seen that typically 10–20% of the SiO gas formed will produce condensates, while the rest will go through the charge into the off gas system (Broggi, 2021). This shows that the condensation reactions according to the reversed reaction [2.4] and [2.5] are not in equilibrium. Broggi (2021) calculated the SiO-pressure based on the starting SiO pressure and the condensed material found in the experiments, as shown in Figure 2.30. The results show that the real SiO pressure in the gas is much higher than the equilibrium pressure for the condensation reactions. This agrees with industrial experience that the off-gas out of the furnace has a much higher SiO-content compared to the condensation equilibrium reactions.

The condensation reactions are exothermic, with a high absolute reaction enthalpy at 1500°C: -616.6 kJ/mol for $2\text{SiO(g)} = \text{SiO}_2 + \text{Si}$ and -1404 kJ/mol for $3\text{SiO(g)} + \text{CO(g)} = 2\text{SiO}_2 + \text{SiC}$. This means that both reactions have an adiabatic product temperature above 6000°C. This heat will of course be distributed to the surrounding gas and charge particles. However, this distribution takes time, and the condensation will therefore stop locally. If the high temperature zone is about 1950°C (the SiO-pressure in the high temperature zone is about 0.5), then 20% of the SiO gas is condensed. The condensation reaction will then have increased the bulk temperature in the low temperature zone by about 200°C and this may also stop condensation from occurring. It is therefore believed that a total condensation of about 10%–20% of the SiO in the gas is possible, as was also found in the experimental setup (Broggi, 2021).

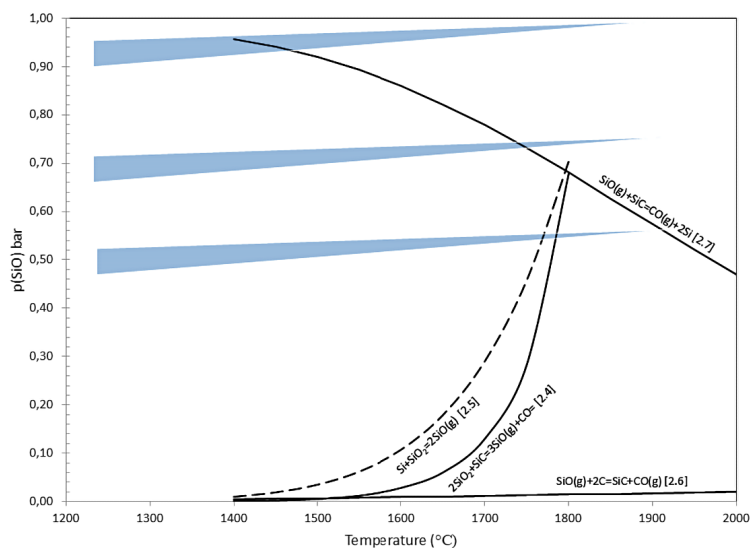


Figure 2.30 Calculated SiO pressure during cooling of SiO- and CO-gas starting at 1 bar SiO pressure, 0.75 bar SiO pressure and 0.55 bar SiO pressure starting at 1900°C based on amount of SiO and CO condensed experimentally. Adapted from (Broggi, 2021). [Used with permission from A. Broggi].

In industrial furnaces, the condensate can clog the charge materials and stop the raw materials descending in the furnace. The clogging will also prevent the gas from being distributed evenly in the charge. Clogging of the charge material is seen to occur mainly between 1500 and 1750°C (Broggi, 2021, Vangskåsen, 2011). At higher temperatures, the SiO_2 will be liquid, and the strength of the condensate will be low. At lower temperatures, the condensate will not be dense, but more a cottonlike structure. It is also in this temperature area that the brown $\text{Si} + \text{SiO}_2$ condensate forms, which seems to be tougher and more effective in gluing the charge together. The strength of the condensate was measured by Vangskåsen (2012), and it was found to be in the range 120–500 MPa when the condensate was excavated from the area below the 1670°C isotherm. For comparison, Portland cement is about 40 MPa and natural quartz in the area 130–370 MPa. When the condensate was extracted at higher temperatures, the strength decreased to 30–120 MPa, and this was believed to be due to the drainage of the Si particles and the softening of the silica.

Metal producing reaction – $\text{SiO(g)} + \text{SiC} = 2\text{Si} + \text{CO(g)}$, reaction [2.7]

Traditionally, it is assumed that Si is produced in the metal pool area, where SiO_2 reacts with Si and SiC, producing SiO gas. This gas then reacts with SiC to produce silicon. This may still be the main reaction producing silicon, however, in the last years this view has been challenged. As mentioned in the previous subchapter, the silicon produced in the $\text{Si} + \text{SiO}_2$ condensate will separate from the condensate and end up in the tapped silicon. It was estimated that this can be as much as 10% of the total silicon produced (Vangskåsen, 2012). Next, as will be mentioned in Chapter 6 Electric operation, the arcs may go to the SiC-crusts surrounding the electrodes. When this happens, the energy will be developed in the SiC crusts. This means that when the SiO_2 meets the crust, SiO will be developed, and Si may be produced. This has been seen in the samples excavated from an industrial FeSi75 furnace, as shown in Figure 2.31.

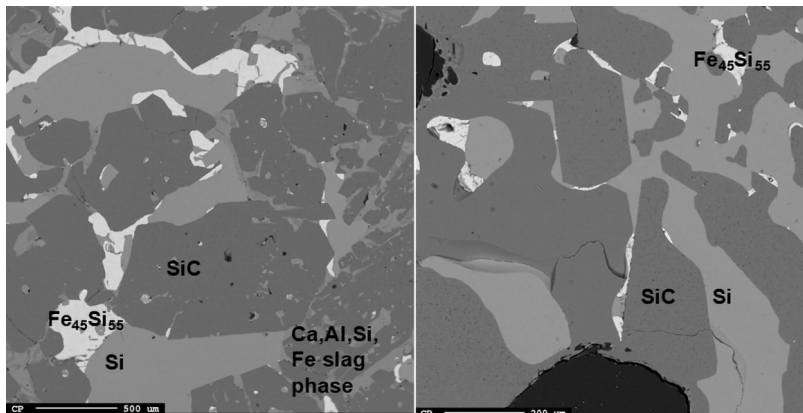


Figure 2.31 FeSi produced in the SiC crust high up in an industrial FeSi75 furnace 400 mm from the charge top and 250 mm and 550 mm horizontally from the electrodes (Tranell et al., 2010).

According to the equilibrium calculations shown in Figure 2.9, the SiO pressure is only high enough to produce elemental silicon above about 1800°C. Below this temperature, the condensation reactions give too low an equilibrium SiO pressure. As discussed in the last sub-chapter, the condensation

reactions may, however, be slow, and a higher SiO pressure may therefore be present. Si production in SiC at lower temperatures has also been observed. Tangstad *et al.* (2010) reported silicon produced as low as 1500°C in SiC particles. Tangstad *et al.* (2010) also reported elemental silicon at 1760°C, which is more in agreement with the findings of Jayakumari (2020), where Si was found in the SiC particles between 1600 and 1700°C. It was also found that SiC from charcoal produced more elemental silicon than SiC from coal and petroleum coke (Jayakumari, 2020; Jayakumari and Ringdalen, 2022). Both Tangstad *et al.* (2010) and Jayakumari (2020) used Si + SiO₂ mixtures to produce SiO gas, giving a high SiO pressure in the set-up. Sindland *et al.* found that β -SiC from charcoal reacted faster and produced more silicon than commercial α -SiC and α -SiC from crust material at temperatures above 2000°C (Sindland *et al.*, 2026).

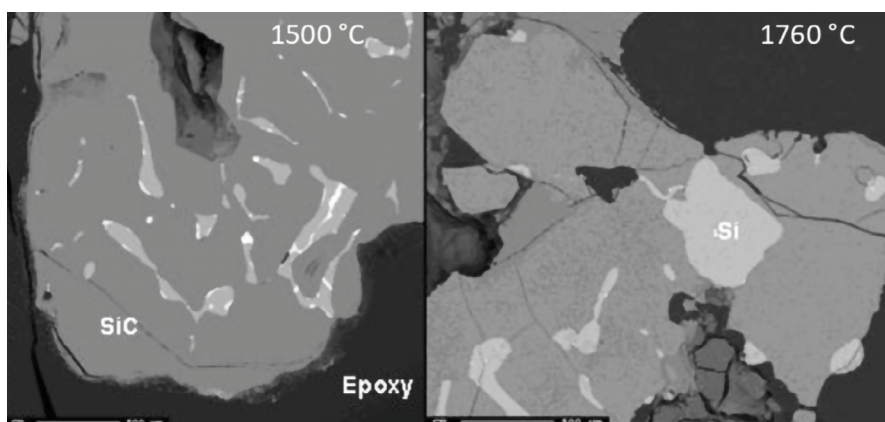


Figure 2.32 SiC particles from a 75 kVA Si-simulator showing that elemental silicon can be found inside the SiC particles as low as 1500°C (Tangstad *et al.*, 2010) (Light grey is silicon, mid-grey is SiC and black is epoxy-filled cavities).

Silicon has, however, also been seen in the SiC pores in pilot scale experiments where the gas contains both SiO and CO (Vangskåsen, 2012), as shown in Figure 2.33. Sample 6, where silicon is formed in the SiC pores, was extracted high up in the charge material. The quartz is, however, melted, which means that the temperature was higher than 1700°C. As the particles descend in the furnace, the silicon content in the SiC particles gradually increases. Silicon

in the SiC particles was also seen in the low temperature area of a pilot scale experiment reported by Myrhaug (2003). It may be debated whether the metal in the SiC particles is from condensate reaction [2.5], where SiO gas produces silica and silicon. SiO₂ has, however, never been found together with the silicon in the SiC pores and it is therefore believed that this is not the case.

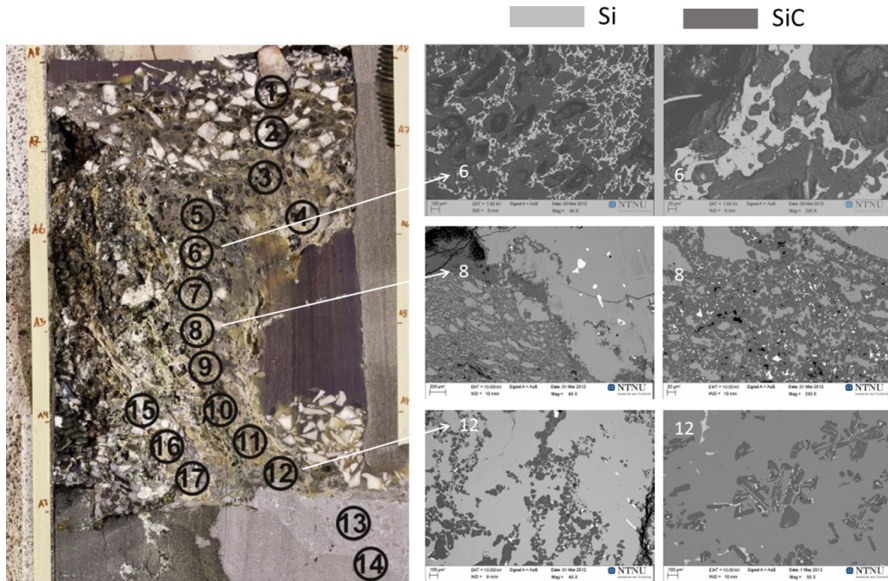


Figure 2.33 SiC particles taken out at different positions in the partly transformed charge materials in a 150 kW pilot scale experiment with a top and bottom electrode. It is seen how the amount of silicon in the SiC particles increases as the materials are getting closer to the high temperature area (Vangskåsen, 2012) [Permission from J. Vangskåsen].

As will be discussed in Chapter 4, there is also more slag in the furnace than was previously assumed. This may also mean that, when liquid SiO₂ comes down into the area below the electrode tips, it will dissolve in the slag. The dissolved SiO₂ may form SiO gas or silicon when it reacts with SiC. This has, however, not been experimentally investigated and is still a theory.

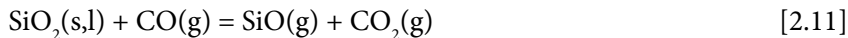
To sum up the areas where the metal producing reactions occur:

1. In the metal pool below the electrodes, where molten quartz produces SiO gas with Si or SiC, hence, the Si is produced from the SiO gas from reaction [2.7]. This will happen above 1800°C.
2. In the metal pool below the electrodes, where dissolved SiO₂ in slag produces SiO gas with Si or SiC and hence, the Si is produced from the SiO gas from reaction [2.7]. This will happen above 1800°C.
3. In the SiC crater wall next to the electrodes, where molten quartz produces SiO gas with SiC. Hence, the Si is produced from the SiO gas from reaction [2.7]. This will probably happen above 1800°C, as the crater wall may be quite warm. This can happen quite high up in the furnace when SiC crusts are produced.
4. In the SiC particles in most of the charge area, probably above 1600–1700°C. This will again probably occur according to reaction [2.7].
5. When the SiO gas is condensed to silicon and silica according to reaction [2.5], the silicon will perspire out of the condensate and may contribute up to 10% of the total silicon production. Reaction [2.5] will mainly be happening between 1500 and 1800°C.

Reaction between SiO₂ and C

Motzfeldt investigated the reaction between SiO₂ and C based on the hypothesis that it is a solid-state reaction (Motzfeldt and Steinmo, 1973). Particles of 1–2 mm of SiO₂ and C (graphite) were heated together in vacuum. A slow reaction started at 1450°C. The reaction pressure over SiO₂–C–SiC is then about 0.5 bar. After the reaction, the SiO₂ grains were apparently unchanged, but the C grains had a thin layer that was identified as β-SiC (cubic). SiC was also present outside the points of contact between SiO₂ and C and therefore, this cannot be a solid-state reaction. They also showed that the reaction could proceed without direct contact. Here, they heated a silica rod in vacuum while it hung at a predetermined distance from the walls in a graphite tube. The reaction started at about 1450°C, as with the particle mixture. The reaction

must hence be through the gas phase. The proposed reaction mechanism for the reaction between SiO_2 and C gives



with the expected overall reaction

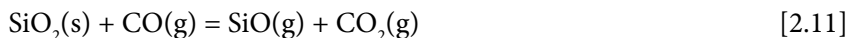


Here, the SiO partial pressure increases and reaches a value where SiC becomes stable. Calculation shows that the content of CO_2 at equilibrium is very low at 1 bar:

$$\frac{p_{\text{CO}_2}}{p_{\text{CO}}} \approx 10^{-4} \text{ (Nearly independent of the temperature)}$$

Wiik (1990) investigated the reaction thoroughly and showed beyond doubt that when solid SiO_2 is heated in an atmosphere containing CO, it reacts to form SiO and CO_2 . He ran a systematic set of experiments to elucidate the mechanism of the reaction between SiO_2 and C, and his results seem to be reasonably well explained by a model that assumes a local equilibrium content of CO_2 close to the surface of the SiO_2 and the C particles.

Ozturk and Fruehan investigated the gasification of SiO_2 in a stream of CO, He-CO and Ar-CO at 1650°C (Ozturk and Fruehan, 1985). They treated spheres of diameter 0.60–0.95 cm made from ‘commercially available fused quartz’ with the gas in a thermobalance and monitored the weight loss by the reaction:



The active modification of SiO_2 is uncertain, since the fused SiO_2 may gradually change to cristobalite during the run. The SiO flux reported per unit surface was almost independent of the sphere diameter, gas velocity and gas composition. Therefore, Ozturk and Fruehan concluded that the rate was

not controlled by gas-phase mass transfer. They indicated that the formation of CO_2 on the silica surface may be rate-determining. The numerical value of the SiO flow was $\sim 6.5 \cdot 10^{-8}$ moles $\text{cm}^{-2} \text{s}^{-1}$. This is not a rate constant that applies to all conditions, but it can be taken as an indication of the largest rate that can be obtained from an available surface at a temperature below the melting point of SiO_2 .

The SiO gas produced may also react with any available C present according to reaction [2.6]:



In pellets with intimate contact between the SiO_2 and the carbon, the SiO has time to react with the carbon and will therefore not leave the system. Weimer *et al.* (1993) proposed the reaction mechanism given by reactions [2.22] and [2.6], as illustrated by Figure 2.34. They also included an initial reaction at the contact point directly between the SiO_2 and the C particles, reaction [2.3].



The total reaction in the pellets will hence be according to reaction [2.23].

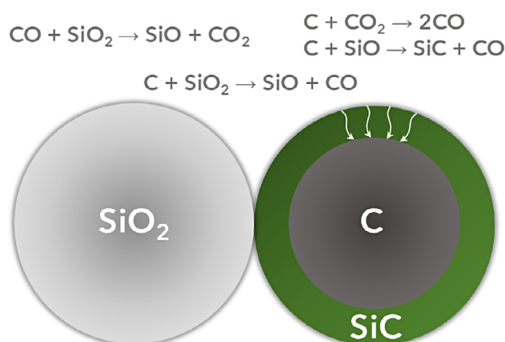
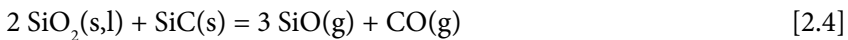


Figure 2.34 Proposed mechanism forming SiC from SiO_2 and C materials.

Li and Tangstad investigated the reaction mechanism between SiO_2 and carbon in SiO_2 -C composite pellets for various carbon contents at 1650°C (Li and Tangstad, 2018, 2017). The reactions can be visualized by the weight loss, as shown in Figure 2.35. The weight loss is seen to be in two steps: first, a rapid step where the SiO_2 and C react to SiC according to the overall reaction [2.23]. It can be mentioned that very small amounts of SiO gas escape the system in this step, as the weight loss in the transition between the fast and slow step is very close to this reaction. This was also shown by chemical analyses at this point. When all the carbon is transformed to SiC, the SiO will be the main product according to reaction [2.4].



Several authors have investigated the SiC formation from fine materials of SiO_2 and carbon, reviewed by Weimer *et al.* (1993) and Li (2017), to mention a few. The particle size is typically less than 1 μm ; however, some investigate materials up to 40 μm . As seen in Figure 2.36, the temperature dependency (the activation energy) varies between the various works and the various carbon agents, and the literature reports activation energies in the area of 250 to 550 kJ/mol. Looking at the large picture, the temperature dependency can, however, be averaged according to the line marked as 3 in the figure, and gives an activation energy of 307 kJ/mol. It is also seen that when the SiO_2 melts, at about 1700°C, the rate will not continue to increase with temperature. As seen in the figure, carbon black fits quite good with the activation energy of 307 kJ/mol, while the charcoal seems to be higher and the coke seems to be lower. Whether this is a real difference or a result of experimental variation is unclear.

Within the same experimental investigation, investigating various carbon materials with the same sizing, Li *et al.* (2018) found that the charcoal reacted faster than coal and coke, which is in accordance with the SiO reactivity of the various carbon materials, as well as the CO_2 reactivity. Carbon black typically has a lower reactivity, however, as carbon black is typically of smaller size particles, the reactivity may still be in the same area. To obtain the highest amount of SiC, it is not only the reaction rate of the SiO gas with the SiC that is important, the SiO loss should also be minimized. It is hence important that the SiO production rate is in the same order of magnitude as the SiC production.

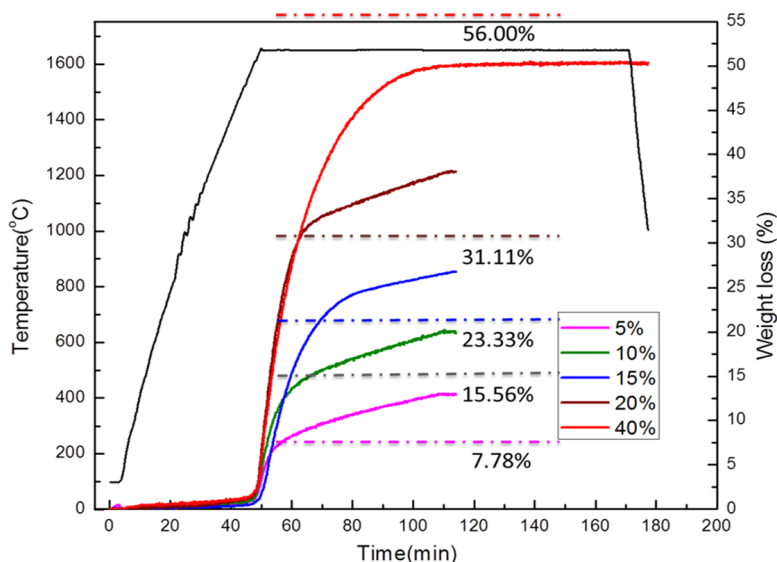


Figure 2.35 Weight loss of SiO_2 pellets deposited with carbon with varying carbon contents ranging from 5 to 40% at 1650°C (Li and Tangstad, 2017). The weight loss is divided into two reaction steps where the first rapid stage is the SiC production with the total reaction $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO(g)}$ (as indicated by the horizontal lines) and the second slow reaction step is the SiO producing step where the total reaction is $2\text{SiO}_2 + \text{SiC} = 3\text{SiO(g)} + \text{CO(g)}$. Reproduced with permission from Springer Nature.

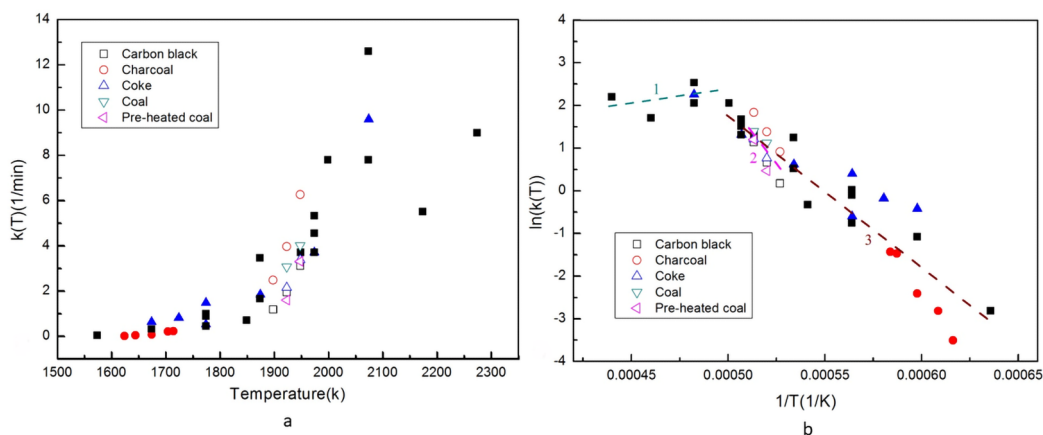


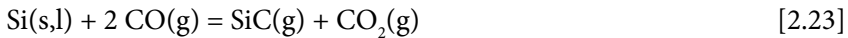
Figure 2.36 Rate constant for reaction [2.23] $\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO(g)}$ after the review of Weimer et al. (1993) and the work of Li (2017). (Solid icons – review of Weimer et al. (1993) and open icons – experimental work of Li (2017)).

There has been an increasing interest in using natural gas as a carbon raw material. Methane (CH_4) will decompose when heated, and the investigations with carbon black and deposited carbon described above (Weimer *et al.* (1993) and Li and Tangstad (2017)) are a part of this. Methane may also be used directly as a gas and, as hydrogen is also present, this will change the reaction mechanism. This will further be discussed in Chapter 9 – Modified carbothermic processes.

The reaction between SiO_2 and C has been believed to be restricted in today's silicon production furnaces. However, as we are moving towards more use of waste materials, and hence the use of carbon and quartz composite agglomerates, this reaction will be of more interest. With a surplus of carbon, it is seen that the quartz in the agglomerates will react to SiC already at low temperatures and could be a valuable material in today's furnaces (Straum *et al.*, 2026).

Reaction between Si and CO gas

Produced Si and FeSi can also react back to SiC when CO-gas is present, as seen in lab-scale experiments (Ksiazek and Bao, 2024; Wintervoll, 2026). In CO-containing atmospheres, SiC may form through the reaction between liquid silicon and carbon monoxide (CO), as described in Equation [2.23]. In addition, the equilibrium between CO, CO_2 and solid carbon is governed by the Boudouard reaction, shown in Equation [2.22]:



with the expected overall reaction:



Calculations show that the content of CO_2 at equilibrium is very low at 1 bar:

$$\frac{p_{\text{CO}_2}}{p_{\text{CO}}} \approx 10^{-4} \text{ (Nearly independent of the temperature)}$$

The rate of SiC formation increased with increasing temperature. Even when the experiments were operated in Ar, a thin SiC layer (1–10 μm) formed on the silicon surface. This is believed to be due to trace elements of oxygen in the Ar gas reacting with the carbon parts in the furnace.

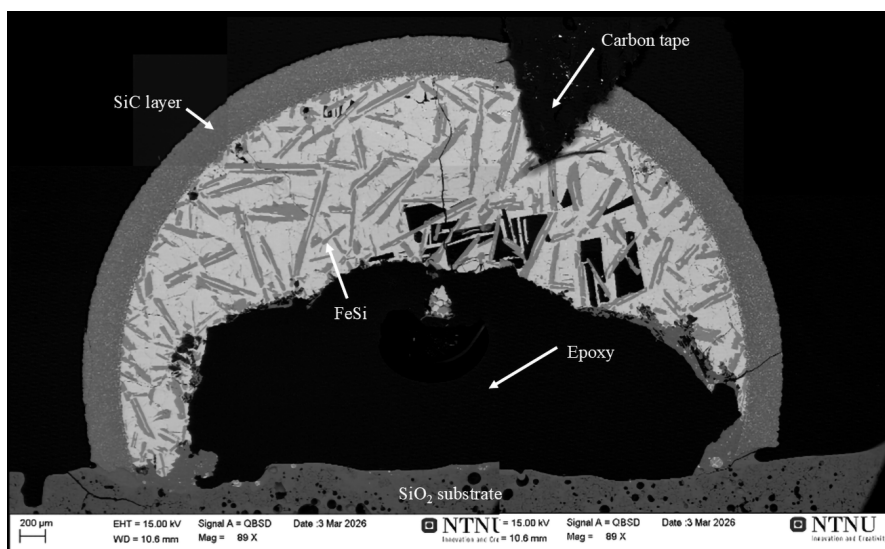


Figure 2.37 SiC layer developed on a FeSi₇₅ drop at 1650°C after 15 minutes in CO gas (Wintervoll, 2026).

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