Mechanism of reaction of silica and carbon for producing silicon carbide

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Abstract
The reaction kinetics of carbon reduction of silica were investigated using thermodynamic concepts and by fitting to relevant models the experimental data obtained for this reduction using a thermogravimetric unit in the temperature range of 1566 to 1933 K. The results show that the only way to produce SiC in this reduction is the reaction of Si, SiO, or SiO₂ at the surface or by diffusion of SiO inside the carbon particles while CO and CO₂ have no direct effect on the process. The controlling step of this reduction at temperatures lower than 1750 K is the chemical gas–solid or solid–solid reaction at the surface of the carbon particles, while at higher temperatures, the rate of SiO diffusing inside the carbon particles controls the rate of this reduction.

Keywords
Silica, carbon, reduction, mechanism, TGA

Introduction
Several mechanisms have been defined for the production of silicon carbide (SiC) using the reaction of silica (SiO₂) and carbon (C) at high temperatures.¹⁻⁹ Among these mechanisms, some cases have been widely accepted in the temperature range of 1500 to 2000 K.⁷⁻⁹ Nevertheless, attending to the complexity of this reaction, there is no complete investigation for obtaining this mechanism, based on the thermodynamic and kinematic of this reaction.

Shimoo et al.¹⁰ studied the reaction of silica and graphite in argon atmosphere for producing SiC and SiO. They concluded that, in the first stage, an interfacial reaction (a chemical process on the surface of graphite particles) controls this reduction; then, diffusion of
carbon in the produced layer of SiC controls this reduction. Agarwal and Pal\textsuperscript{11} resulted that, at temperatures above 1773 K, this reduction has been composed of three reactions with effects of CO as the major component, and the reaction rate is controlled by a combination of reduction reaction of silica and the Boudouard reaction (i.e. \( \text{C} + \text{CO}_2(\text{g}) \leftrightarrow 2\text{CO(\text{g})} \)). Vodopanov et al.\textsuperscript{12} investigated the reaction of silica and graphite in different atmospheres, such as CO, Ar, or vacuum. They observed that this reaction is too fast in the CO atmosphere, slow in the Ar atmosphere, and too slow in the vacuum condition. It was opposite to the Agarwal and Pal\textsuperscript{11} results that reported a higher reaction rate in Ar atmosphere than in CO atmosphere. Some studies also indicated that the initial stages of this reaction are correlated by the evolution of CO.\textsuperscript{13,14} In some of laboratory studies,\textsuperscript{10,13,14} the presence of CO\textsubscript{2} in outlet gases was not observed; however, experimental results of Sahajwalla et al.\textsuperscript{14} reveal this component in the discharge gas. Wegrzyn\textsuperscript{15} collected the experimental data from various articles and concluded that the initial stage of this reaction is controlled by the reaction on the surface of carbon particles. Chen and Lin\textsuperscript{16} have a similar study on the effect of contact area on synthesis of SiC through carbothermal reduction of SiO\textsubscript{2}. Biernacki and Wotzak\textsuperscript{13} investigated the reduction of crystalline and amorphous SiO\textsubscript{2} using simultaneous thermogravimetric analysis (TGA) and mass spectroscopy. They concluded that this reaction has two stages. First, SiC is produced by small amounts of SiO, then SiO\textsubscript{2} reacts with SiC and produces SiO or Si. Several researchers\textsuperscript{17–26} indicated that this reaction involves SiO\textsubscript{2} effects as an intermediate component. Filsinger and Bourrie\textsuperscript{27} studied most possible reactions between SiO\textsubscript{x} and C compounds using the TGA at temperatures below 2273 K. They found four sequential intermediate reactants. They investigated 17 possible reactions,\textsuperscript{28} specially, two reaction schemes that proposed by Muller et al.\textsuperscript{29} and Schei.\textsuperscript{30–33} Wiik and Modzfeldt\textsuperscript{34} investigated this reaction at 1831 K in CO and Ar atmospheres using TGA. They considered a reaction between SiO\textsubscript{2} and CO to produce SiO and CO\textsubscript{2} and a reaction between CO\textsubscript{2} and C to produce CO. Baird and Taylor\textsuperscript{35} measured the pressure of produced CO in this reaction at temperatures between 1673 and 1853 K to obtain the activity of SiO\textsubscript{2} in slug solution. Klinger et al.\textsuperscript{36} had a similar study in vacuum condition at the temperatures 1718 to 2038 K. They observed that, at low temperatures, the reaction followed a linear rate law (i.e. zero-order reaction) and at higher temperatures, the reaction showed a nucleation and growth process. Therefore, this reaction involves as a key intermediate SiO molecules and its subsequent reaction with C.

Attending to the existence of several differences among the presented theories in the mentioned relevant references, and also importance of improving the production rate and also quality of the produced SiC in different processes, such as the Acheson process, it is necessary to present a complete study for obtaining the mechanism of this reaction. In this study, the stoichiometric reaction of SiO\textsubscript{2} and C has been investigated at temperatures between 1533 and 1966 K. First, all the thermodynamically possible reactions in this reduction have been obtained using their Gibbs energy changes (i.e. \( \Delta G \)). These reactions help us to recognize the possible mechanisms for this reduction. Then, we investigated the rate of this reduction using a TGA experimental study to obtain the possible reaction mechanisms.

**Experiments**

In this section, experimental procedure for reduction of silica using carbon powder is described. Carbon powders had a high purity (more than 99 %w total carbon, from Merck
Company; silica powder (crystalline quartz from Mount Rose, Canada) contained more than 95%w SiO$_2$; and Helium gas with 99.999% purity (from Air Products Company) was used to minimize effects of impurities on the reaction. Each of the solid particles having a nominal particle size of 1 μm.

A commercial TGA device with a gas detector at the exhaust line was used to reduce a mixture of 1 mol of silica powder by 3 mol of carbon powder in a small crucible that contained 100 mg of mixed powder, which provides a solid bed with 9-mm height and 6-mm diameter. A computer-recorded weight change of the solid content of the crucible over time and the reaction temperature was measured using accurate thermocouples that were located at the outside surface of the crucible inside the reactor. Flowing of the helium gas caused a ±0.2-K temperature variation during the experiments. Exhaust gas of the reactor passed through a gas detector for measuring the CO and CO$_2$ content of this gas. The furnace heated up the reactor with the rate of 50 K.min$^{-1}$ to the target temperature, and at a same time, 100 L.hr$^{-1}$ of helium purged air content of the reactor.

**Results and discussions**

**Thermodynamic**

Thermodynamic approach involves study of equilibrium states. This study tests the possibility of a reaction and indicates whether this reaction is a spontaneous process or not. Changes of the Gibbs energy of a reaction may approve the possibility of occurrence of this reaction in the evaluated thermodynamic condition. Figure 1 displays the equilibrium curves relevant to possible equilibrium compositions in the solid, liquid, and gas phases at the temperature range of 1566 to 1933 K relevant to the reaction between 1000-mol SiO$_2$ and 3000-mol C.$^{37}$ Based on this graph, the reduction of these solid particles produces solid Si and SiC, and also CO and SiO gases at these temperatures. However, escaping of these gases from the formed
pores in the reduced solid phase prevents a complete equilibrium conditions occurrence. In addition, other components, such as CO₂ gas, have intermediate effects on the occurred reactions for producing these components.

Spontaneous processes have non-positive ΔG at constant temperature and pressure. Figure 2 shows ΔG of the possible reactions relevant to this reduction at different temperatures.³⁷ (Some greyscale figures have been presented in this article. In these figures, the darkness of each line or bar indicates the importance of them.) As seen in this figure, the following reactions have chances of occurrence in this reduction (the reactions with ΔG < 0, which have been shown with dark lines in this figure)

\[
\begin{align*}
\text{SiO}_2 + 3\text{C} & \leftrightarrow \text{SiC} + 2\text{CO(g)} \quad (1) \\
\text{SiO(g)} + \text{C} & \rightarrow \text{Si} + \text{CO(g)} \quad (2) \\
\text{SiO(g)} + 2\text{C} & \rightarrow \text{SiC} + \text{CO(g)} \quad (3) \\
2\text{SiO(g)} + 3\text{C} & \leftrightarrow 2\text{SiC} + \text{CO}_2(g) \quad (4) \\
\text{SiO(g)} + \text{CO(g)} & \rightarrow \text{SiO}_2 + \text{C} \quad (5) \\
\text{SiO(g)} + \text{CO}_2(g) & \rightarrow \text{SiO}_2 + \text{CO(g)} \quad (6)
\end{align*}
\]
This list indicates that the only way for producing SiC in this reaction is the reaction of solid carbon (and not CO or CO₂ gases) with the silicon components (i.e. Si, SiO, or SiO₂). Therefore, SiC is formed by the reaction of solid Si or SiO₂ at the surface of the carbon particles, or by the reaction of diffused SiO gas with C inside graphite particle. Therefore, CO and CO₂ have no direct effects on the SiC production, and these components may have intermediate effects on this reaction.

**Mechanism**

The reaction of carbon with silica removes its oxygen contents and decreases its weight. Therefore, a common method for study progress of this reaction is TGA. The extent of this reaction can be defined by comparing weight loss of the sample at any time (Wᵢ− W, where Wᵢ is the initial weight of the sample) with the final amount of weight loss (Wᵢ− Wᵢ) when the weight loss is stopped experimentally (X = Wᵢ− W/Wᵢ− Wᵢ). Figure 3 shows the measured weight loss of the solid sample, detected carbon monoxide concentration (CₖO) in the exhaust gas, and their differential variations with temperature, in a non-isothermal TGA experiment. It is clear that there are two different mechanisms for this reaction. At temperatures less than 1750 K, the solid sample weight loss and the increment of the CO concentration are too low and linear with a constant slope of their variations with changes of the reactor temperature, vice versa their variations at the temperatures more than 1750 K. It is also observed that the final weight changes of the solid sample at the temperatures less than 1750 K were too low (i.e. maximum 5%), which indicates low progress of this reaction at these temperatures, in comparison with its changes at temperatures more than 1750 K (that was more than 80%). Therefore, the defined X for this reduction indicates reaction progresses with different Wᵢ at different temperatures less and more than 1750 K.

The reduction kinetics of silica with carbon has been studied using the existing models (see Table 139–54), which are based on a single-step kinetic equation:

\[
\frac{dX}{dt} = k(T)f(X)
\]
where \( t \) is time, \( T \) is temperature, \( X \) is solid conversion and \( f(X) \) is reaction model as a function of the solid conversion, and \( k(T) \) is reaction rate constant as a function of temperature. Dependency of this constant to the temperature has been defined by the Arrhenius equation \( k = k_0 \exp(-E/RT) \). Where \( E \) and \( R \) are activation energy and universal gas constant, respectively. Substituting these functions into equation (17) and isothermal integration of this equation give the following equation

\[
g(x) = \int_0^x [f(x)]^{-1} \, dx = k_0 \exp\left(\frac{-E}{RT}\right) t
\]

which \( k_0 \) is pre-exponential factor and \( g(x) \) is an integral form of the reaction model. One of the common methods of mechanism analyzing of such reactions is fitting the experimental data (isothermal conversion vs time) with the conventional models and validating this fitting using correlation coefficient.\(^5\)

Figures 4–8 show fitting of the presented models in Table 1 with the experimental reduction data at different temperatures. The obtained \( k \) values by these models and their relevant \( R^2 \) have been presented in these figures. Fitted curves that have more importance (attending to the calculated \( R^2 \) values) have darker lines in these figures. Figures 9 and 10 show logarithmic form of the calculated \( k \) versus \( T^{-1} \) for the reactions at temperatures less and more

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**Figure 3.** Measured weight loss of the solid sample, detected carbon monoxide concentration in the exhaust gas, and their differential variations with temperature.
than 1750 K, respectively. The accordance of these fitted straight lines with the experimental data (that were shown as markers in these figures) has been presented by R² values. Lower importance models (based on their R² values) were presented with lighter lines in this figure. Now, the reaction activation energy and pre-exponential factor can be calculated by each one of these models. Figures 11 and 12 compare the calculated activation energies as the vertical bars for the reactions at temperatures less and more than 1750 K, respectively. Width of each bar has been calculated using the presented values of R² in Figures 9 and 10, and the darkness of each bar has been calculated using the average value of the presented values of R² in Figures 4–8 for that model. Therefore, the darkness of each bar shows the accordance of that model with the experimental data and the width of each bar indicates the acceptability degree of calculated E value. It is clear from these figures that the reaction has suitable accordance with different models and follows their defined mechanisms at temperatures less and more than 1750 K. This reduction follows a combination of the nucleation and growth and also the geometrical contracting area mechanisms, and it is a second-order reaction at the temperatures lower than 1750 K, which indicates that the controlling step of this reduction process is the chemical gas–solid or solid–solid reaction at the surface of the carbon

Table 1. The conventional models39–54 for solid-state reactions to determine reduction mechanism of silica with carbon.

| Number | Model                      | f(x)                     | g(x)                     |
|--------|----------------------------|--------------------------|--------------------------|
| 1      | Power law                  | 2 x ½                    | x³                      |
| 2      | 2x²                        | x²                      |
| 3      | 3x⁴                        | x⁴                      |
| 4      | 4x⁴                        | x⁴                      |
| 5      | Avrami-Erofe‘ev            | ¾ (1 – x)[−ln(1 – x)]™½ | [−ln(1 – x)]²           |
| 6      |                            | 2(1 – x)[−ln(1 – x)]™½  | [−ln(1 – x)]²           |
| 7      |                            | 3(1 – x)[−ln(1 – x)]™³  | [−ln(1 – x)]³           |
| 8      |                            | 4(1 – x)[−ln(1 – x)]™⁴  | [−ln(1 – x)]⁴           |
| 9      | Contracting area           | 2(1 – x)½                | 1 – (1 – x)²            |
| 10     | Contracting volume         | 3(1 – x)³                | 1 – (1 – x)³            |
| 11     | 1D diffusion               | (2x)⁻¹                  | x²                      |
| 12     | 2D diffusion               | [−ln(1 – x)]⁻¹           | (1 – x)ln(1 – x) + x   |
| 13     | 3D diffusion               | ¾ (1 – x)[1 – (1 – x)²]⁻¹ | [1 – (1 – x)]³²       |
| 14     | Ginstling–Brounshtein      | [−ln(1 – x)]⁻¹           | 1 – ½ x – (1 – x)²    |
| 15     | Zero-order                 | 1                       | x                       |
| 16     | First-order                | (1 – x)                  | −ln(1 – x)             |
| 17     | Second-order               | (1 – x)²                 | (1 – x)⁻¹ – 1          |
| 18     | Third-order                | (1 – x)³                 | ½ [(1 – x)⁻² – 1]      |
Figure 4. Fitting of the power law models with the experimental data at different temperatures.

Figure 5. Fitting of the Avrami-Erofe’ev models with the experimental data at different temperatures.
Figure 6. Fitting of the geometrical contraction models with the experimental data at different temperatures.

Figure 7. Fitting of the diffusion models with the experimental data at different temperatures.
Figure 8. Fitting of the reaction-order models with the experimental data at different temperatures.

Figure 9. Logarithmic form of $k$ versus $T^{-1}$ at temperatures less than 1750 K.
Figure 10. Logarithmic form of $k$ versus $T^{-1}$ at temperatures more than 1750 K.

Figure 11. Calculated activation energy of SiO$_2$-Carbon reduction at temperatures less than 1750 K, using the presented models in Table I.
particles. On the other hand, at more temperatures, this reduction is a first-order reaction and follows the 3D diffusion mechanism, which indicates that the reaction rate is fast enough at these temperatures and rate of the diffusing of SiO gas inside the carbon particles controls the total rate of the reaction.

**Conclusion**

In this study, the reaction kinetics of carbon reduction of silica particles was investigated. For this purpose, a TGA unit was used to study the reaction kinetics at the temperature range of 1566 to 1933 K. Fitting method was used to obtain the mechanism of this reaction. The spontaneity of the possible reactions has been tested using the thermodynamic concepts attending to the change of their Gibbs energy. It was resulted that the only way for producing SiC in this reaction was the reaction of the silicon components at the surface or by diffusion inside the carbon particles, and CO and CO₂ have no direct effects on this production. It was also resulted that the controlling step of this reduction process at temperatures lower than 1750 K is the chemical gas–solid or solid–solid reaction at the surface of the carbon particles. At temperatures more than 1750 K, the reaction rate of this reduction process is fast enough and the rate of SiO diffusing inside the carbon particles controls the total rate of the reaction.

**Declaration of conflicting interests**

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