Finely dispersed silicon carbide synthesis model in the electrothermal reactor with periodic batch loading

V S Kuzevanov, S S Zakozhurnikov, G S Zakozhurnikova, A B Garyaev

1 National Research University «MPEI», Volzhsky branch, Russia, 404110 Volzhsky, Lenin Ave., 69
2 MIREA – Russian Technological University, Russia, 119454 Moscow, Vernadsky Avenue, 78.
3 Volgograd State Technical University, Russia, 400005 Volgograd, Lenin avenue, 28
4 National Research University «MPEI», Russia, 111250 Moscow, Krasnokazarmennaya, 14
galya.vlz@mail.ru

Abstract. Fine silicon carbide is used in metallurgy, electronic devices and the aviation industry. Reactors where the synthesis of finely dispersed carbides is organized in an electrothermal fluidized bed (ETKS reactors) have several advantages over resistance furnaces used for mass production of carbides. The basic advantage is the direct production of a finely dispersed fraction of carbide-containing particles with lower specific costs of electric energy. In this article, there were studied non-stationary processes in an ETKS reactor operating in the mode of periodic loading into the reaction volume of components of chemical reactions for the synthesis of silicon carbide: finely dispersed carbon-containing particles and SiO2 particles (batch). A mathematical model of synthesis for non-stationary conditions is developed. Relations are obtained for calculating changes in the process of silicon carbide synthesis not only of the sizes of solid (liquid) particles participating in chemical reactions, but also of the concentrations of volatile components that affect the rates of these reactions in the working volume of the ETKS reactor. There were carried out calculations to identify the influence of determining factors on the yield of the final product and the analysis of these results. A comparison of the calculation results with the available experimental data on the yield of silicon carbide in an ETKS reactor with a periodic charge loading was presented.

1. Introduction
Reactors where the synthesis of finely dispersed carbides is organized in an electrothermal fluidized (fluidized) bed (ETKS reactors) have several advantages over resistance furnaces used for the mass production of carbides. The basic advantage is the direct production of a finely divided fraction of carbide-containing particles with lower specific costs of electric energy [1], [2], [3].

In [4], a model of continuous synthesis of silicon carbide in a fluidized bed was proposed. When creating the model, the condition of stationary production of the final product in the fluidized reaction bed was used, in particular, the concentration of volatile components of chemical reactions was unchanged.
In this paper, there were presented the model and the results of studies of non-stationary processes based on it in the ETKS reactor operating in the periodic mode of loading into the reaction volume of the components of chemical reactions for the synthesis of silicon carbide: finely dispersed carbon-containing particles and SiO\textsubscript{2} particles.

2. **The main provisions of the model of non-stationary process in the reactor ETKS**

2.1. **System status after loading components**
There were considered that immediately after loading the following conditions were met:

- heating of all carbon-containing particles was completed;
- the temperature of the fluidizing gas \( T \) was higher than the temperature of the onset of the chemical reaction of carbide formation;
- the temperature of free carbon-containing particles \( c_1 \) was equal to the temperature of the fluidizing gas;
- the temperature of the charged particles of SiO\textsubscript{2} was equal to the melting temperature of silicon dioxide \( T_{\text{m}} \);
- the temperature of the carbon-containing particles \( c_2 \), which entered into interaction (contact) with SiO\textsubscript{2} particles, was equal to the temperature \( T_{\text{m}} \).

We assumed that particles of all solid components of the production process had an initial spherical shape. The initial size of all carbon-containing particles \( (c_1 \text{ and } c_2) \) was the same, the radius of the particles was equal to \( R_c \). The initial radius of all SiO\textsubscript{2} particles was the same and equal to \( R_{\text{SiO2}} \).

2.2. **Silicon Carbide Synthesis Process and Model Assumptions**
- the synthesis process of silicon carbide is mainly determined by the following chemical reactions [1], [4]:
  \[
  \begin{align*}
  \text{C} + \text{SiO}_2 &= \text{SiO} + \text{CO} \quad (1) \\
  2\text{C} + \text{SiO} &= \text{SiC} + \text{CO} \quad (2)
  \end{align*}
  \]
- the participants in the synthesis process are solid carbon-containing particles \( c_1 \) and \( c_2 \), as well as SiO\textsubscript{2} particles and a fluidizing gas of varying composition due to the generation of volatile components in reactions (1) and (2);
- particles of all solid (liquid) components retain their spherical shape;
- the amount of carbon-containing particles \( c_2 \) attached to the evaporating particles of SiO\textsubscript{2} does not change;
- solids with fluidizing gas are not carried out; the gas composition changes only due to the generation of gaseous components — CO and SiO;
- the evaporation of any solid SiO\textsubscript{2} particle is limited by the influx of heat to it due to thermal conductivity, convection, and the radiation component; the gas phase of SiO\textsubscript{2,g} remains attached to the system of interacting particles \( c_2 \) and SiO\textsubscript{2};
- the reaction of formation of SiO with the participation of carbon-containing particles of \( c_2 \) can continue with the complete evaporation of solid particles of SiO\textsubscript{2}, but in the presence of non-removable vapors of SiO\textsubscript{2,g};
- carbon-containing particles \( c_1 \) participate in the reaction of formation of silicon carbide and do not enter into another reaction;
- mixing of particles in the reaction volume does not destroy the system of interacting particles \( c_2 \) and SiO\textsubscript{2} or \( c_2 \) and SiO\textsubscript{2,g}.

The assumptions were the basis for using the phenomenological approach in the analysis of the non-stationary process [5] of SiC synthesis, in particular, considering the transformation of only single particles representing groups of particles of solid components of chemical reactions and changing the average fluidization gas parameters \( \tilde{V}_{\text{RO}} \) for the reaction volume.
3. The mathematical formulation of the model
The main parameters that determine the dynamics of the production of finely dispersed silicon carbide, in addition to the temperature and composition of the reaction medium, as well as the conditions of heat transfer, are the sizes of dissimilar particles and the concentration of participants in chemical reactions.

3.1. Variation of the radii \( r_i \) of dispersed particles
It can be shown [4], [6] that, within the framework of the adopted model, a differential equation is valid that describes the change in the size of a spherical particle, written in the generalized form:

\[
\frac{dr_i}{dt} = -\Psi^*_i f_{r,i},
\]

where "i" is the particle type index: \( c_1, c_2 \) or SiO2; \( \Psi^* \) is a constant; \( f_r \) are the functions of time; \( \tau \) is the time.

For particles that have undergone the formation of silicon carbide \( (c_1) \), [4]:

\[
\Psi^*_{c1} = 2 M_c c_k D_1/\rho_c,
\]

\[
f_{r,c1} = C_{SiO},
\]

where \( M_c \) is the molar mass of carbon; \( c_k \) is the carbon fraction in the carbon-containing particle; \( k_{D1} \) is the rate constant of the chemical reaction \( (2) \); \( C_{SiO} \) — concentration of gaseous SiO; \( \rho_c \) is the density of the carbon-containing particle.

For \( c_2 \) particles attached to evaporating SiO2 particles, [4]:

\[
\Psi^*_{c2} = M_c c_k D_2/\rho_c,
\]

\[
f_{r,c2} = C_{SiO2},
\]

where \( k_{D2} \) is the rate constant of the chemical reaction \( (1) \); \( C_{SiO2} \) — vapor concentration of SiO2.

The change in the radius of the SiO2 particle is associated with the intensity of evaporation into the reaction volume from the melting surface, limited by the influx of heat to the particle from the outside. In the case of a constant heat flux density \( q \), the load to the particle is valid, [4], [7]:

\[
\Psi^*_{SiO2} = b/p_{SiO2},
\]

\[
f_{r,SiO2} = (r_{SiO2} + \Delta h_{SiO2}/q b)^{-1}.
\]

Marked here

\[
b = \frac{2 M_{SiO2} \sigma p_{SiO2}}{RT p_{SiO2}^*} \left( \frac{\bar{R}T}{2 \pi M_{SiO2}} \right)^{1/2},
\]

where \( \bar{R} \) is the universal gas constant; \( \sigma \) is the surface tension of SiO2; \( M_{SiO2} \) is the molar mass; \( \Delta h_{SiO2} \) is the heat of the phase transition of SiO2; the indices "'" and """" refer to the densities of the liquid and vapor phases of SiO2 on the saturation line; \( T \) is the absolute temperature of the process.

3.2. Change in concentrations of gaseous components of chemical reactions
The change in the concentration of gaseous components of chemical reactions over time fundamentally depends on the loading order of particles \( c_1, c_2 \) and SiO2. We took the option of organizing the synthesis of silicon carbide, when all carbon-containing particles are loaded at a time, and solid SiO2 particles are introduced into the reaction volume with a certain periodicity in relatively small portions until the formation of SiC is completed [3]. We believed that in this loading mode, the concentrations of the gaseous components \( C_{SiO} \) and \( C_{SiO2} \) of the synthesis process are proportional to the relative size \( R_{i1}^{rel} \) of the solid carbon-containing particle participating in the chemical reaction, i.e. \( C_{SiO} \sim R_{c1}^{rel}, C_{SiO2} \sim R_{c2}^{rel} \). Moreover,

\[
R_{i1}^{rel} = \frac{r_i - r_{cr}}{r_i - r_{cr}^o},
\]

where the index "i" corresponds to the index "c1" or "c2"; the "o" index refers to the value of the particle radius at the time of the introduction of the next portion of SiO2; the "cr" index reflects the size of the particle with complete absorption of the gaseous participant in the reaction.

Consideration of the generation of SiO by reaction \( (1) \), as well as the absorption of SiO in the reaction of formation of silicon carbide \( (2) \) and removal of SiO from the reaction volume with a fluidizing gas,
gives the following equation for determining the change in $C_{SiO}$ in the period $\Delta \tau$ between two consecutive inputs of SiO:

$$C_{SiO} = C_{SiO}^0 \eta_{c_1} \exp \left( -L_{c_1} \eta_{c_1} \tau \right).$$

Here

$$L_{c_1} = \frac{\Psi_{c_1}^* C_{SiO}^0}{\rho_{c_1} \tau_{c_1} \eta_{c_1}} - f_1(\tau_{c_1}^{cr})$$

$$\left( r_{c_1}^{cr} \right)^3 = \left( r_{c_1}^0 + f_1(\tau_{c_1}^{cr}) \right)^3$$

where $f_1$ is the function of time $\tau_{c_1}^{cr}$ the total evaporation of a portion of SiO$_2$ and times $\tau_{c_1}^{cr}$, $\tau_{c_1}^{cr}$ effective flow of chemical reactions (2) and (1), respectively; $f_2$ is the function of the portioned flow rate of particles SiO$_2$ ($\delta$ is the fraction of the mass of one portion in the total mass of SiO$_2$ involved in the synthesis); $f_3$ is the function of the volumetric flow rate $V_{in}$ of the fluidizing gas, the rate of the carbide formation reaction and the radius $r_{c_1}^{cr}$ characterizing the completion of the effective interaction of the reaction components (2).

The concentration $C_{SiO}$ of the gaseous component of SiO$_2$ of the synthesis process fundamentally depends on the number $p_{c_2}$ of particles $c_2$ attached to the evaporating particles of SiO$_2$. We assume that for $p_{c_2} = 1$, upon instant evaporation of the introduced portion of SiO$_2$, a local region of chemical interaction of reaction components (1) with the maximum possible concentration $C_{SiO} = C_{SiO}^n$ ("n" is the saturation index) is provided. Assuming that the particle system formed after the first portion of SiO$_2$ particles is introduced into the reaction volume does not break down, and the gaseous component of the SiO$_2$ reaction belonging to this system is not removed from the reaction volume, we obtain the following equation for calculating $C_{SiO}$ in the period $\Delta \tau$ between two consecutive inputs of SiO:

$$C_{SiO} = C_{SiO}^n \eta_{c_2} \exp \left( -L_{c_2} \eta_{c_2} \tau \right).$$

Here

$$L_{c_2} = \frac{\Psi_{c_2}^* C_{SiO}^0}{\rho_{c_2} \tau_{c_2} \eta_{c_2}} - f_2(\tau_{c_2}^{cr})$$

$$\left( r_{c_2}^{cr} \right)^3 = \left( r_{c_2}^0 + f_2(\tau_{c_2}^{cr}) \right)^3$$

where $f_2$ is the function of the time of complete evaporation of a portion of SiO$_2$ and the time of effective interaction of the components of the chemical reaction (1).

4. Design study of the synthesis process and verification of the SiC synthesis model

4.1. Initial data

The calculation of the synthesis of finely divided silicon carbide was carried out according to an algorithm constructed according to the above equations for the connection of process parameters. In numerical calculations, the total amount of $\delta = 10$ was assigned equal to the mass of SiO$_2$ portions of identical mass introduced into the reaction volume. The conditions are indicated when the chemical reactions (1) and (2) can be considered effective:

$$C_{SiO}^0 \geq C_{SiO} \geq 0.01 C_{SiO}^0$$

$$C_{SiO}^0 \geq C_{SiO} \geq 0.01 C_{SiO}^0$$

The limiting value of the concentration $C_{SiO}^n$ in the system of attached particles SiO$_2$ and $c_2$ was taken from the saturation state taking into account the relative number of particles $c_2$:

$$C_{SiO}^n = \frac{\rho_{SiO}}{M_{SiO} \times p_{c_2}}$$

The maximum value of the SiO gas concentration was calculated by the ratio

$$C_{SiO} = \frac{\rho_{SiO} \times 273 \times r_{c_2}^0 \times \gamma}{\delta}$$

where the "norms" index corresponds to normal conditions; the factor in parentheses takes into account the effect on the limiting concentration of the surface area of the generating particle SiO particles $c_2$; $\gamma$ is a correction factor that takes into account the technological features of $\tilde{V}_{RO}$. 

4
The initial mass adopted in the calculations for the carbon-containing particles \((c_1, c_2)\) loaded in the reaction volume with the size \(R_c = 1.075 \cdot 10^{-4} \text{ m}\) was 0.5 kg. The total mass of SiO\(_2\) loaded in portions with a particle size of \(R_{\text{SiO}_2} = 6.5 \cdot 10^{-5} \text{ m}\) is 0.25 kg. The process temperature is \(T = 1873 \text{ K}\).

Figure 1 shows the time variation of the sizes of particles \(c_1, c_2\) and the radius of the carbide-forming particle \(R_{\text{SiC}}\) involved in the synthesis of silicon carbide. Figure 2 demonstrates the change in the dynamics of carbide formation with a 4-fold decrease in the concentration of \(C_{\text{SiO}}^o\) in comparison with the value obtained from dependence (15).

4.2. Model verification

Variant calculations were carried out with the model checked for adequacy to physical ideas about the SiC synthesis process.

The initial data on the parameters of the charge components, the conditions of the formation of a fluidized bed, heat transfer, and the characteristics of chemical reactions in the calculations according to the author's model were taken from the following publications: [8], [9] — SiO\(_2\) parameters in the liquid and gaseous state; [6], [10] - velocity of the beginning of fluidization; [11] - heat supply to the liquid particle; [12] and [13] is the reaction rate constant (1); [14] is the exponential factor and activation energy for the chemical reaction (2).

![Graph](image)

**Figure 1.** The change in the size of carbon-containing particles in the synthesis of SiC.
1 - changing \(r_{c_1}\); 2 - changing \(r_{c_2}\); 3 - changing \(R_{\text{SiC}}\); \(p_{c_2} = 4\); \(C_{\text{SiO}}^o\) - according to equation (15) with \(\gamma = 1\).
Figure 2. Resizing of carbon-containing particles during the synthesis of SiC. 
1 - changing $r_{c1}$; 2 - changing $r_{c2}$; 3 - changing $R_{SiC}$; $p_{c2} = 4$; $C_{SiO2}^0$ - according to equation (15) with a correction factor $\gamma = 0.25$.

The calculation results were compared with the results of an experimental study of the synthesis process in an installation with an electrothermal fluidized bed (ETKS), [2], [3]. The data on the yield of silicon carbide in experiments at a temperature of 1600–1650 °C were taken from [3]; the change in the parameters of the carbonization process over time was analyzed in [2]. The silicon carbide yield according to the author's model was calculated according to the dependence:

$$m_{SiC} = m_{c1} \frac{M_{SiC}}{2M_C} \left[1 - \left(\frac{r_{c1}^{out}}{R_{c1}}\right)^3\right],$$

(16)

where $m_{c1}$ is the mass of the loaded particles $c_1$; $r_{c1}^{out}$ - value $r_{c1}^{cr}$ after entering the last portion of SiO2. From equation (16) it is easy to obtain the relation for the radius $R_{SiC}$ of a carbide-forming particle with a carbon core $r_{c1}^{cr}$.

A comparison of the calculation results (Fig. 2) and experiments shows their agreement with satisfactory quantitative agreement with the data of [3] on the yield of silicon carbide: and the data of [2] on the duration of the synthesis process:

- the yield of silicon carbide, as a percentage of the residual mass of the charge, according to the calculation - 25.3, according to the experiment - 22.9;
- the average radius of the carbide-forming particle $R_{SiC}$ in the residual charge was calculated to be $0.105 \cdot 10^{-3}$ m, and according to the experiment, $0.118 \cdot 10^{-3}$ m (weighted average value).

Note that the yield of the final product (mass of SiC) weakly depends on the value of $C_{SiO2}^0$, and is determined mainly by the total amount of SiO2 introduced into the reaction volume, but the concentration of $C_{SiO2}^0$ dictates the duration of the synthesis process, as can be seen from a comparison of fig. 1 and fig. 2. It is obvious that the correction factor $\gamma$ depends on many factors, including the design features of the reaction volume, the unevenness of the temperature field and the distribution of solid particles in the volume, the discreteness and organization of the input of SiO2 particles.

5. Conclusion

Within the framework of the phenomenological approach, a mathematical model and an algorithm for calculating changes in the main parameters of the synthesis of finely dispersed silicon carbide in an electrothermal reactor have been developed. Relations have been obtained for calculating the sizes of particles involved in the synthesis and the concentration of volatile components that affect the rates of
chemical reactions of SiC formation. Satisfactory agreement between the calculated and experimental data on the yield of the final product in the ETKS reactor was shown. The necessity of adjusting the model peak value of the concentration $C_{SiO}$ to determine the correspondence of the calculated synthesis time with the exposure time of the charge in the ETKS reactor was noted.

References
[1] Borodulia V and Vinogradov L et al 2012 Carbidothermal reduction of SiO2 and the formation of silicon carbide in an electrothermal fluidized bed Heat and mass transfer pp 121-127.
[2] Borodulia V and Vinogradov L et al 2015 Synthesis of silicon carbide in an electrothermal reactor with a fluidized bed of carbon particles Combustion and plasma chemistry tom 13 №2 pp 92-102.
[3] Borodulia V and Grebenkov A et al 2019 Features of the formation of various structural modifications of silicon carbide during its carbothermal synthesis in an electrothermal fluidized bed reactor Heat and Mass Transfer
[4] Kuzevanov V and Garyaev A et al 2019 Model of continuous production of fine silicon carbide Materials Science and Engineering International Workshop "Advanced Technologies in Material Science, Mechanical and Automation Engineering" (MIP: Engineering – 2019". Krasnoyarsk Science and Technology City Hall of the Russian Union of Scientific and Engineering Associations) p 32106
[5] Ozherelkova L and Savin E et al 2019 The temperature dependence of unsteady heat conduction in solids Rossiyskiy tehnologicheskiy zhurnal (Russian Technological Journal) 7(2) pp 49-60
[6] Gaevoy V and Ivanov E et al 1996 A simplified model of the process of burning coal in a fluidized bed Mathematical modeling 8 10 pp 71-82
[7] Dohov M 2006 Calculation of the time of evaporation of dispersed particles Fundamental Research 10 pp 65-66.
[8] losilevskiy I and Gryaznov V et al 2014 Properties of high-temperature phase diagram and critical point parameters in silica High Temperatures - High Pressures 43 pp 227–241.
[9] Champagnon B and Martinez V et al 2007 Levelut Density and density fluctuations anomalies of SiO2 glass: comparison and light scattering study Philosophical Magazine 87 (3-5) pp 691-695
[10] Wallis G M 1972 One-dimensional two-phase flows (Publishing house "Mir")
[11] Bukur D and Amundson N 1981 Fluidized-bed char combustion diffusion limited models Chemical Engineering Sciences, v.36 pp 1239-1256
[12] Feng Ni 2015 Kinetics of the reaction between quartz and silicon carbide in different gas atmospheres Light Metals Silicon and Ferroalloy Production Supervisor: Merete Tangstad IMTE Department of Materials Science and Engineering Submission date: June p 90.
[13] Li X and Zhang G et al 2016 Reduction of quartz to silicon monoxide by methane-hydrogen mixtures Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science 47:2197.
[14] Barabanov N and Zemskova V et al 1998 Mathematical modeling of the process of carbidization of synthetic foams Chemistry and chemical technology tom 41 release 5 pp 32-34.