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RESEARCH ARTICLE

Effect of leakage of volatile synthesis products on silicon carbide yield in an electrothermal fluidized bed reactor

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Abstract

Objectives. To calculate the effect of leakage of volatile synthesis products on silicon carbide yield in an electrothermal fluidized bed reactor, as well as to develop a general model of the synthesis of finely divided silicon carbide. This will be achieved by particularizing a mathematical model of leakage of volatile products of chemical reactions from the reaction volume of the reactor with the fluidizing inert gas.

Methods. As a method to produce silicon carbide, synthesis in an electrothermal fluidized bed was studied. The model of leakage of volatile products was validated by comparing the calculation results with existing experimental data on the SiC synthesis in a high-temperature fluidized bed reactor. The comparison parameters were: mass yield of silicon carbide, and the total synthesis time in a reactor with batch loading of silicon dioxide into the reaction volume.

Results. The value of the parameter p in the general model of SiC synthesis in a fluidized bed was established. The parameter p is equal to the ratio of the number of carbon-containing particles involved in the formation of SiO, to the total number of silicon dioxide particles. It also characterizes the composition of stable complexes of particles of the charge at various operating temperatures of the fluidized bed. The discrepancy between the calculated and experimental values of the masses of the synthesized silicon carbide was shown not to exceed 15.5% at a high temperature of the fluidized bed (T = 1800°C) and decreases with a decrease in the operating temperature to 4.7% at T = 1450°C.

Conclusions. The general computational model for silicon carbide synthesis with a built-in procedure for calculating the leakage of volatile products of chemical reactions enables the variants of SiC production in electrothermal fluidized bed reactors to be analyzed. In this case, it is important to establish an energy-efficient working cycle without preliminary expensive experimental studies.

Keywords

synthesis, silicon carbide, fluidized bed, charge, volatile reaction products, model, SiO leakage

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НАУЧНАЯ СТАТЬЯ

Влияние утечки летучих продуктов синтеза на выход карбида кремния в реакторе электротермического кипящего слоя

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Аннотация

Цели. Рассчитать влияние утечки летучих продуктов реакций карботермического синтеза карбида кремния на массовый выход конечного продукта и развить общую модель синтеза мелкодисперсного карбида кремния в части конкретизации математической модели утечки летучих продуктов химических реакций из реакционного объема установки с ожижающим инертным газом.

Методы. В качестве способа получения SiC рассмотрен процесс его производства в электротермическом кипящем слое. Верификация модели утечки летучих продуктов проведена путем сравнения результатов расчета с имеющимися экспериментальными данными по синтезу SiC в реакторе высокотемпературного кипящего слоя. Параметрами сравнения являлись массовый выход карбида кремния и суммарное время синтеза при последовательных вводах порций диоксида кремния в реакционный объем реактора.

Результаты. Конкретизировано значение параметра p общей модели синтеза SiC в кипящем слое — параметр p равен отношению числа углеродосодержащих частиц, участвующих в образовании SiO, к общему числу частиц диоксида кремния и характеризует состав устойчивых комплексов частиц шихты при разных рабочих температурах псевдоожиженного слоя. Показано, что отклонение расчетных и экспериментальных значений масс карбида кремния, получаемого в результате синтеза, не превышает 15.5% при высокой температуре кипящего слоя (T = 1800°C) и уменьшается при снижении рабочей температуры: 4.7% при T = 1450°C.

Выводы. Общая расчетная модель синтеза карбида кремния с встроенной процедурой расчета утечки летучих продуктов химических реакций позволяет проводить анализ вариантов производства SiC в реакторах электротермического кипящего слоя. Важным при этом является организация энергоэффективного рабочего цикла без предварительных дорогостоящих экспериментальных исследований.

Ключевые слова

синтез, карбид кремния, кипящий слой, шихта, летучие продукты реакций, модель, утечка SiO

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INTRODUCTION

Analysis of complex high-temperature processes in heterogeneous systems with chemically reacting components is efficient, if it combines experimental and analytical research methods [1–6]. Mitrofanov *et al*. [7, 8] carried out an experimental and theoretical study of the formation of a fluidized bed of dispersed material, in order to determine patterns and relationships between hydrodynamic processes and the electrical conductivity of the bed. A mathematical model was constructed to predict the structure of the region of fluidized particles in the presence of internal local heat sources. However, in those works [7, 8], the area under study was not reactive; i.e., neither conversion of components was considered, nor the yield of any product.

Borodulya *et al.* [9–11] studied the patterns of formation of silicon carbide in an electrothermal fluidized bed (ETFB) [12] and performed experiments to find process parameters that ensure the necessary properties of the resulting product; however, no theoretical analysis of physicochemical processes in the synthesis of SiC in the ETFB reactor was made in those works.

In our previous works [13–15], we developed a model of the synthesis of finely divided silicon carbide in a high-temperature fluidized bed of components of chemical reactions. This reaction volume consists of randomly moving solid particles, a fluidizing gas, and volatile products of chemical reactions. Together with the fluidizing neutral gas, volatile reaction products are also removed from the reaction volume, which undoubtedly affects the efficiency of the reactor.

In this work, we proposed a model of the process of leakage of SiO, the most important component of the SiC synthesis reaction, which significantly affects the yield of silicon carbide.

Basic provisions of the synthesis model

An ETFB reactor with electrical energy supply was considered, where the reaction volume was designed as a fluidized bed. The solid components of the reaction volume (charge) after loading into the reactor were particles of carbon-containing material (coal or coke, Rexyl) and particles of silicon dioxide (river or quartz sand) [16].

The maximum operating temperature in the fluidized bed was 1800°C. The pressure in the working volume remained close to atmospheric pressure. The SiC synthesis process comprised several stages:

- loading of carbon-containing particles, and their fluidization and heating of the entire reaction volume to the operating temperature;
- batch loading of SiO_2 particles until the full consumption of their entire amount provided for the SiC synthesis.

In the model, the following approximations and assumptions were made:

- in the reaction volume, the gas pressure and temperature do not change during the synthesis of silicon carbide;
- the mixture of gases in the reaction volume is a mixture of ideal gases;
- the only volatile synthesis products are CO and SiO; the gas mixture consists of CO, SiO, and the fluidizing gas (N_2);
- the mass flow rate of the fluidizing gas does not change during the synthesis process;
- the synthesis process is represented in a quasi-stationary approximation.

Mathematical model of SiO leakage

As previously [13–15], we used a phenomenological approach and took into account only two main chemical reactions of the synthesis of silicon carbide:
for particles c_2,

$$C + SiO_2 = SiO + CO; \quad (1)$$

and for particles c_1,

$$2C + SiO = SiC + CO. \quad (2)$$

Herein, c_1 are carbide-forming carbon-containing particles and c_2 are carbon-containing particles reacting with SiO_2 in the gaseous phase.

Since the temperature of melting and intense evaporation of SiO_2 is lower than the temperature of the beginning of carbide formation, c_2 particles are cooled and do not participate in reaction (2).

The amounts of the gaseous product SiO in the same reaction volume in reactions (1) and (2) are different because of the leakage of SiO. Let us define the mass leakage of SiO as:

$$\frac{dm_{SiO}^{leak}}{d\tau} = V_{rem} M_{SiO} C_{SiO}. \quad (3)$$

Herein, m is mass; τ is time; V is volume flow rate; M is molar mass; C is concentration. The subscript *SiO* refers to silicon oxide; the superscript *leak*, to leakage; and the subscript *rem*, to the removal of a mixture of gases from the reaction volume. Then, it follows from reactions (1) and (2) that:

$$-\dot{m}_{c_2} = -\frac{1}{2}\dot{m}_{c_1} + V_{rem} M_c C_{SiO}, \quad (4)$$

where the subscripts c, c_1, and c_2 refer to carbon and carbon-containing particles c_1 and c_2, respectively; $\dot{m}_{c_1} = \frac{dm_{c_1}}{d\tau}$; and $\dot{m}_{c_2} = \frac{dm_{c_2}}{d\tau}$.

Let us take into account that, for the mixture of ideal gases:

$$C_{N_2} + C_{CO} + C_{SiO} = \frac{P}{\tilde{R}T}. \quad (5)$$

Herein, P is the pressure of the gas mixture; T is the temperature of the mixture; $\tilde{R}$ is the universal gas constant; the subscripts N_2 and CO refer to the fluidizing gas and carbon monoxide, respectively.

Transforming the molar balance equation at the outlet of the reaction volume $\dot{V}_{\text{r.v.}}$, where the gas mixture leaves it, and taking into account Eq. (5) for the relationship between the concentrations of volatile products in this volume, we obtain the following equation for the relationship between the concentration C_{SiO} and V_{rem}:

$$V_{\text{rem}} = \frac{\frac{1}{M_{\text{N}_2}} V_{\text{in}} \rho_{\text{in}} - \frac{1}{M_c}\left(\dot{m}_{c_2} + \frac{1}{2}\dot{m}_{c_1}\right)}{a_1 - C_{\text{SiO}}}, \qquad (6)$$

wherein the subscript *in* refers to the fluidizing gas at the inlet of the reaction volume, ρ is the density, and $a_1 = \frac{P}{\tilde{R}T}$.

Equation (4) describes the effect of SiO leakage on the changes in the masses of particles c_1 and c_2 in the reaction volume and, therefore, also shows the relationship between the SiO leakage and the yield of silicon carbide. The integration of Eq. (4) gives the following value of the period Δτ of reactor operation with a single SiO_2 load:

$$\Delta r_{c_2}^3 = \frac{1}{2}\frac{\tilde{n}_{c_1}}{\tilde{n}_{c_2}}\Delta r_{c_1}^3 + \left(\frac{1}{3}a_2\right)^{-1} m_{\text{SiO}}, \qquad (7)$$

wherein $m_{\text{SiO}} = \int_{\Delta\tau}\left\{\dot{m}_{\text{in}} - \dot{m}_{c_2} - \frac{1}{2}\dot{m}_{c_1}\right\}\theta d\tau$;

$$\theta = \frac{C_{\text{SiO}}}{\left(a_1 - C_{\text{SiO}}\right)};\quad \Delta r_{c_2}^3 = \left(r_{c_2}^{\text{act}}\right)^3 - \left(r_{c_2}^{\text{cr}}\right)^3;$$

$$\Delta r_{c_1}^3 = \left(r_{c_1}^{\text{act}}\right)^3 - \left(r_{c_1}^{\text{cr}}\right)^3;\quad \dot{m}_{\text{in}} = \frac{M_c}{M_{\text{N}_2}} V_{\text{in}}\rho_{\text{in}};$$

r is the current radius of the particle, the superscript *act* (actual) refers to the parameters at the moment of loading a batch of SiO_2, the superscript *cr* (critical) refers to the time of loading the next batch or the end of the SiC production process, $a_2 = 4\pi\rho_c\tilde{n}_{c_2}$, and $\tilde{n}$ is the number of particles in the reaction volume.

The main difficulty in resolving the problem of the effect of SiO leakage on the yield of silicon carbide is to integrate the right-hand side of Eq. (7) for m_{SiO}. Let us use a model proposal, in order to describe the change in the radii of particles c_1 and c_2 [14, 15] in the representation of the components $\dot{m}_{c_1}$ and $\dot{m}_{c_2}$ of integrand (7). As a result, we have a function which when integrated gives the product of the beta function and the hypergeometric series [17, 18]. After transformations, we obtain the following:

$$\Delta r_{c_2}^3 = \frac{1}{2}\frac{\tilde{n}_{c_1}}{\tilde{n}_{c_2}}\Delta r_{c_1}^3 + a_{\text{I}}\ln\frac{1}{1-\beta^*} + a_{\text{II}}\left\{\left(r_{c_2}^{\text{cr}}\right)^2 S_1 + 2r_{c_2}^{\text{cr}}\Delta r_{c_2} S_2 + \left(\Delta r_{c_2}\right)^2 S_3\right\} + a_{\text{III}}\left\{\left(r_{c_1}^{\text{cr}}\right)^2 S_4 + 2r_{c_1}^{\text{cr}}\Delta r_{c_1} S_5 + \left(\Delta r_{c_1}\right)^2 S_6\right\}. \qquad (8)$$

Herein, $\beta^* = \frac{C_{\text{SiO}}^{\max}}{a_1}$; $a_{\text{I}} = \dot{m}_{\text{in}}\frac{R_c^3}{m_{c_2}^0 L_{c_1}}$; $a_{\text{II}} = 3l\Delta r_{c_2}\beta^*$;

$a_{\text{III}} = \frac{3}{2}\frac{\tilde{n}_{c1}}{\tilde{n}_{c2}}\Delta r_{c_1}\beta^*$; $\Delta r_{c_1} = r_{c_1}^{\text{act}} - r_{c_1}^{\text{cr}}$; $\Delta r_{c_2} = r_{c_2}^{\text{act}} - r_{c_2}^{\text{cr}}$;

and Sj (j = 1, …, 6) are the hypergeometric series with the general form

$$S_j = \sum_{i=1}^{\infty}\frac{\left(\beta^*\right)^{i-1}}{k_j + i}, \qquad (9)$$

wherein $k_1 = l$, $k_2 = 2l$, $k_3 = 3l$, $k_4 = 1$, $k_5 = 2$, $k_6 = 3$, $l = \frac{L_{c_2}}{L_{c_1}}$. The subscript *0* in the definition of a_{I} means the time at which the synthesis begins after the reaction volume has been heated to the operating temperature of the process. R is the initial average radius of particles loaded into the reactor, $L_{c_1} = \psi_{C_1}^*\frac{C_{\text{SiO}}^{\max}}{\Delta r_{c_1}}$, and $L_{c_2} = \psi_{C_2}^*\frac{C_{\text{SiO}_2}^{\max}}{\Delta r_{c_2}}$. The functions $\psi_{C_1}^*$ and $\psi_{C_2}^*$ describe the rates of chemical reactions (2) and (1), respectively [19, 20][1]. The maximum concentration $C_{\text{SiO}_2}^{\max}$ of SiO_2 vapor is calculated according to the data from [14]. The definition of the concentration $C_{\text{SiO}}^{\max}$ of the volatile product of the SiC synthesis immediately after loading the next batch of silicon dioxide into the reaction volume should be refined in accordance with the mathematical model of SiO leakage.

Determination of the maximum SiO concentration in the reaction volume

Let $\dot{m}_{\text{SiO}}$ and $\dot{m}_{\text{CO}}$ be the mass flow rates (generations) of SiO and CO, respectively, in $\dot{V}_{\text{r.v.}}$ at the time of

[1] Feng N. *Kinetics of the reaction between quartz and silicon carbide in different gas atmospheres*: Master Thesis. Norwegian University of Science and Technology (NTNU). Trondheim. 2015. 90 p.

loading a batch of SiO_2 ($\tau = 0$). Then it follows from reactions (1) and (2) that

$$\frac{C_{SiO}^{max}}{C_{CO}^{max}} = \left(1 + \frac{1}{2}\frac{\dot{m}_{c_1}}{\dot{m}_{c_2}}\right)^{-1}\Bigg|_{\tau=0}. \quad (10)$$

Equation (5) at $\tau = 0$ taking into account relation (10) takes the form

$$a_1 = C_{N_2}\Big|_{\tau=0} + C_{SiO}^{max}\left(2 + \frac{1}{2}\frac{\dot{m}_{c_1}}{\dot{m}_{c_2}}\right)\Bigg|_{\tau=0}. \quad (11)$$

The established concentration $C_{N_2}\big|_{\tau=0}$ of the fluidizing gas after loading a batch of SiO_2 particles into the reaction volume is found through the concentration C_{SiO}^{max} from the relationship of the generations of the volatile products:

$$\frac{C_{N_2}}{C_{SiO}^{max}}\Bigg|_{\tau=0} = -\frac{\dot{m}_{вх}}{\dot{m}_{c_2}}\frac{M_c}{M_{N_2}}. \quad (12)$$

The mass flow rates $\dot{m}_{c_1}$ and $\dot{m}_{c_2}$ are calculated using the general model of the synthesis of silicon carbide [14, 15]. As a result, from Eqs. (10)–(12) and the expressions for $\dot{m}_{c_1}$ and $\dot{m}_{c_2}$, we obtain the following equation and solution, which are quadratic in the intended parameter C_{SiO}^{max}.

$$C_{SiO}^{max} = \frac{\tilde{\rho}}{2}\left[\left(1 + \frac{4\tilde{q}}{\tilde{\rho}^2}\right)^{\frac{1}{2}} - 1\right], \quad (13)$$

where $\tilde{\rho} = \dfrac{2b_2 + b_3}{b_1}$; $\tilde{q} = a_1\dfrac{b_2}{b_1}$; $b_1 = M_{N_2}\sigma_{c_1}$;

$b_2 = M_{N_2}\sigma_{c_2}C_{SiO_2}^{max}$; $b_3 = \dfrac{1}{3}V_{in}\rho_{in}R_C^3\rho_c$;

$\sigma_{c_1} = m_{c_1}^0\left(r_{c_1}^{act}\right)^2\alpha_{c_1}k_{c_1}$; $\sigma_{c_2} = m_{c_2}^0\left(r_{c_2}^{act}\right)^2\alpha_{c_2}k_{c_2}$; α is the fraction of the surface of a particle that participates in the chemical reaction; and k_{c_1} and k_{c_2} are the rate constants for reactions (2) and (1), respectively.

General scheme of calculations

As in our previous works [14, 15], the general model of silicon carbide synthesis was used to calculate all the main process parameters, in order to determine the change in the characteristics of the charge over time. These are: the size of solid particles, the concentration of volatile components in the reaction volume and the yield of the final synthesis product. However, unlike those works, each variant calculation of the masses m_{SiC} of the synthesized silicon carbide was carried out for two cases: with SiO leakage in the working process; and without such leakage. The effect of SiO leakage was determined by comparing the values of the following dimensionless parameter:

$$Y = \frac{m_{SiC}^{max} - m_{SiC}^{p}}{m_{SiC}^{*}}, \quad (14)$$

where the superscript * refers to the absence of SiO leakage in the synthesis process. The superscripts *max* and *p* indicate the mass yield of the synthesis product with minimum leakage and various values of the parameter *p*, respectively. In this case, the maximum yield of silicon carbide, m_{SiC}^{max}, is always observed at the minimum *p* value. This depends on the physical properties of carbon-containing particles and SiO_2 particles. For example, for Rexyl and river sand, $p^{min} \simeq 0.2$.

The variable parameters in the calculations were the mass m_{ch}^0 and composition of the initial charge; the operating temperature of the synthesis; the number δ of loaded batches of SiO_2; and the relative number of particles c_2 entering into reaction (1), $p = \dfrac{\tilde{n}_{c_2}}{\tilde{n}_{SiO_2}}$. Since the parameter *p* cannot be determined within the framework of phenomenological approaches when modeling processes with a multiple number of particles, this parameter was determined by comparing the integral characteristics found in the experiments [11] and calculations. These characteristics were the mass yield of silicon carbide and the synthesis time under the same initial data of the experiments and calculations.

RESULTS AND DISCUSSION

General initial data

All calculations were carried out at three values of δ (δ = 2, 5, and 10). The weights of batches of SiO_2 particles loaded into the reaction volume were assumed to be equal. The carbon-containing particles were Rexyl (ρ_C = 500 kg/m^3). Silicon dioxide as a component of the initial charge was coarse river sand. The processes at different operating temperatures *T* in the reaction volume (1450, 1600, and 1800°C were considered separately). The particles of the charge component in the initial state in all calculations had the same average size: $R_C = 10.75 \cdot 10^{-5}$ m and $R_{SiO_2} = 6.5 \cdot 10^{-5}$ m. The mass flow rate of the fluidizing gas was calculated according to Wallis' monograph [21].

Calculation at variable values of the parameter *p*

Table 1 shows the results of calculations of the yield of silicon carbide in the synthesis processes in the case of SiO leakage, and in the hypothetical situation when there is no such leakage and the product yield is maximum. The initial masses of solid components of the charge are m_c^0 = 0.32 kg and $m_{SiO_2}^0$ = 0.3 kg. The operating temperature of the process was T = 1600°C.

Similar calculations were made at other operating temperatures of silicon carbide synthesis: T = 1450°C and T = 1800°C. The results are presented in Fig. 1. Table 1 and Fig. 1 show that, at the considered operating temperatures of SiC synthesis, an increase in the parameter p is accompanied by a decrease in the yield of the final product.

The explanation for this effect is quite simple. An increase in the parameter p means the formation of stable complexes of particles c_2 + SiO_2 at a lower temperature

Table 1. The main characteristics of the SiC synthesis process and the particle sizes of the residual charge

m_{SiC}, kg	Mass yield, %	Time, s	$r_{c_1}^{yield} \cdot 10^5$, m	δ	p	m_{SiC}, kg	Mass yield, %	Time, s	$r_{c_1}^{yield} \cdot 10^5$, m	$r_{c_2}^{yield} \cdot 10^5$, m
With SiC leakage				–	–	Without SiC leakage				
0.108	35.724	10589	6.685	10	0.6	0.195	57.716	32127	5.708	9.413
0.114	37.381	9146	7.626	10	0.5	0.195	57.770	19876	7.216	9.095
0.119	38.713	8025	8.264	10	0.4	0.195	57.796	14733	7.980	8.572
0.124	39.958	7531	8.734	10	0.3	0.195	57.812	11962	8.460	7.523
0.132	42.222	7202	8.952	10	0.2	0.195	57.822	10574	8.795	2.595
0.124	40.152	9836	6.724	5	0.6	0.195	57.563	31079	5.779	9.413
0.130	41.602	8694	7.975	5	0.5	0.195	57.639	16792	7.244	9.095
0.136	43.109	7538	8.308	5	0.4	0.195	57.688	11746	7.995	8.572
0.142	44.703	6377	8.865	5	0.3	0.195	57.719	9446	8.470	7.523
0.147	46.005	5741	9.009	5	0.2	0.195	57.739	8187	8.802	2.595
0.141	44.637	7870	7.121	2	0.6	0.195	57.490	30146	5.883	9.413
0.142	44.816	6881	8.002	2	0.5	0.195	57.439	12467	7.297	9.095
0.144	45.295	5523	8.586	2	0.4	0.195	57.492	8461	8.026	8.572
0.148	46.315	4865	8.929	2	0.3	0.195	57.535	6745	8.491	7.523
0.163	50.036	4606	9.185	2	0.2	0.195	57.566	5618	8.817	2.595

Note: The yield (%) is calculated as $\left(\frac{m_{SiC}}{m_{ch}}\right) \cdot 100\%$; the subscript *yield* refers to the time at which the synthesis is completed.

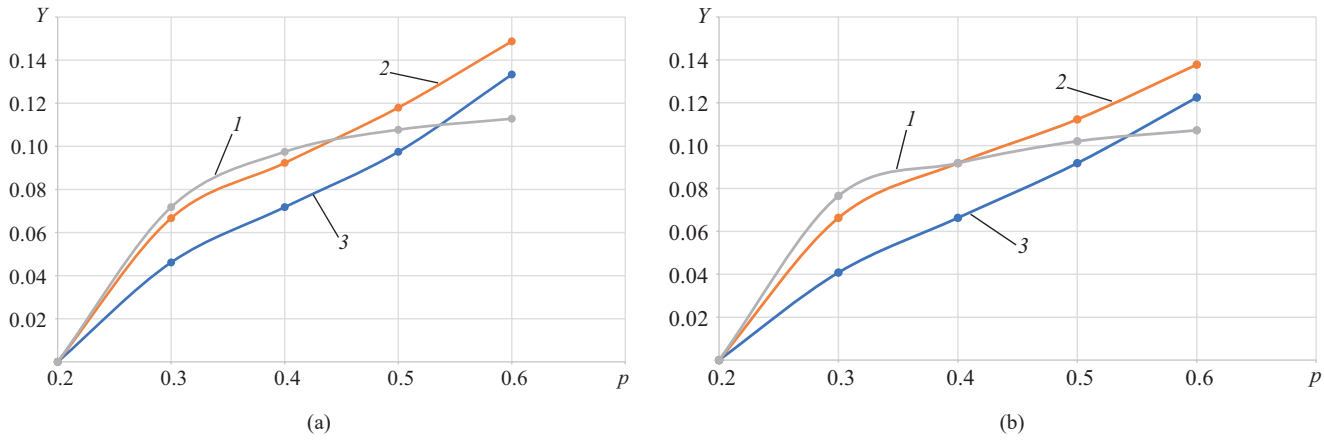

Fig. 1. Effect of SiO leakage on silicon carbide yield at operating temperatures of (a) 1450 and (b) 1800°C. Function $Y = Y(p)$: (*1*) δ = 2; (*2*) δ = 5; (*3*) δ = 10

with an increasing number of particles c_2. In the case of a constant initial number of carbon-containing particles, the number of carbide-forming particles c_1 decreases, and the thickness of the silicon carbide layer formed on the core of c_1 increases with the inevitable increase in diffusion resistance and decrease in the rate of main reaction (2). The synthesis process becomes longer with an increased loss of SiO, an important volatile component of chemical reaction (2).

Figure 2 illustrates the relationship between the SiO leakage and the time of the synthesis process as the dependence of Y on the relative time X of additional SiO leakage. This corresponds to the increase in the parameter p from its minimum value:

$$X = \frac{\tau^p - \tau^{\max}}{\tau^*}. \quad (15)$$

In definition (15), τ^p, $\tau^{\max}$, and τ^* are the times at which the yields of the final product are m^p_{SiC}, $m^{\max}_{SiC}$, and m^*_{SiC}, respectively. The dependencies shown in Fig. 2 also characterize the effect of both the number δ of loadings of equal-mass batches of SiO_2 into the reaction volume, as well as the operating temperature of the working process on the loss of the component of chemical reactions in the synthesis of silicon carbide.

Validation of calculation results

The variables X (Eq. (15)) and Y (Eq. (14)), which are the argument and the calculation function in Fig. 2 respectively, are convenient for analyzing the effect of SiO leakage on the loss of the final product in the synthesis of SiC. This effect largely depends on the synthesis time. This in turn, is determined by the ratio of reacting particles p in the resulting stable complexes c_2 + SiO_2 and the number δ of loadings of batches of SiO_2 particles during the entire process.

Albeit not in the calculated (virtual) but in the real silicon carbide production process, the parameter p takes a very specific value, related to the model representation of the physicochemical process. However, this value cannot be detected directly in the reaction volume in the experiment due to the lack of workable techniques for the corresponding measurements. In turn, at a given composition of the charge, with known constants for chemical reactions (1) and (2), a specific operating temperature of the synthesis, and a specified number of loadings of batches of silicon dioxide into the reaction volume, the parameter p and the time of synthesis of the final product are uniquely related. This can be seen from a comparison of Figs. 1 and 2.

As show by experiments [9–11], in an electrothermal fluidized bed reactor during the high-temperature synthesis of silicon carbide, the changes in the following parameters of the reaction medium, in particular, were measured: operating temperature of the fluidized bed, fluidizing gas flow rate, and CO concentration (at the reactor outlet). At the end of each experiment, the mass of the residual charge was measured. Then, after

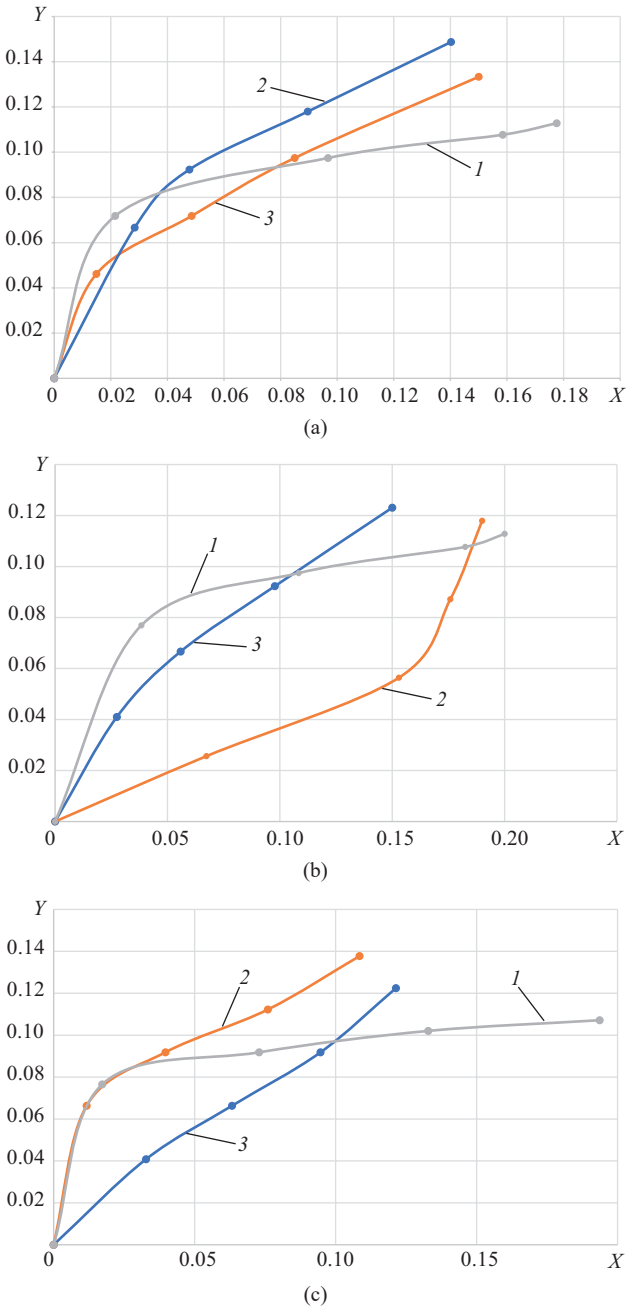

Fig. 2. Effect of synthesis time on silicon carbide yield at operating temperatures of
(a) 1450,
(b) 1600, and
(c) 1800°C.
$Y_1 = Y_1(p)$:
(*1*) δ = 2,
(*2*) δ = 5,
(*3*) δ = 10

annealing, the mass of the resulting final product was measured. A thorough morphological analysis was also carried out. The data [11] was taken as the basis for validating the calculation results in this study with the simultaneous determination of the model value of the parameter p.

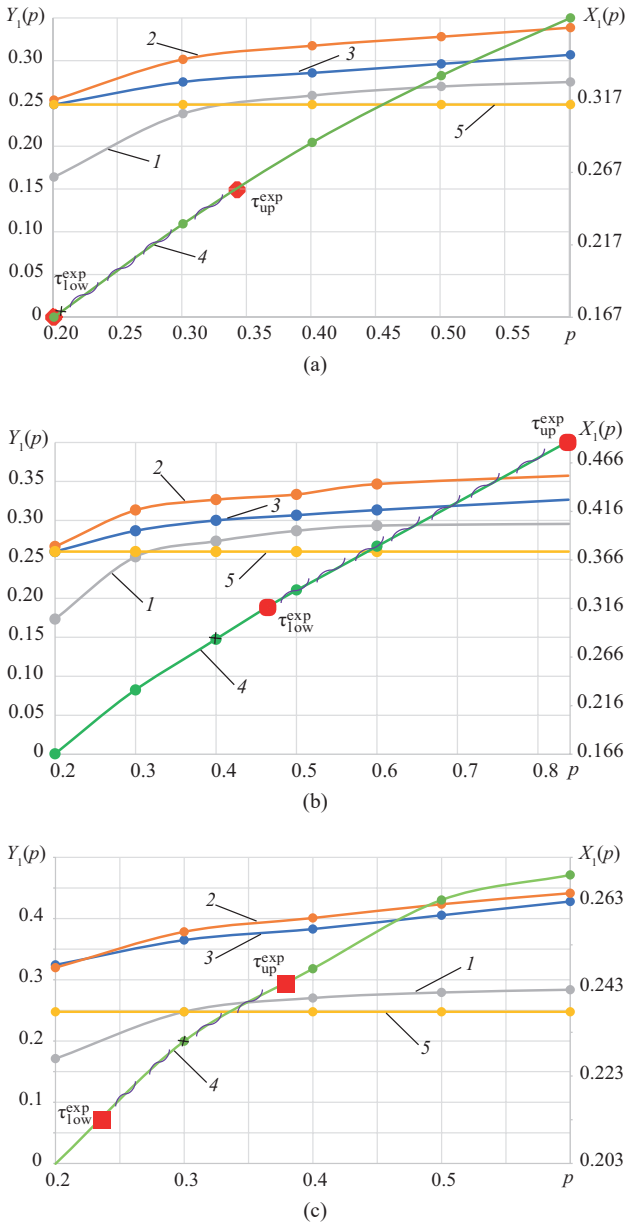

Fig. 3. Relative loss of end product (SiC) because of SiO leakage:
(a) T = 1450°C, m_c^0 = 0.570 kg, $m_{SiO_2}^0$ = 0.290 kg;
(b) T = 1600°C, m_c^0 = 0.500 kg, $m_{SiO_2}^0$ = 0.230 kg;
(c) T = 1800°C, m_c^0 = 0.400 kg, $m_{SiO_2}^0$ = 0.340 kg;
(⁓) range of experimental value of synthesis time;
(+) calculated synthesis time, δ = 10. Function $Y_1 = Y_1(p)$: (*1*) δ = 2; (*2*) δ = 5; (*3*) δ = 10; (4) function $X_1 = X_1(p)$ at δ = 10; (*5*) experimental data [11]

Figure 3 compares the experimental and calculated values of SiC yield and synthesis time at the experimental initial parameters. The calculated graphs in Fig. 3 are plotted in relative coordinates $Y_1 = Y_1(p)$ and $X_1 = X_1(p)$, where

$$\begin{cases} X_1 = \dfrac{\tau^* - \tau^p}{\tau^*} \\ Y_1 = \dfrac{m_{SiC}^* - m_{SiC}^p}{m_{SiC}^*} \end{cases}. \qquad (16)$$

The horizontal lines represent experimental data and are constructed by the elementary change of τ^p and m_{SiC}^p by the experimental (superscript *exp*) values τ^{exp} и m_{SiC}^{exp} in definition (16).

Estimates of synthesis time in experiments were made according to the following two criteria:

- according to the time during which the operating temperature in the reaction volume exceeded the value assigned in a specific experiment;
- according to the time during which CO as a volatile product of reactions (1) and (2) was detected at the outlet of the reaction volume.

Since the estimates do not coincide, in the graphs $X_1 = X_1(p)$ in Fig. 3, both upper (τ_{up}^{exp}) and lower (τ_{low}^{exp}) estimates of the synthesis time are indicated for each experiment. The experimental data was compared with the calculation results at δ = 10. This is due to the number of pulse changes in the operating temperature and CO concentration in the experimental curves [9–11].

Table 2 analyzes the agreement between the results of experiments and calculations.

The right hand column of Table 2 shows the parameter p values averaged over the synthesis time, which were taken to compare the results of experiments and calculations. We assessed the efficiency of our model taking into account the leakage of SiO in the calculations of SiC synthesis at $\bar{p}$ = 0.2 at T = 1450°C, $\bar{p}$ = 0.4 at T = 1600°C, and $\bar{p}$ = 0.3 at T = 1800°C in terms of the discrepancy between the calculated and experimental values of the masses of the synthesized silicon carbide, $\left(1 - \dfrac{m_{SiC}^{\bar{p}}}{m_{SiC}^{exp}}\right) \cdot 100\%$, to obtain 4.7% ($T$ = 1450°C), 5.4% (T = 1600°C), and 15.5% (T = 1800°C). Note that the SiC loss calculated by the leakage model is somewhat higher than that observed in experiments. This is quantitatively demonstrated by the discrepancy $\left(1 - \dfrac{m_{SiC}^{\bar{p}}}{m_{SiC}^{*}}\right) \cdot 100\%$ which is 3.6% (T = 1450°C), 3.9% (T = 1600°C), and 11.5% (T = 1800°C).

Table 2. Calculated and experimental parameters of SiC synthesis

T, °C	m_{ch}, kg	m_{ch}^{exp}, kg	$m_{SiC}^{\overline{p}}$, kg	m_{SiC}^{exp}, kg	$\tau_{low}^{exp} \cdot 10^{-4}$, s	$\tau_{up}^{exp} \cdot 10^{-4}$, s	$\tau^{\overline{p}} \cdot 10^{-4}$, s	$\overline{p}$
1450	0.589	0.565*	0.142	0.149*	1.00	1.20	1.13	0.2
1600	0.523	0.509*	0.105	0.111*	1.23	1.38	1.20	0.4
1800	0.382	0.418*	0.141	0.167*	1.25	1.40	1.31	0.3

*Impurities in the charge are ignored [22].

CONCLUSIONS

The process of SiC formation at variable parameters of chemically reacting media in a high-temperature fluidized bed is very complex. The yield of the final product is not determined by the volumetric balance of the interacting components of the closed system and significantly depends on the loss of any reacting component from the reaction volume. This work demonstrated the adequacy of the first model, as well as the calculation algorithm for the leakage of a volatile product of silicon carbide synthesis.

The leakage of SiO, an intermediate volatile product of the synthesis of silicon carbide, from the reaction volume of the ETFB reactor ultimately leads to the loss of the final product, SiC. However, a decrease in the amount of SiO as a reagent is accompanied by a decrease in the synthesis time of silicon carbide, i.e., a decrease in energy costs for the production of a unit of product.

A computational model of the synthesis of silicon carbide with a validated procedure for calculating the leakage of volatile products of chemical reactions, presented in this work in the form of the SiO leakage model, will allow for computational studies aimed at optimizing the SiC production process in ETFB reactors. In turn, this will determine the validity of recommendations on the composition of the initial charge, the number of loadings of SiO_2 batch into the reaction volume, and the operating temperature of the production process. In this case, it is of the utmost importance to design an energy-efficient operating cycle without preliminary expensive experimental studies.

Authors' contributions

V.S. Kuzevanov—developing the research concept and methodology and writing the text of the manuscript.

S.S. Zakozhurnikov—software and validation.

G.S. Zakozhurnikova—carrying out calculations, analyzing literature sources, and searching and analyzing experimental data.

All authors have read and agreed to the published version of the manuscript.

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