Modeling of the synthesis of ‘core-shell’ composite particles based on segregated oxidation of titanium and silicon tetrachlorides in flow-type plasmachemical reactor

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Abstract. The simulation of single-stage synthesis of composite titania-silica nanoparticles in the working zone of flow-type plasmachemical reactor has been performed based on segregated oxidation of titanium and silicon tetrachlorides, with each precursor being preliminarily mixed with air oxygen by means of bubbling. Within the framework of the developed model of the synthesis, the data regarding core size of composite particles, their shell thickness as well as ratio of particles with and without shell have been extracted.

1. Introduction
Synthesis of nanocomposite powders of oxide ceramics is one of the most promising trends in modern technologies. These products belong to new class materials with controlled physico-chemical properties ranged depending on their applications. In particular, nanosized titania (TiO\textsubscript{2}) powders are being widely used in industry. In many applications it is required to extremely inhibit photocatalitic activity of TiO\textsubscript{2} nanoparticles. For instance, it is the case when TiO\textsubscript{2} pigments are used to modify physico-chemical properties of paint films, plastic materials, in paper manufacturing as well as that of sun blocking agents. In these it is necessary to reduce an area of photo-active free surface of titania pigment as much as possible, with titania optical properties being unchanged. This requirement might be met by the synthesis of nanocomposite ‘TiO\textsubscript{2} core – SiO\textsubscript{2} shell’ particles. In these powders the greater thickness of silica amorphous layer and the lesser its microporosity, the lower photoactivity of the composite powder [1]. In [2] first time the simulation of single-stage synthesis of composite TiO\textsubscript{2}/SiO\textsubscript{2} nanoparticles in the working zone of plasmachemical reactor has been performed providing segregated oxidation of titanium and silicon tetrachlorides. In this work molar concentrations of reacting components fed into the reactor were chosen regardless of actual technique of mixing. In addition, the range of varying the flow rate of mixture of air and silicon tetrachloride allowed a decrease of reacting flow temperatures below 1200 K at which a formation of chlorosiloxanes (SiO\textsubscript{x}Cl\textsubscript{y})\textsubscript{z} is possible [3]. Moreover, in the model a minimal shell thickness is not restricted.

In this work the results of simulation of aforementioned single-stage synthesis of composite TiO\textsubscript{2}/SiO\textsubscript{2} nanoparticles have been presented taking into consideration above aspects.
2. Formulation of the problem

In figure 1 the schematic of the working zone of a flow-type reactor is shown (actually, the reactor is positioned vertically). Nitrogen jet with a temperature \( T_1 \) and flow rate \( Q_1 \) is injected through the channel of the reactor to its working zone. Titanium tetrachloride vapors mixed with air (temperature \( T_2 \), total flow rate \( Q_2 \)) are supplied into the reactor through first side slot. In the mixing zone of the reactor, the synthesis of gaseous titania is followed by a formation of \( \text{TiO}_2 \) particles. While moving along the reactor, the particles grow due to the surface reaction and coagulation. In [4, 5] the results of numerical and experimental studies of this stage are presented. \( \text{SiCl}_4 \) vapors mixed with air with temperature \( T_3 \) and flow rate \( Q_3 \) are injected via second side slit.

In this mixing zone both the homogeneous reaction of synthesis of gas-phase silica which is condensed on titania particles and heterogeneous reaction with formation of solid silica on \( \text{TiO}_2 \) particles and \( \text{TiO}_2/\text{SiO}_2 \) composite particles occur. In contrast to the model presented in [2] in the model implemented here the possible quantity of solid-phase silica is preliminarily calculated in current computational cell. Based on this quantity, a surface area of titania particle which might be covered with this amount of solid-phase silica is estimated, with shell thickness being not less than \( \text{SiO}_2 \) monomer diameter. Then a fraction of titania particles with formed silica layer is evaluated. If both titania and composite particles are present in a computational cell, their fractions are proportional to a number of particle of each sort.

Next step for model generalization is consideration of a possibility of partial covering of titania particles. An adequacy of each variant of the model should be further checked in experiments to be conducted on the lab set-up, the operating parameters of the experiments being as those assigned for calculations. The assumption of absence of coagulation of composite particles is to be also examined empirically.

3. Mathematical model

A flow of a viscous heat-conducted compressible gas mixture is considered. The mixture consists of following species: \( \text{O}_2 \), \( \text{N}_2 \), \( \text{TiCl}_4 \), \( \text{SiCl}_4 \), \( \text{TiO}_2 \), \( \text{SiO}_2 \), and \( \text{Cl}_2 \). The last three components are the products of following generalized gas-phase reactions of synthesis of titania and silica with kinetic rates \( k_T \) and \( k_S \), respectively:

\[
\begin{align*}
\text{TiCl}_4 + \text{O}_2 & \xrightarrow{k_T} \text{TiO}_2 + 2\text{Cl}_2, \\
\text{SiCl}_4 + \text{O}_2 & \xrightarrow{k_S} \text{SiO}_2 + 2\text{Cl}_2.
\end{align*}
\]

A single-fluid flow is assumed. It is defined by a system of quasi-gas dynamic equations (QGD) [4] in which the external forces and the heat sources are accounted for as follows:
\[
\frac{\partial \rho}{\partial t} + \text{div } \mathbf{j} = 0, \\
\frac{\partial (\rho \mathbf{u})}{\partial t} + \text{div } (\mathbf{j} \otimes \mathbf{u}) + \nabla p = \rho \mathbf{F} + \text{div } \Pi, \\
\frac{\partial (E)}{\partial t} + \text{div } (\mathbf{j} H) + \text{div } \mathbf{q} = (\mathbf{j} \cdot \mathbf{F}) + \text{div } ((\Pi \cdot \mathbf{u}) + Q).
\]

Here all quantities are normalized: \( \mathbf{u}, \rho \) and \( p \) are the velocity vector, density and averaged pressure of the mixture flow, respectively. \( \mathbf{F} \) is the mass force density vector, \( H \) is the total specific enthalpy, \( \Pi \) is the viscous stress tensor, \( Q \) is the specific heat. The mass flux density vector \( \mathbf{j} \) is determined as following:

\[
\mathbf{j} = \rho \mathbf{u} - \tau \left[ \text{div } (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla p - \rho \mathbf{F} \right], \quad \tau = \frac{M}{\text{Re } \text{Sc}} \frac{T}{p}.
\]

where \( \tau \) is the relaxation parameter, \( \text{Re} \) – Reynolds number, \( \text{Sc} \) – Schmidt number, \( M \) – Mach number, \( T \) – gas mixture normalized temperature.

The system is supplemented with continuity equations for the species in the mixture:

\[
\frac{\partial \rho_i}{\partial t} + \text{div } \mathbf{j}_i = \sum_j J^{(ji)}(i) \tag{2}
\]

where \( \rho_i \) – normalized density of \( i \)-th species, \( J^{(ji)} \) is the normalized rate of transformation of the mass of the \( j \)-th species to the \( i \)-th species in a unit volume of the mixture, \( \mathbf{j}_i \) – normalized mass flux density vector of \( i \)-th species.

In addition, the equations for the volumetric concentration \( c_p \) of the solid phase should be considered for this system:

\[
\frac{\partial c_p}{\partial t} + \text{div } (c_p \mathbf{u}) = \sum_j J^{(jp)} \tag{3}
\]

Here \( J^{(jp)} \) is the normalized rate of transformation of the mass of the \( j \)-th species to the solid phase.

On the right-hand sides of (2), (3) there are accounted for the kinetic relations which describe variations of the concentrations of titanium tetrachloride and titanium dioxide in the gas and solid phases as well as those of silicon tetrachloride and silicon dioxide in the gas and solid phases due to the homogeneous and heterogeneous reactions and to the phase transition:

\[
\frac{dC_1}{dt} = -k_{T}^{1}C^{1} = - \left( k_{T}^{2} + k_{T}^{3} A \right) C^{1}, \quad \frac{dC_2}{dt} = k_{T}^{2}C^{1} - k_{T}^{3}C^{2},
\]

\[
\frac{dC_3}{dt} = k_{T}^{4}C^{1}A + k_{S}^{4}C^{2}, \quad \frac{dC_4}{dt} = -k_{S}^{4}C^{4} = - \left( k_{S}^{5} + k_{S}^{6} A \right) C^{4},
\]

\[
\frac{dC_5}{dt} = k_{S}^{5}C^{4} - k_{S}^{6}C^{5}, \quad \frac{dC_6}{dt} = k_{S}^{6}C^{4}A + k_{S}^{6}C^{5}.
\]

\( C_1, C_2, C_3, C_4, C_5, C_6 \) stand for corresponding mass concentrations of titanium tetrachloride and titanium dioxide in the gas phase and of titanium dioxide in the solid phase, silicon tetrachloride and silicon dioxide in the gas phase and of silicon dioxide in the solid phase. \( k_{T}^{1}, k_{S}^{1} \) are the rates of the generalized reactions of synthesis of titania and silica, respectively, \( k_{T}^{2}, k_{S}^{2} \) are the corresponding rates of the homogeneous reactions, \( k_{T}^{3}, k_{S}^{3} \) are the rates of the surface reactions, \( k_{T}^{4}, k_{S}^{4} \) – the rates of the phase transitions of titania and silica correspondingly, and \( A \) is the relative area of particles.
The additional relations including ideal gas mixture law to provide a closure of the system of equations are as follows:

\[ p = \rho R_m T \frac{m_g}{1 - \epsilon_p}, \quad \alpha_i = \rho_i / \rho, \quad R_m = R_g \left( \sum_i \alpha_i / m_i \right). \]

In these relations, \( R_m \) is the universal gas constant of the mixture, \( R_G \) is the specific gas constant, \( \alpha_i \) is the mass fraction of the \( i \)-th species, \( m_g \) is the mass fraction of the gas, and \( m_i \) is the molar weight of the \( i \)-th species.

If we supply (1)-(4) with the equation for the number of particles \( N \) per a unit volume:

\[ \frac{dN}{dt} = k_B C_N N_{AV} - \frac{\beta N^2}{2}, \quad \text{(5)} \]

where \( N_{AV} \) is the Avogadro constant. Taking into account the known nuclei diameter and a total mass of particles, their number and molar concentration in an elementary volume, we can calculate the average size of particles there at an arbitrary time point. Coagulation parameter \( \beta \) is evaluated in accordance with [5, 6]:

\[ \beta = 8\pi d_B d_p \left[ \frac{d_p}{d_p + g \sqrt{2}} + \frac{4d_B \sqrt{2}}{u_p d_p} \right]^{-1}, \]

where \( g = \left( \frac{1}{3d_p l_a} \right) \left[ \left( d_p + l_a \right)^3 - \left( d_p + l_a \right) \frac{3}{2} \right] - d_p, \quad l_a = \frac{8d_B}{\pi u_p}, \quad d_B = \frac{3\sqrt{mkT / 2\pi}}{2\rho d_p^2 (1 + \alpha \pi / 8)}. \]

Here \( d_B \) – diffusivity of Brownian particle, \( d_p \) – particle diameter, \( u_p \) – particle velocity, \( l_a \) – particle mean free path parameter for the coagulation process, \( m \) – mass of the molecule of carrier gas, \( k \) – Boltzmann constant, \( \alpha \) – accommodation coefficient.

### 4. Boundary conditions

On the reactor walls, we imposed the no-slip conditions, the absence of the heat flux of the wall temperature, and a zero value of the normal derivative of pressure (this additional condition is caused by specific features of the QGD system). The flow rates and temperatures were specified for the jets. To calculate the pressure, density, and velocity at the inlet boundaries of the jets, we used the boundary conditions based on using the Riemann invariants for the Euler equations.

With the purpose of numerical integration of equations (1)–(3), they are rewritten in the cylindrical coordinate system (the axisymmetric problem is considered) and are brought to the dimensionless form. As the main dimension parameters of the problem, the radius of the reactor channel, the velocity of sound in quiescent air at temperature of 300 K, and the density of this air are considered.

The QGD system of equations is solved numerically using a difference scheme explicit in time. The time derivatives are approximated by upwind differences with the first order of accuracy, and the spatial derivatives are presented as central differences of the second order of accuracy.

### 5. Results of calculations

The main series of calculations whose results could be validated against experimental data was performed in the following formulation. At first, the quasi-steady flow field in the reactor, which was formed by injection of the jet from the plasma torch, was computed. After that, side jets were injected.

The reactor has the following geometry: \( L_R = 444 \text{ mm}, \ d_R = 32 \text{ mm}, \ L_C = 38 \text{ mm}, \ d_C = 14 \text{ mm}, \ L_T = 33 \text{ mm}, \) and half angle of opening of the zone with variable cross-section \( \alpha = 15^\circ \). Axial coordinates of injection of centers of side jets: \( z_1 = 28 \text{ mm}, \ z_2 = 292 \text{ mm} \). Here \( d_C, \ d_R \) – channel and...
reactor diameters, respectively. \( L_C, L_R, L_T \) – corresponding lengths of channel, reactor and zone of variable area of cross-section.

Operating parameters of the set-up: \( T_1 = 4500 \text{ K}, Q_1 = 1 \text{ g} \cdot \text{s}^{-1}; T_2 = 300 \text{ K}, Q_2 = 2.5 \text{ g} \cdot \text{s}^{-1}; T_3 = 300 \text{ K}, Q_3 = 1.0–1.2 \text{ g} \cdot \text{s}^{-1} \). The molar composition of species of first side jet: air – 99.5\%, TiCl\(_4\) – 0.5\%; the molar composition of species of second side jet: air – 99.2\%, SiCl\(_4\) – 0.8\%.

The values of the kinetic rate constants in (4), (5) were given in compliance with [6, 7] as follows:

\[
k_1^T = 8.26 \cdot 10^4 \exp\left(-\frac{-10 681}{T}\right), \quad k_3^T = 4.9 \cdot 10^3 \exp\left(-\frac{-8993}{T}\right), \quad k_1^P = 1.2 \cdot 10^{10} \exp\left(-\frac{-10 681}{T}\right),
\]

\[
k_3^P = 8.0 \cdot 10^{14} \exp\left(-\frac{-400 000}{T}\right), \quad k_3^S = 4.0 \cdot 10^{13} \exp\left(-\frac{-40 828}{T}\right), \quad k_5^S = k_5^P.
\]

In figure 2 profiles of particle diameter averaged over their number

\[
d_i = \frac{1}{N_i} \sum_j d_{ij} N_{ij},
\]

as well as profiles of logarithm of number

\[
N_i = \sum_j N_{ij}
\]

of particles along the reactor are presented as a function of axial distance for three flow rates of mixture air+SiCl\(_4\) vapors and two axial locations of the second slit side jet. Here \( d_{ij} \) and \( N_{ij} \) – size and number of particles in \( j \)-th computational cell of \( i \)-th cross-section. It is evident from the figure that there are two kinds of nanoparticles at the reactor outlet: titania particles and composite ‘TiO\(_2\) core – SiO\(_2\) shell’ ones.

The results of the computations show that a ratio between a number of titania particles and that of composite ones depends on a ratio between flow rates of \( Q_3 \) and \( Q_2 \) (for instance, see figures 2a and 2b) as well as locations of the jet slit through which a mixture of air and SiCl\(_4\) vapors are injected (see figures 2a and 2c). The same parameters affect the size of composite particles and their shell thickness. Apart of resultant higher rate of the synthesis of gaseous silica, increasing the flow rate \( Q_3 \) leads to formation of a stagnant zone nearby the reactor walls upstream of the plane of injection of mixture air+ SiCl\(_4\) vapors. In this zone titania particles grow and this would result in corresponding increase of core size of composite particles. This may be explained with lower flow velocity in the vicinity of walls and consequently with a rise of residence time of particles therein, they become larger because of surface reaction and coagulation. Downstream of this zone a monotonous character of distributions of parameters of composite particles is established owing to an entrainment of titania particles from mainstream into the zone of propagation of silica vapors. The axial displacement of the slit of injection of mixture air+SiCl\(_4\) upstream causes an increase of time of formation of a shell. This has an influence on both a number of composite particles and shell thickness on their surface. For example, even for 20\% reduction of the flow rate \( Q_3 \) in case presented in figure 2d compared to that drawn in figure 2b a number of composite particles increased up to 40\% of total number of particles at reactor outlet (in case depicted in figure 2b number of composite particles is equal to 20\% of all particles).
Figure 2. Distribution of mass average particle diameter (nm) and the logarithm of the number of particles along the reactor; (a) – calculation for $z_2 = 292$ mm, $Q_3 = 1.2$ g·s$^{-1}$; (b) – calculation for $z_2 = 292$ mm, $Q_3 = 1.0$ g·s$^{-1}$; (c) – calculation for $z_2 = 192$ mm, $Q_3 = 1.0$ g·s$^{-1}$; (d) – calculation for $z_2 = 192$ mm, $Q_3 = 0.8$ g·s$^{-1}$. 1 – logarithm of number of titania particles; 2 – logarithm of number of composite particles; 3 – the diameter of TiO$_2$ particles; 4 – the diameter of composite particles; 5 – the core diameter of composite particles.

6. Conclusion

Based on segregated oxidation of TiCl$_4$ and SiCl$_4$ the simulation of single-stage synthesis of composite ‘TiO$_2$ core – SiO$_2$ shell’ particles in working section of plasmachemical reactor has been conducted. Precursor flow rates and their fractions in gas mixtures injected thru side jet slits are in accordance with those which might be assigned to provide preliminary mixing of reagent components using bubbling procedure. These parameters will be crucial for experimental validation of applied physicomathematical model of the synthesis of composite particles. In addition, the results of calculations will
enable us to examine an extent of influence of operating parameters of the set-up on mean particle size and particle shell thickness as well.

Acknowledgments
The research was partly carried out within the framework of the Program of Fundamental Scientific Research of the state academies of sciences in 2013-2020 (project No. AAAA-A17-117030610120-2). This work was also carried out with partial financial support from the Russian Foundation for Basic Research (grant No. 18-08-00219 a).

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