

Analytical estimation of particle shape formation parameters in a plasma-chemical reactor

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Abstract. Analytical estimation of particle shape formation parameters in a plasma-chemical reactor implementing the process of thermochemical decomposition of liquid droplet agents (precursors) in the flow of a high-temperature gaseous heat-transfer medium was obtained. The basic factor which determines the process is the increase of concentration of a dissolved salt precursor component at the surface of a liquid particle due to solvent evaporation. According to the physical concept of the method of integral balance the diffusion process of concentration change is divided into two stages: the first stage is when the size of gradient layer does not reach the center of a spherical droplet and the second stage when the concentration at the center of a liquid droplet begins to change. The solutions for concentration fields were found for each stage using the method of integral balance taking into account the formation of salt precipitate when the concentration at the surface of the droplet reaches certain equilibrium value. The results of estimation of the influence of various reactor operation parameters and characteristics of initial solution (precursor) on the morphology of particles formed – mass fraction and localization of salt precipitate for various levels of evaporation.

1 Introduction

The use of ultra-fine powders of metal oxides for production of ceramic composite materials makes it possible to synthesize multipurpose products with unique strength characteristics, create construction materials replacing metals as well as protective coatings, filters, membranes, heat-insulation and catalytic materials with specified pore size. Plasma-chemical synthesis is one of the most promising techniques with controlled parameters, including thermochemical decomposition of liquid-droplet agents (precursors) in the flow of a high-temperature gaseous heat-transfer medium [1-3].

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The basic process parameters which determine the structure of obtained final product are represented by reactor operation characteristics (droplet speed, time inside the reactor, heat-transfer medium temperature), as well as relationship K between characteristic times of evaporation t_{vap} and intra-droplet diffusion t_{dif} :

$$K = \frac{t_{vap}}{t_{dif}} .$$

It is shown in papers [3-5] that in the process of precursor droplet movement in the flow of heat-transfer medium the temperature of a liquid particle increases up to the point where solvent evaporation begins at its surface relatively fast and the temperature profile becomes homogeneous. Then the concentration of salt near the surface increases and salt diffuses to the center of the droplet and at certain concentration value a condensed precipitate is formed.

2 Numerical Simulation

The rate u of change of radius R of the droplet due to solvent evaporation can be found in the framework of reduced film model [4, 6, 7]:

$$u = \frac{dR}{dt} = \frac{\lambda_g}{2\varrho} \frac{Nu}{R c_V} \ln(1+B) = K \frac{D}{R} , \quad (1)$$

where B – Spalding number; Nu – Nusselt number; D – diffusion coefficient; λ_g – thermal conductivity of gas at boiling point; ϱ – gas density; c_V – specific heat capacity of solvent vapors at constant volume.

As the temperature of the surface of precursor droplet reaches the equilibrium point of evaporation (boiling) its radius R starts to reduce. Then it is assumed that the temperature of the surface of the droplet remains constant and equal to the temperature of equilibrium evaporation. The concentration C of salt at the surface increases due to solvent evaporation and diffusion process described by the following equation begins.

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right), \quad r \in [0; R] , \quad (2)$$

where r – coordinate oriented from the center of the droplet.

The initial condition (moment of time $t=0$) for equation (2) is.

Boundary conditions in the center of the droplet:

$$\left. \frac{\partial C}{\partial r} \right|_{r=0} = 0 . \quad (3)$$

Boundary conditions on the surface of the droplet in the regime of solvent evaporation:

$$D \left. \frac{\partial C}{\partial r} \right|_{r=R} = -C_s \frac{dR}{dt} = u C_s , \quad (4)$$

where $C_s = C(R)$ – concentration on the surface of the liquid particle.

Using the analogy of heat and diffusion processes the method of integral (in this case mass) balance [8, 9] can be used to solve equation (2). The method assumes the following

concentration profile for considered conditions in the gradient zone with the thickness δ (Fig. 1, a):

$$C(r) = C_0 + \frac{\Delta C}{\delta^2} \frac{R}{r} (r - r_*)^2, \quad r_* \leq r \leq R, \quad (5)$$

where δ – thickness of gradient zone of concentration; $r_* = R - \delta$,
 $\Delta C = C_s - C_0$.

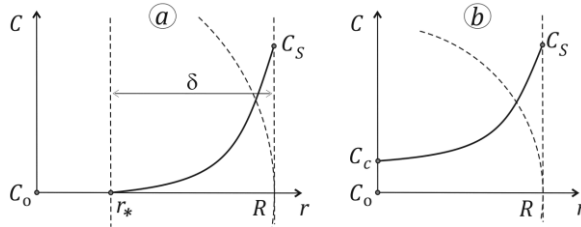


Fig. 1. Solution region scheme.

Integrating the equation (2) over the coordinate r

$$\int_{r_* = R - \delta}^R r^2 \frac{\partial C}{\partial t} dr = \int_{r_* = R - \delta}^R D \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) dr,$$

Taking into account relationship (5) in the limits of variable droplet radius R and length δ of the gradient zone according to Leibniz's rule

$$\frac{d}{dt} \left[\frac{C_0}{3} R^3 - \frac{C_0}{3} R_0^3 + \Delta C R^3 \left[\psi(R) - \psi(r_*) \right] \right] = 0,$$

where $\psi(r) = \left(\frac{r}{\delta} \right)^2 \left[\frac{1}{4} \left(\frac{r}{R} \right)^2 + \left(1 - \frac{\delta}{R} \right) \left[\frac{1}{2} \left(1 - \frac{\delta}{R} \right) - \frac{2}{3} \frac{r}{R} \right] \right]$.

Integrating the obtained ordinary differential equation over time we can obtain the final relationship between the concentration at the droplet surface and the size of the gradient zone

$$C_s = \frac{C_0}{3} \left[3 + \frac{(1 - \varphi) \left(\frac{R_0}{R} \right)^3 - 1}{\psi(R) - \psi(r_*)} \right]. \quad (6)$$

Another relationship between C_s and δ can be obtained from differentiation of the temperature profile (5), boundary conditions (4) taking into account the relation (1)

$$C_s = C_0 \frac{2 - \frac{\delta}{R}}{\left(2 - \frac{\delta}{R}\right) - \frac{\delta}{R} K} . \quad (7)$$

Thus, from expressions (6) and (7) for any current droplet radius R surface concentration C_s and gradient layer thickness δ can be determined if condition $R \geq \delta$ is satisfied.

In case when concentration disturbance reaches the center of the droplet the following relationship can be used [8] instead of the profile (fig. 1, b)

$$C(r) = C_c + (C_s - C_c) \left(\frac{r}{R}\right)^2, \quad 0 \leq r \leq R,$$

where C_c – concentration in the center of a liquid particle.

After the transformations analogous to the ones described above an ordinary differential equation can be obtained for this case

$$\frac{d}{dt} \left[C_c \frac{R^3}{3} + \frac{C_s - C_c}{5} R^3 \right] = 0,$$

solving which we can determine the concentration C_c at the center of a liquid particle and at the droplet surface C_s :

$$C_c = \frac{5(2-K)}{2(5-K)} (1-\varphi) C_0 \left(\frac{R_0}{R}\right)^3, \quad C_s = \frac{2}{2-K} C_c . \quad (8)$$

Parameter φ , from equations (6) and (8), determines the fraction of precipitating salt mass (regarding the initial mass).

3 Analysis of the results

The algorithm for finding concentration distribution parameters and the fraction of precipitated salt is as follows.

1. On the basis of thermophysical properties of materials and reactor's geometry characteristics using averaged heat-transfer medium flow parameters from formula (1) the following values are found: a dimensionless criterion K – ration between characteristic times of evaporation and diffusion, evaporation rate u , the time of a liquid particle inside the reactor and radius R of a particle leaving the reactor.

2. Concentration C_s on the droplet surface is calculated for $\varphi=0$ using expressions (6), (7) or (8).

3. If $C_s > C^*$ (C^* – equilibrium concentration after which salt formation starts), then we choose the value of parameter φ , providing $C_s = C^*$. Thus, we can determine all characteristics of a liquid-droplet particle leaving the reactor including the coordinates of salt precipitation.

The evolution of the droplet of low-concentration ($C_0=0.04$) water solution of the salt with the radius $R_0=20 \mu\text{m}$ in the process of diffusion $D=2 \cdot 10^{-9} \text{m}^2/\text{s}$ and conditional value $C^*=1$. is considered as an example.

Figure 2 shows the dependence of concentration C_s on evaporation level R_0/R for various values of K criterion. As it can be seen the higher the value of K the sooner the

concentration at the surface reaches the equilibrium point C_* , which determines the beginning of salt precipitation process. The dependence of mass fraction of salt precipitate on evaporation level for various values of K criterion is shown Figure 3. The data correspond to development of physical process shown in Figure 2 and illustrate the size and location of the area (in the particle volume) of salt precipitation. Figure 4 shows the diagram for localizations of 80% salt mass precipitation characterizing the condensate area after precursor solvent evaporation.

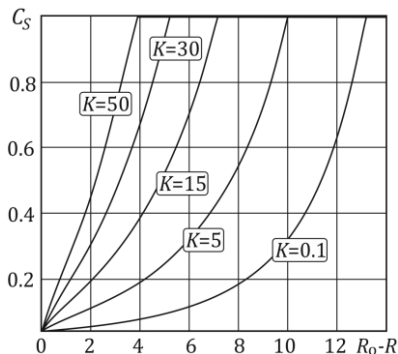


Fig. 2. Dependence of concentration C_s on evaporation level.

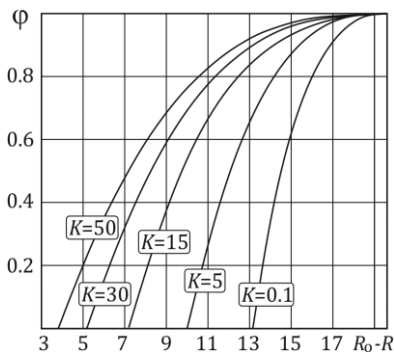


Fig. 3. Dependence of mass fraction of salt precipitate on evaporation level.

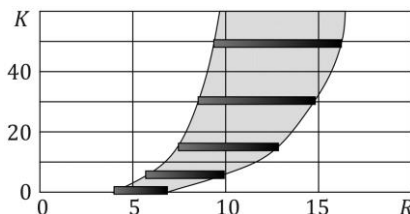


Fig. 4. Localizations of 80 % salt mass precipitation for a particle with initial size of 20 μm .

Thus, the algorithm for analytical estimation of parameters of particle shape formation in the plasma-chemical reactor based on solving the problem of diffusion in the intra-droplet precursor volume in the process of solvent evaporation is described in the paper. The offered approach makes it possible to determine mass fraction and localization of salt precipitate for various evaporation levels.

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