Morphology of ceramic particles produced by plasma-chemical synthesis

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Abstract. Thermal and diffusion processes in the droplet weakly concentrated metal salt solution during its heating in the plasma chemical reactor, in order to synthesize metal oxide powders are considered. Numerical study is based on previously proposed physical-mathematical model. The results of numerical calculations are analyzed to assess the possible influence of the operation parameters of the reactor and the characteristics of the initial solution (precursor) on the morphology of the particles formed.

1. Introduction

The use of fine powders of metal oxides in the preparation of ceramic composite materials enables to synthesize products for various purposes with unique mechanical properties, create metal-substituting construction materials and protective coatings, as well as filters, membranes, and thermoinsulating and catalyst structures with a specified pore size. One of the most promising technologies for producing ceramic powders with controlled parameters is plasma-chemical synthesis, including the thermochemical decomposition of liquid-drop reagents (precursors) in a flow of high-temperature gaseous heat carrier [1, 2]. This technology is known as “spray pyrolysis” [3]. Depending on the chemical composition of the precursor, a wide range of metal oxide powders can be obtained: Al₂O₃ from an aluminum nitrate Al(NO₃)₃ solution, zirconium oxide ZrO₂ from a zirconium nitrate Zr(NO₃)₄ (or zirconium chloride ZrOCl₂) solution, as well as mixed oxides, such as ZrO₂ + MgO, ZrO₂ + Y₂O₃, ZrO₂ + CaO, ZrO₂ + Y₂O₃ + Al₂O₃, etc. [1–3].

Electron microscopic studies of powder particles prepared by the plasma chemical method revealed that their morphology may vary, featuring solid spherical single-crystal formations, hollow spheres and their fragments, films, and porous or foamed particles [2, 3]. The internal structure of ceramic particles is the most important parameter that determines the quality of the product. While the production of construction ceramics requires fine spherical solid particles, the manufacture of heat-shielding materials and catalysts preferably uses porous and hollow particles.

Clearly, the particle morphology is defined by both the precursor characteristics (dispersion of drops, solution concentration) and thermochemical process parameters (speed of drops, time of their residence in the reactor, temperature regime, aerodynamic pattern of the two-phase flow in the reactor, thermophysical properties of the reagents, etc.). To ensure a controllable mode of operation of the plasma-chemical reactor in order to produce particles with desired characteristics, it is necessary to develop physical-mathematical models of the processes occurring in it. The development of such a mathematical apparatus involves multivariate analysis of the problem of calculating the parameters of a multicomponent two-phase chemically reacting medium with a detailed description of heat and mass transfer in the individual spray drops and between the drops and the gaseous heat carrier. However, the available studies are based on physical-mathematical models involving a number of serious simplifications in describing the processes within the solution drops [1–4], an approach that significantly reduces the possibility of predicting the characteristics of the synthesized powders of metal oxides, in particular, their morphology (internal structure).
The physical-mathematical model of heat and diffusion processes in a drop of slightly concentrated solution of a metal salt during heating in a plasma-chemical reactor is presented in [5]. This model is designed to predict the morphology of the particles of ceramic powders depending on the characteristics of the solution and gaseous heat carrier.

2. Problem statement

The plasma-chemical synthesis of ceramic powders is a multistage process that includes the atomization of liquid precursor to form polydisperse drops in the reactor, the movement of the drops in the gaseous heat carrier flow, heating and evaporation of the drops (accompanied by the diffusion and crystallization of the metal salt in the drop bulk), the thermolysis of the salt, leading to the formation of a microporous metal oxide structure at high temperature, and finally, its sintering to form solid particles with a specific morphology (Figure 1).

![Figure 1](image)

Figure 1. Effect of the conditions of salt precipitation on the morphology of the particle formed: (1) heating and evaporation, (2) precipitation and dehydration of the salt, and (3) thermolysis and sintering.

Figure 1 shows that plasma-chemical synthesis produces particles of different structures, depending on the conditions of salt deposition and the characteristics of the precursor salt. Solid particulates are produced by bulk deposition (Figure 1a). During surface deposition, either hollow particles (Figure 1b), if the gas permeability of the deposited salt layer is high enough, or fragments of hollow spheres (Figure 1c) are formed. In the latter case, because of a low permeability of the salt layer, the pressure of solvent vapor generated inside the particle destroys it, whereby producing polydisperse shell fragments.

When an aqueous solution of aluminum nitrate nonahydrate $\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}$ is used, the thermolysis of the salts crystallized in the drop bulk begins above 135°C. In this, the $\text{Al(OH)}_2\text{NO}_3 \cdot 1.5\text{H}_2\text{O}$ basic salt is first formed, while at higher temperatures (above 200°C), it decomposes to yield an amorphous alumina:

$$4\text{Al(NO}_3\text{)}_3 = 2\text{Al}_2\text{O}_3 + 12\text{NO}_2 \uparrow + 3\text{O}_2 \uparrow.$$  

Analysis of the individual steps of the plasma-chemical synthesis revealed that the morphology of the powder particles arises at the stage of evaporation of the drop. Consider the main processes occurring simultaneously in the solution drop at the stage of evaporation, such as the temperature evolution of the drop during its heating, solvent evaporation from the drop surface, salt diffusion towards the drop center, salt crystallization, and removal of the remaining solvent (drop dehydration).

When a solution drop moves in the gaseous heat carrier flow, it is heated so that water evaporates from its surface. As a result, the dissolved salt concentration increases near the drop surface, thereby causing the salt to diffuse to the center of the drop. When the concentration of the salt reaches a certain value, it begins to crystallize to form a condensed precipitate.

The formation of the precipitate, a process determining the morphology of the final product particle, proceeds in two stages. During the first stage, the primary structure of the particle is formed. Let us assume that, when the concentration of salt in solution at the drop surface reaches a certain critical supersaturation concentration $C_{cr}$, the salt crystallizes instantaneously in the part of the drop where $C \geq C_{cr}$ ( $C$ is the salt concentration, and $C_{cr}$ is the equilibrium concentration at a given temperature). In this case, depending on the rate of solvent evaporation and salt diffusion rate, there are two possibilities: bulk and surface precipitation.

Bulk precipitation, producing a solid particle, occurs if by the time $t_{cr}$ of reaching $C_{cr}$ at the surface of the drop, the inequality $C > C_{cr}$ holds throughout its volume. Surface precipitation, producing a hollow
spherical particle occurs if $C > C_r$ only for the peripheral part of the drop, within the layer limited by the critical radius $R_c(t_0)$ and the actual radius $R(t)$ of the drop. The thickness of the wall of the hollow particle is $\delta_1 = R(t) - R_c(t_0)$.

During the second stage, the solvent vapor is removed from the resulting porous structure. Assume that the primary precipitate has a finely porous structure permeable to water vapor.

In the case of bulk precipitation, removing the water vapor does not alter the primary structure of the particle: it is only densified due to the salt remaining in the solution. In the case of surface precipitation, we assume that the salt remaining in the hollow particle, with a mass of

$$m = 4\pi \int_0^R C(r)r^2 dr$$

is uniformly deposited on the inner surface of radius $R_c(t_0)$, forming an additional precipitate layer of thickness $\delta_2 = R_c(t_0) - R_1$, where $R_1$ is the radius of the spherical cavity inside the particle formed. The radius $R_1$ is given by

$$R_1 = [R_c^3(t_0) - \delta_2]^{\frac{1}{3}},$$

where $\rho_s$ is the density of the salt precipitate.

3. Evaluation of the characteristic times

To construct a mathematical model of the processes at the stage of evaporation, we estimated their characteristic times.

• The characteristic time of the dynamic relaxation of the drop, indicating the lag between its velocity and the velocity of gaseous heat carrier is given by \[6\]

$$t_1 = 2\rho R_0^2/\mu,$$

where $\rho$ is the fluid density, $\mu$ is the dynamic viscosity of the gas, and $R_0$ is the initial radius of the drop.

• The characteristic time of temperature equilibration throughout in the drop is \[7\]

$$t_2 = R_0^2/\kappa,$$

where $\kappa$ is thermal diffusivity of the solution.

• The characteristic time of diffusion of salt in the drop bulk reads as

$$t_3 = R_0^2/D,$$

where $D$ is the diffusion coefficient.

• The characteristic time of evaporation of liquid from the drop surface according to the stagnant film model for evaporation can be written as \[8\]

$$t_4 = \frac{2\rho R_0^2 c_v}{\lambda_g \text{Nu} \ln(1 + B)},$$

where $B = c_v (T_e - T_v) / L$ is the Spaulding number, $\text{Nu}$ is the Nusselt number, $\lambda_g$ is the thermal conductivity of the gas at the boiling point, $c_v$ is the specific heat at constant volume of solvent vapor, $L$ is the latent heat of vaporization, is the temperature of the gaseous heat carrier, and is the temperature of equilibrium vaporization (boiling).

Note that the ratio between the characteristic times is independent of the initial radius $R_0$ of the drop and that, with increasing $\text{Nu}$ and temperature difference $T_e - T_v$, the evaporation time decreases. Therefore, we can assume that, under all conditions, the following relationships hold:

$$t_1 \sim t_2 << t_3 \sim t_4.$$

Let us consider, as an example, a drop of a low concentration aqueous metal salt solution with an initial radius of $R_0 = 25$ $\mu$m. At atmospheric pressure and boiling temperature, the following values of the parameters must be used: $D = 10^{-5}$ $m^2/s$, $\rho = 10^3$ $kg/m^3$, $\kappa = 1.58 \cdot 10^{-7}$ $m^2/s$, $c_v = 2.0 \cdot 10^3$ $J/(kg K)$, $L = 2.26 \cdot 10^6$ $J/kg$, $\text{Nu} = 2$, $T_e - T_v = 50$ $K$, $T_v = 373$ $K$, $\lambda_g = 3.3 \cdot 10^{-2}$ $W/(m K)$, and $\mu_g = 2.2 \cdot 10^{-5}$ Pa s.

In this case, the characteristic times of the problem were found to be $t_1 = 6.3 \cdot 10^{-3}$ s, $t_2 = 4.0 \cdot 10^{-3}$ s, $t_3 = 0.63$ s, and $t_4 = 0.88$ s.

As shown in [5], the results depend on the parameter $K$.
4. Analysis of the results

When considering the heating and evaporation of a drop and the diffusion of salt in the drop prior to its crystallization, we assumed that:

• the drop has a spherical shape during the entire process;
• the thermophysical and transport properties of the solution are invariable;
• the density and specific heat of the solution and solvent are the same;
• thermal diffusion is ignored.

Assuming that evaporation of the drop begins only after reaching the boiling point of the solution, we can specify two stages of the process.

(1) The stage of initial heating, when the drop is heated but no evaporation occurs. The concentration of salt is uniform and the diffusion does not occur.

(2) When the surface temperature reaches the equilibrium vaporization temperature (boiling point), solvent evaporation starts, being accompanied by the decrease of the drop size, increase of the salt concentration near the surface, and occurrence of the diffusion process. The surface temperature of the drop remains constant and equal to the equilibrium temperature of evaporation.

Note that the proposed model adequately describes the thermal and diffusion processes for dilute solutions (initial concentration of salt is less than 5 wt %). Under these conditions, the assumptions underlying the formulation of the problem are correct. In many practical applications, the initial concentration of the solution ranges within 5–10 wt % [1–3].

The dimensionless mathematical formulation and numerical method of its solving are presented in [5]. Results of calculations show that the radial distributions of the salt concentration in a drop vary depending on the parameter $K$. At small $K$ values, when the critical concentration $C_{cr}$ at the drop surface is reached, the salt concentration inside the drop is greater than the equilibrium concentration $C_{e}$ so that solid particles are formed. At $K \sim 1$, there is a region inside the drop where the concentration is below the equilibrium concentration $C_{e}$, and therefore, the process of crystallization produces a hollow particle.

Figure 2 displays the crystallization layer thickness normalized by the drop radius at the time of reaching the critical concentration $C_{cr}$ at the drop surface as a function of $K$. The calculation results showed that, for the assumed initial concentration $C_0$ of the solution, the boundary value that separates the modes of formation of hollow and solid particles is $K_c = 0.75$. At $K < K_c$, vaporization is slower than diffusion, so solid particles are formed. At $K > K_c$, vaporization process is faster than diffusion, and therefore, hollow particles are produced. At fixed values of the thermal properties of the salt and solvent, the value of $K$ is mainly determined by the temperature difference between the drop and carrying medium. At a small temperature difference, solid particles are formed, whereas at a large difference, hollow particles. At a large temperature difference, evaporation is faster than diffusion ($K$ increases), and crystallization has time to occur only in the surface layer, and vice versa, at a low temperature difference, the salt concentration reaches an equilibrium value throughout the drop. Note that the ratio of the thicknesses of the primary deposited layer $\delta_1$ and the layer $\delta_2$ formed from the residual salt is determined by the value of the parameter $K$. 

$$K = \frac{t_3}{t_4} = \frac{\lambda_s \text{Nu} \ln(1 + B)}{2\rho Dc_v}.$$
5. Conclusions

(1) Analysis of the results of numerical calculations within the framework of this model showed that the only dimensionless parameter that determines the structure (morphology) of the particle formed is the ratio of the characteristic times of diffusion and evaporation: $K = \frac{t_3}{t_4}$. At $K < K_*$, diffusion is faster than evaporation, and therefore, solid particles are formed; at $K > K_*$, hollow spherical particles are formed.

(2) In the case of the formation of hollow particles, the process of salt crystallization occurs in two stages: the primary precipitation to form a layer of thickness $\delta_1$ followed by the deposition of the remaining salt onto the inner surface of the particles to form a layer of thickness $\delta_2$. The ratio between $\delta_1$ and $\delta_2$ is determined by the value of $K$.

(3) In producing ceramic powders with a given morphology, the main parameters of the controlled plasma-chemical synthesis are the initial concentration of the precursor salt (salt solubility), temperature difference between the gaseous heat carrier and the precursor, as well as the difference between the critical supersaturation concentration $C_{cr}$ and equilibrium saturation concentration $C_*$.

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