Similarity criteria of HOSP formation at plasma processing of agglomerated particles

O P Solonenko
Khristianovich Institute of Theoretical and Applied Mechanics, Siberian Branch of RAS, Novosibirsk, 630090, Russia
E-mail: solo@itam.nsc.ru

Abstract. The theoretical analysis of basic phenomena at plasma processing of the agglomerated powders, in context of hollow microspherical particles production, was fulfilled. With the use of the obtained theoretical solutions for the first time the key similarity criteria were derived that allow to formulate the requirements to plasma flow, characteristics of agglomerate and its material as well as condition of quenching of the formed hollow microdroplet which realization provides the formation of hollow microsphere with necessary characteristics, in particular, of maximal diameter and minimum thickness of shell.

1. Introduction
In the present-day industry of structural and protective materials, powders made up by hollow spheres (HOSP), or hollow powders, gain increasing acceptance. Hollow particles can be obtained by various methods [1-17], etc. Ceramic powders that are used in the production of plasma-sprayed thermal barrier coatings, composite heat- and sound-insulating materials, light construction fillers and backfills, buoyancy materials, and explosive mixtures, deserve special attention. Such powders are also used as catalysts carriers, adsorbents, filter elements, encapsulating media, etc. Application of hollow powders has entered a stage at which the range of scientific and engineering problems to be solved widens permanently.

Over the recent decade, in connection with permanently increasing interest in hollow powders and widening application fields of such powders, considerable efforts of researchers have been focused on the development of new approaches to the problem of formation of hollow microspheres in thermal plasma. In this connection, guaranteed plasma synthesis of hollow microspheres with desired morphology, chemical composition, and mechanical properties becomes an urgent matter.

As it was noted in [18], the simplest production method of hollow powders implies processing of void-free, or dense, particles in plasma. For instance, for a number of materials such as oxides, their densities \( \rho_p^{(s)} \) and \( \rho_p^{(l)} \) in the solid (s) and liquid (l) state may differ substantially. As a result, the particle with \( \rho_p^{(l)} < \rho_p^{(s)} \), as it melts, grows in volume, so that its effective size increases. The radius of the completely melted particle increases by \( \Delta R_p = R_{p0} \left( \sqrt[3]{\rho_p^{(s)}} / \rho_p^{(l)} - 1 \right) \), where \( R_{p0} \) is the initial particle radius. If overheated melt droplet did undergo subsequent fast quenching, its solidification starts from the surface, so that the particle size turns out to be fixed at \( R_{p,end} = R_{p0} + \Delta R_p = R_{p0} + \sqrt[3]{\rho_p^{(s)}} / \rho_p^{(l)} \).

Following solidification-induced volume shrinkage, a spheroidal cavity forms inside the particle, the corresponding radius of the cavity being \( R_h = R_{p0} + \Delta R_p - A_p \), and the shell thickness \( \Delta_p = R_{p0} \left( 1 - \sqrt[3]{1 - \rho_p^{(s)}} / \rho_p^{(l)} \right)^{1/3} \left( \rho_p^{(s)} / \rho_p^{(l)} \right) \).
Using these dependences at hand, we can obtain numerical estimates, for instance, for $\alpha$-Al$_2$O$_3$ (corundum) particles. Analyzing available experimental data, the authors of [19] proposed the following dependence for $\alpha$-Al$_2$O$_3$ density in liquid state: 

$$\rho_p^\ell(T) = 3030 - 1.08(T - 2327),$$

where the dimension of density is kg/m$^3$, and the dimension of temperature $T$ is K. For the density of $\alpha$-Al$_2$O$_3$ in solid state, we adopt the value $\rho_p^{(s)} = 3960$ kg/m$^3$. Then, for the droplet of radius 50$\mu$m at the melting point $T_{pm}=2327$K we have: $\rho_p^{(l)}(2327) = 3030$ kg/m$^3$, $\Delta R_p \approx 4.7 \mu$m, $R_{p, end} \approx 54.7 \mu$m, $A_p \approx 20.9 \mu$m, and $R_h \approx 33.8 \mu$m. For the same droplet overheated over the melting point by 400K, we similarly obtain: $\rho_p^{(l)}(2727) = 2598$ kg/m$^3$, $\Delta R_p \approx 7.5 \mu$m, $R_{p, end} \approx 57.5 \mu$m, $A_p \approx 17.2 \mu$m, and $R_h \approx 40.3 \mu$m.

Hence, the characteristics of hollow spheres solidified from overheated molten particles are fully defined by the densities of the particle material in the solid and liquid state, and also by the overheating value of the droplets. Provided that the particle shell is impermeable, a spheroidal vacuum cavity is formed inside each particle.

In paper [17] technological capabilities of thermal plasma are shown when processing various agglomerated powders for the purpose of obtaining the hollow microspheres of metals, alloys and oxide ceramics. Despite great practical and scientific interest to such powders [1, 2, 12, 20-22], etc., so far there are no physical and theoretical bases allowing a priori to optimize the mode of plasma processing and for certain to predict diameter and thickness of shell of obtained hollow microspheres.

2. Analysis of basic processes

In the present paper as the initial particles are considered the agglomerated particles of decamicrometer sizes obtained by means of spray drying. Such particles are formed of large number of randomly packed ultra-fine particles (UFPs) and are characterized by open porosity. Their processing in plasma jet can lead to formation, both hollow microspheres, and microspheres with distributed gas inclusions. Implementation of this or that scenario depends on the intensity of interphase heat transfer "agglomerated particle - plasma" and agglomerate residence time in plasma jet. As it was noted in [17], irrespective of method of obtaining the agglomerated particles (spray drying, mechanoactivation in high-energy planetary-type mills, etc.) formation of hollow microspheres has much in common. This process consists of following stages (see figure 1):

1) heating the agglomerate until its surface reaches the melting point; at the same time, owing to the thermal expansion, there is the free outflow of gas from porous frame of particle in environment;

2) formation of stable surface film of the melt encapsulating remained gas in porous frame of particle; as it will be shown further, mass of the gas $m_g^{(c)}$ which has remained in volume of agglomerated particle in many respects determines the final diameter of hollow microsphere and thickness of its shell;

3) further heating of particle and melting of UFPs directed from its surface to the center, their merge and involvement in growing layer of melt, owing to ideal wetting and minimization of surface
of the front of melting; at the same time there is gas displacement in solid porous frame by moving front or capture of gas inclusions by melt;

4) completion of melting of agglomerate, formation of either internal gas cavity and liquid spherical shell, or spherical droplet with distributed gas bubbles, further heating of droplet-balloon;

5) the subsequent quenching at which the hollow microspherical droplet solidifies from surface.

The purpose of the present work is obtaining the key similarity criteria allowing the formulation of the requirements to heat flux density $q^{(+)} (\text{W/m}^2)$ from plasma to particle, taking into account the properties of heterogeneous material of the agglomerate, which realization is necessary for formation of hollow microdroplet of controlled diameter and thickness of shell.

Besides, the criterion condition which realization provides preservation of size and thickness of hollow droplet shell as a result of obtained hollow droplet quenching is derived.

3. Similarity criteria characterizing the stages of HOSP production

At first, we will consider the processes of heating and melting of spherical agglomerated particle of size $D_{p0}$ of several tens microns, formed of solid spherical UFPs with characteristic size $d_p<<D_{p0}$.

Let’s assume that $P$ is its volume open porosity, and $T_{p0}$ is initial temperature at the moment of input in plasma flow characterized by the heat flux density $q^{(+)}$. Let’s take into consideration the effective properties of heterogeneous material: $\rho P c_1 + \rho c_2$ is specific volumetric heat capacity, where $(\rho c)_1$ and $(\rho c)_2$ are specific heat capacities of UFPs material and gas; $\rho$ and $c$ are density and heat capacity; inferior indexes of $i=1,2$ correspond to UFPs material and gas, respectively; superscripts “s” and “l” characterize the values of parameters for solid and liquid state of material. We will define thermal conductivity $\lambda_p^{(s)}$ of particle porous material in accordance with [23], i.e. $\lambda_p^{(s)} = \lambda_{1}^{(s)}/[1+P(\lambda_{1}^{(s)}/\lambda_2^{(s)}-1)]$. We consider that effective thermophysical properties $(\rho c)_p^{(s)}$, etc. of porous material do not depend on temperature and are obtained by averaging in interval of temperatures [$T_{p0}$; $T_{1m}$], $T_{1m}$ is melting point of UFPs; $\sigma_p^{(s)} = \rho c_1^{(s)}(\rho c)_p^{(s)}$ is thermal diffusivity. Under $L_{1m} = (1-P)L_{p0}$ we understand efficient melting heat of heterogeneous material ($L_{im}$ is heat of melting of the UFPs material). Thus, we have evaluated all required thermophysical characteristics of the heterogeneous material. Those characteristics parametrically depend on the porosity $P$, which is the parameter to be set a priori.

Below, in figures, we will omit the upper line under variables. As a model ceramic material we will use practically interesting to many technologies $\alpha$-$\text{Al}_2\text{O}_3$ which properties are rather well studied both for solid, and for liquid states. Let’s consider that the gas filling pore space of agglomerates is air and ambient pressure is equal to atmosphere pressure.

3.1. Heating of agglomerated particle before melting

Apparently, under other equal conditions, final diameter $D_p$ and thickness of shell $\Delta_p$ of hollow droplet will depend on the mass of gas $m_{g0}^{(c)}$ remained (encapsulated) in porous volume of agglomerate by the time $t_f$ of formation of the surface film of melt, and also on the degree of the subsequent overheating of hollow droplet formed after complete melting of agglomerate. It is evident, that overheating of hollow droplet is limited by boiling point $T_{1b}$ of UFPs material. On one hand, the value $m_{g0}^{(c)} < m_{g,\text{max}} = \pi \rho_{g} (T_{p0}) D_{p0}^2 P / 6$, i.e. is limited above the initial mass of gas, and, on the other hand $m_{g0}^{(c)} \geq m_{g,\text{min}} = \pi \rho_{g} (T_{1m}) D_{p0}^2 P / 6$ that answers the case when by the time $t_f$ agglomerated particle is uniformly heated, and its temperature is equal to $T_{1m}$. The actual mass of gas depends on
temperature distribution on particle radius at the time \( t = t_r \), i.e. 
\[
m_{g0}^{(c)} = 4\pi \int_0^{R_{p0}} \rho_g(T) r^2 \, dr,
\]
\( R_{p0} = D_{p0} / 2 \). Therefore, value \( m_{g0}^{(c)} \) is defined by thickness \( \delta(t_r) = \sqrt{2\pi R_{p0}/t_r} \) of the thermal boundary layer in particle which at the moment \( t_s = R_{p0}^2/12a_p^{(s)} \) is equal to \( R_{p0} \), i.e. at \( t = t_s \) thermal disturbance will reach the particle center.

For consideration of the irregular stage of heating of agglomerated particle, that we are interested in, we will formulate the following boundary value problem:

\[
\frac{\partial T}{\partial t} = \frac{a_p^{(s)}}{r^2} \cdot \frac{\partial}{\partial r} r^2 \frac{\partial T}{\partial r}, \quad T(r,0) = T_{p0}, \quad r \in [0; R_{p0}]; \quad \frac{\partial T}{\partial r} \bigg|_{r=R_{p0}=0} = \frac{q^{(s)}}{\lambda_p^{(s)}}, \quad 0 < t \leq t_s.
\]

Taking into consideration the dimensionless variables \( \bar{r} = r / R_{p0} \), \( \text{Fo} = \bar{a}_p^{(s)} t / R_{p0}^2 \), \( \vartheta^{(s)} = [T(\text{Fo},\bar{r}) - T_{p0}] / [T_{im} - T_{p0}] \), we will formulate the boundary value problem characterizing heating of solid agglomerated particle:

\[
\frac{\partial \vartheta^{(s)}}{\partial \text{Fo}} = \frac{1}{\bar{r}^2} \cdot \frac{\partial}{\partial \bar{r}} \bar{r}^2 \frac{\partial \vartheta^{(s)}}{\partial \bar{r}}; \quad \vartheta^{(s)}(0,\bar{r}) = 0, \quad \bar{r} \in [0;1];
\]

\[
\frac{\partial \vartheta^{(s)}}{\partial \bar{r}} \bigg|_{\bar{r}=1} = 0, \quad \frac{\partial \vartheta^{(s)}}{\partial \bar{r}} \bigg|_{\bar{r}=0} = K_{i_p}^{(s)}, \quad 0 < \text{Fo} \leq \text{Fo}_a,
\]

where \( K_{i_p}^{(s)} = q^{(s)} R_{p0}^{(s)} / \lambda_p^{(s)} (T_{im} - T_{p0}) \) is Kirpichyev’s similarity criterion [24]. By analogy with work [25], the approximate solution of the boundary value problem (1), (2) characterizing dynamics of surface temperature of spherical particle at the stage of its irregular heating (\( \text{Fo} \leq \text{Fo}_a = 1/12 \)), looks like:

\[
\vartheta^{(s)}(\text{Fo},1) = K_{i_p}^{(s)} \cdot (\text{Fo} + 2\sqrt{\text{Fo}/3}),
\]

Having used (3), we will find the value of time \( \text{Fo}_f = (\sqrt{1+3/K_{i_p}^{(s)}} - 1)^2 / 3 \) necessary for heating of particle surface to the melting point, solving the equation (3) at \( \vartheta^{(s)}(\text{Fo}_f,1)=1 \). Let’s demand the realization of the condition \( \text{Fo}_f / \text{Fo}_\vartheta = 1 \), where \( \text{Fo}_\vartheta = \bar{\vartheta}^2 / 12 \) is an instant of time for which the dimensionless thickness of thermal boundary layer in agglomerated particle is equal to \( \bar{\vartheta} = \vartheta / R_{p0} \), \( 0 < \bar{\vartheta} \leq 1 \). As a result we will obtain the condition in similarity criterion and dimensional forms

\[
K_{i_p}^{(s)} (\bar{\vartheta}) = 3 / [(1 + \bar{\vartheta}^2 / 2)^2 - 1],
\]

\[
q^{(s)}(\bar{\vartheta}) = 3\lambda_p^{(s)} (T_{im} - T_{p0}) / [(1 + \bar{\vartheta}^2 / 2)^2 - 1]R_{p0}.
\]

In figure 2a,b are presented the generalized dependences for Kirpichyev’s similarity criterion \( K_{i_p}^{(s)} \) and the relative mass of gas \( \bar{m}_{g0}^{(c)} = m_{g0}^{(c)} / m_{g,\text{max}} \), which has encapsulated in porous volume of agglomerated particle by the instant of time \( t_r \), versus dimensionless thickness \( \bar{\vartheta} \). The corresponding generalized correlation between the relative mass of the gas \( \bar{m}_{g0}^{(c)} \), which has remained in particle by the instant of time \( t_r \), and criterion \( K_{i_p}^{(s)} \) is presented in figure 2c.

As appears from the presented data, parameter \( \bar{m}_{g0}^{(c)} \), depending on intensity of particle heating, undergoes essential variation. It should be noted that, other things being equal, the relative mass of gas \( \bar{m}_{g0}^{(c)} \), encapsulated in volume of agglomerated particle in an instant of time \( t_r \), does not depend on
porosity $P$ of agglomerate, and is defined by temperature distribution in it. But, as appears from (3), the heat flux density $q^{(+)}(\overline{\delta})$ demanded for ensuring the given thickness $\overline{\delta}$ of thermal boundary layer in an instant of time $t_f$, depends in direct proportion on effective thermal conductivity $\lambda_p^{(s)}$ which, in turn, depends on porosity of agglomerate.

In accordance with [26], for random dense packing arrangements of spherical UFPs of the set size in the agglomerated particle their volume concentration $1-P$ ranges from 0.59 to 0.65. Therefore, when studying the influence of porosity $P$ of agglomerates on dynamics of their heating and phase changes, as minimum value of porosity it is possible to assume the value $P=0.35$.

The values of the heat flux density $q^{(+)}$ are given in Figure 3, demanded for providing stated above conditions of heating of agglomerated particles $\alpha$-$Al_2O_3$ of sizes $D_{p0}=50$, 100 and 150 µm at their porosity of $P=0.35$. We consider that in initial instant of time the porous volume of agglomerates is filled with air at temperature $T_{p0}=300$ K. It is clear that requirements to heat flux density $q^{(+)}$ significantly increase with decrease of size $D_{p0}$ of agglomerated particle and mass of gas $m^{(c)}_{g0}$.

![Figure 2](image_url)

**Figure 2** Generalized dependences of Kirpichyev's similarity criterion (a) and relative mass of encapsulated gas (b) vs. the relative thickness of thermal boundary layer in agglomerated particles; generalized dependence of relative mass of encapsulated gas vs. Kirpichyev's criterion (c); required values of the heat flux density when processing agglomerates $\alpha$-$Al_2O_3$ of sizes $D_{p0}=50$, 100 and 150 µm (porosity $P=0.35$) vs. the relative thickness of thermal boundary layer in agglomerated particles.

3.2. Melting of agglomerate and hollow droplet formation

Let's make an estimation of the relative values of diameter $\overline{D}_{p,m} = D_{p,m} / D_{p0}$ and thickness of shell $\overline{A}_{p,m} = A_{p,m} / D_{p,m}$ of hollow microspheres, having assumed that agglomerates $\alpha$-$Al_2O_3$, obtained at $t = t_f$, then are completely melted, and their temperature of $T_p$ is equal to melting point of $\alpha$-$Al_2O_3$ ($T_{m1} = 2327$ K). According to [27], the equilibrium value of hollow droplet radius $R_p$ can be defined from the equation
\[
\begin{align*}
p_{g} & \geq \frac{2\sigma^{(l)}_{m}}{R_{p}} \left( 1 + \frac{1}{1 - A_{p} / R_{p}} \right) - \frac{3m_{g}(c)RT_{g}}{4\pi R_{p}^{3}M_{g}(T_{g})} \left( 1 - A_{p} / R_{p} \right)^{3} = 0, \quad 1 - A_{p} / R_{p} = \sqrt[3]{1 - 3m_{p,0} / 4\pi R_{p}^{3}R_{p}^{3}}, \quad (6)
\end{align*}
\]
derived from the equality of initial agglomerated particle mass and mass of hollow droplet formed.

Here \( m_{p,0} = 4\pi R^{3} \rho (1 - P) R_{p}^{3} / 3 \) is the mass of UFPs in agglomerate, \( p_{g} \) is the pressure of environment, \( R = 8.314 \cdot 10^{3} \text{J/(kmole-K)} \) is the universal gas constant, \( M_{g}(T_{g}) \) is the relative molar mass of gas at temperature \( T_{g} = T_{p} \). For efficient solution of the non-linear equation (6) the Newton method is used.

As the calculations showed, searching the solution of the equation (6) with relative error \( \varepsilon = 10^{-6} \) at given ambient pressure and temperature of encapsulated gas equal to temperature of the hollow droplet shell, usually requires 5-6 iterations if as an initial approximation to required diameter of hollow droplet the initial size of the agglomerated particle is assumed.

From the data presented in figure 3, it is visible that the mass \( m_{p,0}^{(c)} \) of gas encapsulated in the particle at the moment \( t = t_{r} \), considerably influences the final characteristics of hollow droplet. So, at temperatures \( T_{m} \) their maximal diameter surpasses initial diameter of agglomerated particle by more than 40%. It should be noted that the condition (4) is necessary, but, generally speaking, not sufficient.

For obtaining the hollow droplet it is necessary to melt agglomerate completely and if necessary to overheat it up to temperature \( T_{b} \). Let’s find the time \( F_{m} \) of complete melting of agglomerate at given value \( q^{(r)} \). Having written down for particle the equation of heat balance and having brought it to dimensionless form, we will obtain demanded condition in the similarity criterion form

\[
F_{m} = \frac{2}{3(1 + D_{p,m}^{2})K_{I}^{(i)}} \left[ 1 + \frac{2}{3} \frac{\rho^{(s)}_{p} L_{im}^{3} \left[ (\rho\xi^{(i)}_{p})^{3} \left[ 1 - (1 - T_{p,0}/T_{m})^{3} \right] \right]}{(\rho\xi^{(i)}_{p})^{3} \left[ 1 - T_{p,0}/T_{m} \right]} \right], \quad (7)
\]

where \( \rho^{(s)}_{p} = (1 - P) \rho^{(s)}_{l} L_{im}^{3} \left[ (\rho\xi^{(i)}_{p})^{3} \left[ 1 - (1 - T_{p,0}/T_{m})^{3} \right] \right] \) is the Stefan similarity criterion of phase transition, \( K_{I}^{(i)} = q^{(r)} A_{p,b}/\tilde{\lambda}_{1}^{(i)} T_{b} \) is the Kirpichyev’s similarity criterion characterizing heating the liquid shell of formed hollow droplet in an instant of time \( F_{m} \), \( \tilde{\lambda}_{1}^{(i)} \) is the effective thermal conductivity of melt; absolute values of diameter \( D_{p,m} \) and thickness \( A_{p,m} \) of hollow droplet shell are found from (6).

\[ D_{p,m} = \frac{D_{p,m}}{D_{p,0}} - (a), \quad A_{p,m} = \frac{A_{p,m}}{D_{p,m}} - (b), \]

of hollow droplets \( \alpha-\text{Al}_2\text{O}_3 \), obtained when processing agglomerates of sizes \( D_{p,0} = 50, \ 100 \) and \( 150 \ \mu\text{m} \) (porosity \( P = 0.35 \)), at their heating to melting point \( (T_{m}) \) vs. relative thickness \( \delta \) of thermal boundary layer at the instant of time of the first stage completion.

At deriving (7) it was supposed that temperature distribution in the cross-section of melted shell is
quasi-stationary. Therefore, the temperature of its outer surface at the moment \( t_m = R_p^2 F_{om}/a_p^{(s)} \) is equal to \( T_{sur}^{(t)}(t_m) = T_{im}(1 + K_i^{(s)}) \).

In figure 4, as an example, are provided, calculated according to (6), the value of time \( t_m \) for agglomerated particles \( \alpha\)-Al\(_2\)O\(_3\), characterized by porosity \( P=0.35 \), and generalized processing conditions given in figure 2a. Analyzing the data presented in figure 4, it is possible to conclude that by means of the thermal plasma generated by DC and RF plasma torches, at the corresponding choice of power, working gas, processing conditions and subsequent quenching of hollow microdroplets it is possible to obtain the hollow droplets with demanded characteristics.

![Figure 4](image_url)

**Figure 4** Dependences of time \( t_m \) of the complete melting of agglomerated particles \( \alpha\)-Al\(_2\)O\(_3\) (sizes \( D_{p0}=50, 100 \) and \( 150 \) µm, porosity \( P=0.35 \)): (a) - vs. heat flux density \( q^{(s)}(\bar{\delta}) \) from plasma to particle required for completion of the first stage at relative thickness \( \bar{\delta} \) of thermal boundary layer (see Figure 3); (b) – vs. relative thickness \( \bar{\delta} \) of thermal boundary layer at the instant of time of the first stage completion.

At directed melting of agglomerated particle (from its surface to the center) the current surface of the melting front, generally speaking, is not spherical, and is piecewise both envelope surfaces of completely melted UFPs, and dividing solid and liquid phases in separate, not completely melted UFPs. Owing to merge of the neighbor liquid ultrafine particles randomly distributed in the layer adjacent to the melting front, and to their absorption by the front, space volume in the layer (with initial porosity of \( P \)), filled with gas, decreases. The characteristic time \( t_j \) of the complete coalescence of two liquid UFPs of diameter \( d_p \) corresponds to the closing-time of pore of the same diameter \( t_j = 2 \mu_p d_p / 3 \sigma_p \), where \( \mu_p \), \( \sigma_p \) is dynamic viscosity and the surface intention of the melt. For the melt of alumina \( \mu_p=0.0573 \) Pa·s, \( \sigma_p=0.69 \) N/m, at \( d_p=10^{-6} \) and \( 5\cdot10^{-6} \) m we will have, respectively, \( t_j = 5.5\cdot10^{-8} \) and \( 2.8\cdot10^{-7} \) s that is, at least, three-four orders less than the characteristic time of the complete melting of agglomerate and is one-two orders less than the characteristic time of passing of the melting front through one layer of UFPs. It leads to replacement of the gas having temperature of \( T_g \sim T_{im} \) by porous connected pinholes inside the particle. Depending on UFPs packing in agglomerate, gas is forced out as to the particle center, and crosswise, owing to gas pressure equalization in the porous framework before the melting front.

### 3.3. Overheating of hollow droplet to boiling point

Let’s make an estimation of the relative values of the diameter \( \bar{D}_{p,b} = D_{p,b} / D_{p0} \), and also the thickness of shell \( \bar{A}_{p,b} = A_{p,b} / D_{p,b} \) of hollow microdroplet formed at the melting point and then overheated to the boiling points of \( \alpha\)-Al\(_2\)O\(_3\).

Absolute values of diameter \( D_{p,b} \) and thickness \( A_{p,b} \) of shell of hollow droplet are obtained from
equation (6) at temperature of encapsulated gas $T_g = T_{1b}$.

Figure 5 Relative diameter $D_{p,b} = D_{p,b} / D_{p,0}$ - (a), and relative thickness of shell $\Delta_{p,b} = \Delta_{p,b} / D_{p,b}$ - (b), of hollow microdroplets $\alpha$-Al$_2$O$_3$, obtained when processing the agglomerates of sizes $D_{p,0}$ = 50, 100 and 150 µm (porosity $P$ = 0.35), at their heating to boiling point ($T_{1b}$) of $\alpha$-Al$_2$O$_3$, vs. relative thickness $\delta$ of thermal boundary layer at the instant of time of first stages completion.

From the data presented in the figure 5 it is visible that the mass $m^0_{g,0}$ of gas encapsulated in particle at the moment $t = t_f$, considerably influences the final characteristics of hollow droplet. So, at temperatures $T_{1b}$ its maximal diameter surpasses initial diameter of agglomerated particle more, than for 60%.

3.4. Quenching of hollow droplet to produce HOSP

Let's assume that the formed hollow droplet having diameter $D_{p,\text{end}}^{(l)}$ and shell thickness $\Delta_{p,\text{end}}^{(l)}$, is evenly heated to temperature $T_{p,\text{end}}, T_{pm} < T_{p,\text{end}} \leq T_{1b}$ and is exposed to cooling until achievement by its external surface of the melting point of UFPs material and to the subsequent solidification. Similar to the first stage of the irregular heating, in this case we need to investigate the problem of irregular cooling of liquid shell, i.e. to consider the following boundary value problem:

$$\frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r}\right), \quad T(r,0) = T_{p,\text{end}}, r \in[R_{p,\text{end}}^{(l)} - \Delta_{p,\text{end}}^{(l)}; R_{p,\text{end}}^{(l)}]; \quad \left.\frac{\partial T}{\partial r}\right|_{r=0} = -\frac{q^{(l)}}{A_{p}^{(l)}}, \quad 0 < t \leq t_{\Delta}.$$  

Taking into consideration the dimensionless variables

$$\varphi = \frac{r - R_{p,\text{end}}^{(l)} + \Delta_{p,\text{end}}^{(l)}}{\Delta_{p,\text{end}}^{(l)}}, \quad r \in[R_{p,\text{end}}^{(l)} - \Delta_{p,\text{end}}^{(l)}; R_{p,\text{end}}^{(l)}],$$

$$\text{Fo} = \frac{\varphi(t)}{\Delta_{p,\text{end}}^{(l)}}, \quad \mathcal{G}^{(l)}(\text{Fo},\varphi) = \left[T_{p,\text{end}} - T(\text{Fo},\varphi)\right]/\left[T_{p,\text{end}} - T_{1m}\right],$$

we can formulate the boundary value problem characterizing the initial stage of cooling under formation of final hollow solid microsphere:

$$\frac{\partial \mathcal{G}^{(l)}}{\partial \text{Fo}} = \frac{1}{\varphi^2} \frac{\partial}{\partial \varphi} \left(\varphi^2 \frac{\partial \mathcal{G}^{(l)}}{\partial \varphi}\right), \quad \mathcal{G}^{(l)}(0,\varphi) = 0, \varphi \in[0;1]; \quad \left.\frac{\partial \mathcal{G}^{(l)}}{\partial \varphi}\right|_{\varphi=0} = 0, \quad \left.\frac{\partial \mathcal{G}^{(l)}}{\partial \varphi}\right|_{\varphi=1} = K_{i_{p,\text{end}}}^{(l)}, \quad 0 < \text{Fo} \leq \text{Fo}_1,$$  

where $K_{i_{p,\text{end}}}^{(l)} = q^{(l)} A_{p,\text{end}}^{(l)} / \Delta_{p,\text{end}}^{(l)} (T_{p,\text{end}} - T_{1m})$ is the Kirpichyev’s similarity criterion, characterizing cooling of liquid shell.

The approximate solution of the boundary value problem (8) characterizing dynamics of the external surface temperature of shell at the stage of its irregular cooling ($\text{Fo} \leq \text{Fo}_1 = 1/12$), looks like:

$$\mathcal{G}^{(l)}(\text{Fo},1) = K_{i_{p,\text{end}}}^{(l)} (\text{Fo} + 2\sqrt{\text{Fo}/3})^{1/3},$$

Having used (9), we will find the value of time $\text{Fo}_1 = (\sqrt{1+3/K_{i_{p,\text{end}}}^{(l)}} - 1)^2 / 3$ necessary for the
external shell surface cooling to the melting point, solving the equation (9) at \( \beta^{(i)}(\text{Fo}.,t)=1 \). Let's demand the realization of the condition \( \text{Fo}/\text{Fo}_{.,t} \leq 1 \), where \( \text{Fo}_{.,t} = 1/12 \) is an instant of non-dimensional time for which the dimensionless thickness of thermal boundary layer in shell is equal to \( A_{p,.t}^{(i)} \). As a result we will obtain the condition in similarity criterion and dimensional forms

\[
K_{p,.t}^{(i)} \geq 2.4, \quad q^{(i)} \geq 2.4 A_{p,.t}^{(i)}(T_{p,.t}-T_{1,m})/A_{p,.t}^{(i)}. \tag{10}
\]

Realization of condition (10) means that at the time of the beginning of hollow drops solidification temperature of encapsulated gas does not undergo any changes, and, therefore, the size of solidified hollow particle will also not undergo any changes. At less intensive surface cooling of hollow droplet at the time of achievement of the melting point by external surface of the shell temperature in its cross-section will be distributed more uniformly. It will lead to cooling of encapsulated gas, and, therefore, to decrease in the size of the hollow droplet and increase in thickness of its shell. So, energy consumptions on overheat of hollow droplet will not give the necessary effect as at low rate of cooling the hollow droplet restores its parameters (diameter and thickness of shell) which it had at the moment of formation at temperature close to melting point. As a result of its solidification the hollow microsphere with practically same parameters will be obtained.

Estimates show that characteristic time of heating/cooling of air cavity with a radius \( \leq 50 \) \( \mu \)m at temperature of shell equal to the melting point of alumina is less by at least an order of characteristic time of thermal relaxation of 5 \( \mu \)m thick shell. Therefore, at heating/cooling of hollow droplet temperature of encapsulated gas "follows up" the temperature of shell of hollow microdroplet.

Thus, the final size of hollow microsphere depends not only on intensity of heating of initial agglomerate, its melting and overheating the formed hollow droplet up to the boiling point of UFPs material, but also on the rate of cooling (quenching) of the final hollow droplet formed in plasma flow.

If solidification of hollow drop began at radius \( R_{p,.t} \) and shells thickness of \( A_{p,.t} \), then after solidification and cooling up to temperature \( T_{g,.t} \) of obtained hollow microsphere the internal gas pressure is defined according to dependence

\[
P_{p,.t} = \frac{3m_{g,.t}^{(i)}RT_{g,.t}}{4\pi(R_{p,.t}-A_{p,.t})^3M_g(T_{g,.t})},
\]

which is obtained from (6). Therefore, if hollow droplet of alumina was heated to boiling point and as a result of fast quenching kept the size, after cooling up to the temperature \( T_{g,.t} = 300 \) K then internal gas pressure will be \( p_{p,.t} \approx 0.85 \cdot 10^4 \) Pa. The estimate is obtained at following conditions: \( R_{0,.t} = 50 \) \( \mu \)m, \( P = 0.35 \), \( p_{g,.t} = 10^5 \) Pa, \( q^{(i)} = 3 \cdot 10^8 \) W/m\(^2\), \( \delta = 0.1 \), \( q^{(-)} = 6.9 \cdot 10^8 \) W/m\(^2\), \( m_{g,.t}^{(i)} = 1.85 \cdot 10^{-13} \) kg, \( M_g(T_{g,.t}) = 28.97 \) kg/kmole, \( R_{p,.t} = 76.5 \) \( \mu \)m, \( A_{p,.t} = 6.6 \) \( \mu \)m. As it can be seen, at the given conditions of obtaining the hollow microspheres with impermeable shell, inner gas pressure is lower by at least one order than ambient pressure in which agglomerated particle was treated.

4. Conclusions

1. The engineering physical model which has allowed for the first time to formulate key similarity criteria, responsible for formation of hollow ceramic particles at plasma processing of the agglomerated powders obtained at spray drying is developed.

2. On the example of alumina it is shown that, other things being equal, varying the heat flux density from plasma to the particles of agglomerated powder, and also varying the rate of quenching of the produced hollow droplets, it is possible to control diameter and thickness of shell of obtained hollow microspheres in the wide range.

3. The obtained results allow to formulate requirements to choice of plasma processing mode of any agglomerated powders with decameter particles size for production of hollow microspherical powders with given characteristics.
Acknowledgement. This work was supported in part in the framework of Interdisciplinary Integration Projects No. 2 and 98 of Siberian Branch of the Russian Academy of Sciences for 2012-2014.

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