Thermal Plasma Processes for Production of Hollow Spherical Powders: Theory and Experiment*

Oleg P. SOLONENKO**, Igor P. GULYAEV** and Andrey V. SMIRNOV**

**Khristianovich Institute of Theoretical and Applied Mechanics SD RAS, Novosibirsk 630090, Russia

E-mail: solo@itam.nsc.ru

Abstract

Present paper considers processes of production and treatment of hollow particles in plasma flows. Specifics of agglomerated powders treatment and expansion of hollow droplets are analyzed theoretically. Experimental results on production of hollow micro particles of ZrO_2 , Ni, CoNiCrAlY alloy, SiO_2 are shown here.

Key words: Plasma Spraying, Hollow Spheres, Agglomerated Powders, Suspension Spraying, Zirconia

1. Introduction

In the present-day industry of structural and protective materials, powders made up by hollow spheres, or hollow powders, gain increasing acceptance. Hollow ceramic powders 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. Such powders also form basis for catalysts, 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; in this connection, guaranteed synthesis of hollow microspheres with desired morphology, chemical composition, and mechanical properties becomes an urgent matter.

An analysis of publications presented at major international conferences and in leading foreign and Russian journals shows that, presently, issues concerning the formation of hollow microspheres and the behavior of such microspheres in plasma flows receive insufficient attention.

The main necessary condition to form a hollow particle in plasma flow is sufficient gas content in feedstock powder material. This can be obtained by application of porous particles, binders in agglomerates which evaporate at high temperatures, powders with high specific surface area providing gas adsorption, etc. Our experiments with zirconia powder show that gas to material (particle) mass ratio $m_g/m_p \sim 10^{-4}$ at room temperature and $m_g/m_p \sim 10^{-5}$ at melting point is enough to produce hollow spheres with shell thickness about 10-20% of particle diameter. When such particles enter a plasma flow melting starts at their surface forming a liquid film which catches residual gas. Further heating of a liquid spheres leads to expansion and consolidation of gas cavities and surface tension provides spherical shape of inner void. After a liquid hollow sphere leaves plasma jet and solidifies a position of a gas cavity is fixed and generally it is in the center of the particle, providing uniform shell thickness.

Over the recent decade, in connection with ever increasing interest to hollow powders and widening application field of such powders, considerable efforts of researchers have been focused on the development of new approaches to the problem of formation of hollow

*Received 28 Jan., 2011 (No. 11-0074)
[DOI: 10.1299/jtst.6.219]

Copyright © 2011 by JSME

microspheres in thermal plasma.

The present publication is intended to give an overview of our results that were obtained in recent years in the Laboratory of plasma dynamics and energy conversion in dispersed systems, ITAM SB RAS, in the field of processing various agglomerated powder materials in plasma in the context of obtaining hollow spherical metal, alloy, and oxide-ceramic powders.

2. Analysis of plasma processes involving agglomerated particles

As it was noted in [1], a 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, a particle with $\rho_p^{(l)} < \rho_p^{(s)}$, as it melts, grows in volume, so that its efficient size increases. The radius of a fully molten 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. An overheated melt droplet subsequently given a quench, its solidification starts from the surface, so that the particle size turns out to be fixed at $R_{ps} = R_p + \Delta R_p$. Following crystallization-induced volume shrinkage, a spheroidal cavity forms inside the particle, the relative radius of the cavity being $R_h = R_{p0} + \Delta R_p - h$ and the shell thickness

$$h = R_{ps} \left[1 - \sqrt[3]{1 - (R_{p0} / R_{ps})^3} \right].$$

With the obtained dependences at hand, we can obtain numerical estimates for $\alpha\text{-Al}_2\text{O}_3$ (corundum) particles. Analyzing available experimental data, the authors of [2] proposed the following dependence for the corundum density in liquid state: $\rho_p^{(l)}(t) = 3030 - 1.08(t - 2054)$, where the dimensions of density are kg/m^3 , and the dimensions of temperature t are Celsius degrees. For the density of corundum in solid state, we adopt a value $\rho_p^{(s)} = 3960 \text{ kg/m}^3$. Then, for a droplet of radius $50 \mu\text{m}$ at the melting point $T_{pm} = 2054^\circ\text{C}$ we have: $\rho_p^{(l)}(2054^\circ\text{C}) = 3030 \text{ kg/m}^3$, $\Delta R_p \approx 4.7 \mu\text{m}$, $R_p + \Delta R_p \approx 54.7 \mu\text{m}$, $h \approx 20.9 \mu\text{m}$, and $R_h \approx 33.8 \mu\text{m}$.

For the same droplet overheated over the melting point by 400°C , we similarly obtain: $\rho_p^{(l)}(2454^\circ\text{C}) = 2598 \text{ kg/m}^3$, $\Delta R_p \approx 7.5 \mu\text{m}$, $R_p + \Delta R_p \approx 57.5 \mu\text{m}$, $h \approx 17.3 \mu\text{m}$, and $R_h \approx 40 \mu\text{m}$.

Hence, the characteristics of hollow spheres solidified from overheated molten dense 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 forms inside each particle.

However wider practical possibilities of production of hollow particles can be provided by plasma treatment of agglomerated powders. Several methods for obtaining agglomerated powders with particle sizes in the range of several ten micrometers whose particles comprise several uniformly mixed nano-, submicro-, or micro-sized powder components are presently known. Those methods include: (i) extrusion, (ii) spray drying, (iii) processing of sprayed suspensions and solutions in plasma, (iv) electrolytic deposition of materials, (v) mechanical activation of powder mixtures in high-energy planetary ball mills, etc.

Conditions for obtaining hollow microspheres. Agglomerated particles normally have a heterogeneous structure and a porosity p , which, as a rule, is open-type porosity. However, whatever the production method of particles, their treatment in thermal plasma aimed at obtaining microspheres has many features in common; such a treatment normally comprises the following stages (see Fig. 1):

1) heating of solid particles till the moment the melting point is reached at the particle

surface and a surface melt layer forms there; during this stage, the gas initially contained in the pore space of particles, as it thermally expands, partially leaves the material in the filtration regime;

2) arresting of the remainder gas in the particle as the particle further melts, and subsequent formation of an internal gas cavity and a liquid spherical shell;

3) quenching of obtained hollow droplets, resulting in the formation of hollow microspheres.

Fig. 1. Formation scenario of a hollow particle.

It is worth noting that, in treating agglomerated ceramic, metal, or alloy particles, and also gas-rich metal powders, in plasma, depending on the heating intensity, or density of the heat flux, formation of hollow particles or particles whose volume contains distributed spherical gas cavities is possible.

In this connection, we introduce the following characteristic times: (i) the thermal relaxation time $t_a = R_p^2 / a_p^{(s)}$, which defines the rate of equalization (leveling) of the temperature field inside a particle heated from the surface (here, $a_p^{(s)}$ is the heat diffusivity) and (ii) the time $t_{qm} = \rho_p^{(s)} c_p^{(s)} (T_{pm} - T_{p0}) R_p / q$, which defines the thermal susceptibility of particle material to the heat supplied to the particle surface at the stage of heating of the surface from an initial temperature T_{p0} to the melting point T_{pm} . The ratio of the two characteristic times,

$$t_a / t_{qm} = R_p q / \lambda_p^{(s)} (T_{pm} - T_{p0}), \quad (1)$$

defines the regime of particle heating in plasma. In principle, two heating regimes are possible: gradient heating – $t_a / t_{qm} > 1$, and uniform heating – $t_a / t_{qm} < 1$.

By analogy, one can introduce a dimensionless parameter $L_{qm} = \lambda_p^{(s)} (T_{pm} - T_{p0}) / q$, which defines the characteristic spatial scale of heat transfer during the heating of the particle surface to the melting point at a given heat flux density. If $L_q \ll R_p$, then we have a gradient heating, proceeding with the formation of a melted layer on the particle surface as the surface temperature reaches the melting point, whereas the particle interior still remains cold. Here, the continuous melt film formed on the surface arrests the gas contained in the pore space of the particle; as a result of complete melting of the particle, there forms a spherical droplet, which, as it solidifies from the surface, forms a hollow microsphere. On the contrary, if $L_q > R_p$, then the particle undergoes a gradientless, or uniform, heating. Here, as the particle temperature reaches the temperature T_{pm} , the particle melts uniformly throughout its volume; as a result, suspended gas bubbles remain in the melt, which, on droplet solidification, lead to the formation of microspheres with a distributed closed-type porosity.

This analysis can also be applied to evaluating the possibility of obtaining hollow microspheres from agglomerate particles with a heterogeneous internal structure (particles obtained by spray drying, mechanocomposite particles, particles obtained by plasma treatment of atomized suspensions of the ‘liquid – solid inclusions’ type, etc.). As a result of the analysis, requirements to the operating regime of the plasma torch and requirements to

the working-gas composition are to be formulated.

Evolution of hollow droplets during variation of their temperature and ambient pressure. To proceed with further analysis, consider a simplest formation scenario of a hollow particle based on an assumption of open-type porosity of the initial agglomerate and no disintegration of agglomerate particles occurring during treatment. As an agglomerated particle of diameter D_{p0} enters a plasma jet, both the particle material and the gas contained in the pore space of the particle undergo an intense heating (Fig. 1). On expansion, some amount of the gas initially contained in the particle leaves the particle volume, the pore volume V_{g0} remaining unchanged. At the moment the particle surface reaches the temperature T_{pm} , on the surface of the agglomerated particle a melt film forms, which defines the arrested gas mass m_{g0} . The gas arrested by the thickening shell is forced towards the center of the particle and, on completion of particle melting, it takes a central position, forming an isolated cavity whose size is defined by the droplet temperature and ambient pressure. Let us calculate now the outer diameter of the formed hollow droplet D_{p0} and the relative shell thickness in it, $\delta_{p0} = \Delta_{p0} / D_{p0}$. With p being the initial particle porosity, the total volume of the pores in the particle is $V_{g0} = \pi p D_{p0}^3 / 6$, and the gas mass arrested in the particle at temperature T_{pm} is $m_{g0} = \rho_g(T_{pm}, P_{g0}) V_{g0}$, where ρ_g is the gas density at the initial temperature and pressure.

Subsequent state of the gas volume in the hollow droplet obeys the Mendelev-Clapeyron equation

$$P_g V_g = \frac{m_{g0}}{M_g(T_g, P_g)} R T_g. \quad (2)$$

Here, $V_g = \frac{4\pi R_p^3}{3} \left(1 - \frac{\Delta_p}{R_p}\right)^3$ is the current gas volume after the complete melting of the

particles and its heating to a temperature $T_g > T_{pm}$, R is the universal gas constant, and

M_g is the temperature- and pressure-dependent molar mass of the gas. As a result, equation (2) takes the form

$$P_g = \frac{3m_{g0} R T_g (1 - \Delta_p / R_p)^3}{4\pi R_p^3 M_g(T_g, P_g)}. \quad (3)$$

In view of (3), we can write the following equation of pressure balance at the droplet surface, which relates the equilibrium droplet radius and the equilibrium shell thickness:

$$P_{f0} + \frac{2\sigma_p}{R_p} \cdot \left(1 + \frac{1}{1 - \Delta_p / R_p}\right) = \frac{3m_{g0} R T_g (1 - \Delta_p / R_p)^3}{4\pi R_p^3 M_g(T_g, P_g)}. \quad (4)$$

Here, P_{f0} is the ambient pressure, and σ_p is the melt surface tension coefficient.

Finally, with the additional condition of constant mass of the liquid shell, we obtain:

$$m_{p0} = \frac{4\pi \rho_p R_{p0}^3}{3} \cdot [1 - (1 - \Delta_{p0} / R_{p0})^3], \text{ so that } 1 - \Delta_p / R_p = \sqrt[3]{1 - \frac{3m_{p0}}{4\pi \rho_p R_p^3}}. \quad (5)$$

Thus, solving equation (4) under condition (5), we obtain the current value of the radius R_p and, then, the shell thickness Δ_p for given particular conditions.

Figure 2 shows the calculated values of the outer diameter (a) and relative shell thickness (b) of hollow microsphere versus the size of the initial agglomerated particle. The calculations were performed for ZrO_2 particles of various initial porosities processed in atmospheric-pressure air plasma. In the calculations, data of [3] for air properties were used. It is seen that the outer diameter of the obtained hollow droplet D_p is roughly the size of

the initial agglomerated particle D_{p0} (the former diameter is 2-10% smaller than the latter one), and it is almost independent of the porosity of the initial powder p in the porosity range $p = 0.2 \div 0.7$. Simultaneously, the initial porosity has a pronounced effect on the relative shell thickness δ_p .

Figure 3 shows data that illustrate the dependence of particle shell thickness on the initial porosity of the powder for particles of various diameters D_p . It is seen that in the considered range of particle sizes the shell thickness almost linearly decreases with increasing porosity.

Fig. 2. Diameter (a) and relative shell thickness (b) of hollow particle versus the size of the initial ZrO₂ agglomerate.

The calculated data presented in Figs. 2 and 3 can be used in determining the characteristics of an initial agglomerated powder to be used for obtaining hollow particles of a desired morphology.

A comparison of predicted shell thicknesses of ZrO₂ hollow spheres with measured shell thicknesses is shown in Fig. 4. In the calculations, an experimental estimate of the porosity of the initial agglomerates, $p = 0.45$, was used.

Fig. 3. Shell thickness of formed hollow particle versus the initial porosity of particle agglomerates.

Fig. 4. Shell thickness versus particle size.

It can be concluded that, in a first approximation, the proposed model for the formation of hollow particles well agrees with experimental data: the root-mean-square deviation here is 18%, while the higher measured values of shell thickness could be a consequence of either some fraction of dense particles present in the obtained powder, or particle fragments resulting from disintegration of hollow particles.

3. Production of hollow microspheres in thermal plasma

3.1. Processing of powders obtained by spray drying

As it was noted above, several processes are known suitable for production of hollow particles in thermal plasma. An efficient method here is plasma processing of agglomerated powders obtained by spray drying. A unique material for spraying thermal-barrier and heat-resistant coatings is zirconia stabilized by yttria. The use of a hollow ZrO_2 powder allows one to ease the requirements to plasma facilities and, simultaneously, improve the heat-resisting capability and strength characteristics of sprayed coatings [4, 5].

In tests aimed at obtaining hollow ZrO_2 microspheres it was found that the morphology of such microspheres was largely defined by preparation conditions of the initial agglomerated powder, and also by the thermal and gas-dynamic characteristics of used plasma flows [6-8].

Fig. 5. External appearance of the initial ZrO_2 powder.

Figure 5 shows a SEM image illustrating the external appearance of the initial ZrO_2 powder obtained by the spray drying technique. It is seen that the powder particles range in size from 50 to 150 μm . Here, the sizes of individual microparticles forming the agglomerates cover the range from 3 to 5 μm , with the total number of the microparticles in a single agglomerated particle being 10^3 – 10^5 . The mean volume porosity of the initial powder is $p=0.45$, the

gas-to-particle mass ratio at room temperature being at a level $m_g / m_p \approx 2 \cdot 10^{-4}$, whereas at the melting point of the material ($T_{pm} = 2960 \text{ K}$), $m_g / m_p \approx 2 \cdot 10^{-5}$.

All other conditions being identical, the morphology of plasma-processed powders is largely defined by the thermal and gas-dynamic characteristics of the plasma torch. In this connection, we performed a comparison of characteristics of hollow spherical powders obtained by processing the initial powder in the plasma jet of a linear plasma torch and a two-jet plasma torch (Fig. 6).

Fig. 6. Diagram of powder injection into the plasma jets and the general appearance of the plasma flows: linear plasma gun with radial powder injection (a), two-jet plasma gun with axial powder injection (b).

The thermal power of the nitrogen plasma flows in both cases was about 45 kW, and the powder processing capacity, 20 kg/hour. The operating regime of the linear plasma torch with inter-electrode inserts (IEI) was as follows: working gas feedrate 2 g/s, exit nozzle diameter 14mm, arc current 250A, arc voltage 310V, thermal efficiency 60%. This provided

gas enthalpy about 23 kW/g, which means that average plasma temperature at nozzle exit was about 7000 K, and velocity about 380 m/s. The powder was injected into the plasma jet along the radius into the region under the plasma-gun nozzle exit (Fig. 6, a). The two-jet plasma torch was operated at 0.3 g/s nitrogen feedrate into each of the electrode units, arc current 200 A, arc voltage 250 A, thermal efficiency 90%. Average plasma temperature can be evaluated if no thermal power loss is considered: gas enthalpy 75 kW/g and gas temperature about 12000 K. In the case of the two-jet plasma torch the powder was injected into the region located at a distance $L_f=25$ mm from the merging zone of the electroconductive jets (Fig. 6, b).

In the case of the linear plasma gun, the processed powder proved to be substantially finer than the initial powder: here, the mean particle size was about 20 μm , with almost no fractions coarser than 60 μm being present in the processed powder (Fig. 7, a). This result clearly indicates that, during the treatment, the initial agglomerates underwent disintegration. In the latter case of the two-jet plasma gun the mean particle size was about 45 μm , the size distribution of particles was more homogeneous, i.e. broader, with an appreciable amount of particles with sizes in the range from 10 to 85 μm being present in the powder (Fig. 7, b).

Fig. 7. External view and size distribution of ZrO_2 powder particles processed in the plasma jet of the linear (a) and two-jet (b) plasma torch.

The latter results can be explained by the following factors. *First*, during processing in plasma the initial agglomerated powder particles experienced mechanical stresses resulting from the high temperature and high heating rate; those stresses included (i) the thermal stress induced by the non-uniform thermal expansion of the agglomerate owing to the temperature gradient and (ii) the baric stress induced by the increasing pressure due to the gas and organic binder vapors contained in the pore microvolumes. The amount of the residual gas arrested in the hollow sphere was defined by the gas losses in the agglomerate

owing to the radial filtration flow, which ceased at the moment a continuous outer melt film formed on the agglomerate surface.

Thus, the agglomerated particles of the initial ZrO_2 powder at their radial injection into the plasma torch (case 1) suffered considerable thermal and baric stresses since the mass-mean temperature of the nitrogen plasma at the nozzle exit plane of the plasma gun was about 8000 K (Fig. 8). As a result, the initial particles could disintegrate into several smaller agglomerates, which then passed a spheroidization stage. In the second case, prior to entering the merging zone of the conducting jets the particles experienced rather a soft radiative-conductive heating. As a result, the most probable scenario before the moment the particles entered the hot zone included sintering of microparticles contained in each initial agglomerated powder particle; the sintered agglomerates then entered the mixing zone of the conducting jets, or the hot zone. Under such a heating regime, agglomerates normally display less pronounced tendency to disintegration.

Fig. 8. Diagram of the disintegration process of an agglomerated particles in the plasma torch (schematically).

Second, two other factors deserve mention which could lead to disintegration of already formed hollow melt droplets, and, hence, to a reduced mean particle size of the final spherical powder. Those factors, provoking disintegration of hollow droplets into fragments, which then underwent spheroidization and in-flight solidification, are the following:

- dynamic pressure, acting on the hollow droplet from the side of the gas carrier flow owing to the considerable velocity difference between the particle and the plasma flow;
- heating of the gas contained inside the already formed hollow liquid particle, leading to an increase of its internal pressure, an increase of the outer diameter, thinning of the shell, and shell fracture.

As far as our knowledge goes, those problems as applied to hollow droplets so far have never been considered in the literature, and they call for further investigation.

A comparison of the hollow ZrO_2 powder obtained in our experiments with a commercially available hollow powder is given in Fig. 9. It is seen that the particles in the produced powder (see Fig. 9, a) were shaped as regular spheres and, in contrast to those in the commercial powder (see Fig. 9, b), were all hollow particles. The commercial powder contained a large fraction of non-hollow particles, a considerable fraction of agglomerated particles in it had not passed complete treatment, and the shell thickness in the hollow particles varied over a wide range.

Fig. 9. External and cross-sectional views of particles in the ZrO_2 powders: (a) – powder obtained by the present authors, (b) – commercially available ZrO_2 powder.

An important characteristic of hollow powders is the shell thickness of the microspheres. Within each of the fractions of the ZrO_2 powder obtained with the use of the two-jet plasma torch, we attempted separation of particles with shell thicknesses falling into a certain range; in particular, we tried to organize withdrawal of dense particles. For convenience, we now introduce a new quantity called the effective density of particles ρ_{eff} . This density presents the ratio of the particle mass m_p to the particle volume V_p :

$$\rho_{\text{eff}} = \frac{m_p}{V_p} = \rho_{\text{ZrO}_2} [1 - (1 - 2\delta_p)^3], \quad (6)$$

where $\rho_{\text{ZrO}_2} = 5.6 \text{ g/cm}^3$ is the true density of zirconia particle.

A most reliable method for separating dense from hollow particles is hydrostatic separation, or floatation: particles with an effective density ρ_{eff} greater than the liquid density ρ_l descend to the vessel bottom, whereas particles with a lesser density come to the surface. As for the ZrO_2 powder under consideration, this implies that, for the separation process, a liquid with a density not less than $\rho_l = 3 \text{ g/cm}^3$ is required. One of the methods to increase a density of liquids is using strong solutions of readily soluble, high-density salts. We attempted preparation of a solution of dihydrated potassium iodide in water ($\text{BaI}_2 \cdot 2\text{H}_2\text{O}$, molar mass 426 g/mole, solubility in water at 40°C 322 g per 100 g of water). At room temperature, we were able to reach a density $\rho_l = 2.21 \text{ g/cm}^3$. In using a denser liquid, bromoform (CHBr_3 , density $\rho_l = 2.89 \text{ g/cm}^3$), in each fraction only an insignificant fraction of particles (not more than 1-2%) were found to ascend to the surface; this means that in the majority of particles the wall thickness was greater than 0.11. This method can also be used in treating less dense materials, for instance SiO_2 , whose true density is 2.3 g/cm^3 .

The fraction-average relative shell thickness of the particles $\bar{\delta}_p$ was calculated from their measured mean effective density $\bar{\rho}_{\text{eff}}$:

$$\bar{\delta}_p = \frac{1}{2} \left(1 - \sqrt[3]{1 - \frac{\bar{\rho}_{\text{eff}}}{\rho_{\text{ZrO}_2}}} \right). \quad (7)$$

The mean effective density was determined as follows. A volume V of water was poured into a test tube, graduated in terms of volume, and then the mass of the poured water was determined. Next, the hollow ZrO_2 powder was added to the liquid; the powder was settled to the bottom of the test tube. Then, the change in the tube mass, Δm , and the change in the liquid volume, ΔV , were measured. The mean effective density of the powder was then calculated as $\bar{\rho}_{\text{eff}} = \Delta m / \Delta V$. In our measurements, the mass of the powder loaded into the test tube was 10 grams, and the volume change was 3 ml; this, at a 0.01-g inaccuracy of mass measurements and 0.1-ml inaccuracy of volume measurements, guaranteed a 3-% accuracy in determination of effective density and 4-% accuracy in determination of wall thickness.

Measured values of the mean effective density of hollow ZrO_2 particles, and also measured values of the relative shell thickness in particles of various fractions are summarized in Table 1.

Table 1. Measured shell thicknesses of ZrO_2 hollow microspheres.

$D_p, \mu\text{m}$	45-50	50-56	56-63	63-71	71-80	81-90
$\bar{\rho}_{eff}, \text{g/cm}^3$	4.64	3.76	4.27	3.92	3.43	4.19
$\bar{\delta}_p$	0.22	0.15	0.19	0.17	0.14	0.18

3.2. Processing of mechanocomposite particles

Our first model experiments on plasma spraying of coatings from metal powders given a preliminary high-energy mechanoactivation (MA) treatment and modified with high-melting ultra-fine particles (MA+M), which were reported in [9-11], have allowed us to obtain, at all other conditions being identical, coatings whose microstructure and properties substantially differed from those of coatings sprayed from standard powders.

Yet, until recently it was not possible to give a detailed explanation to the results obtained because of lack of experimental data concerning the behavior in plasma jet, and subsequent interaction with substrate, of initial mechanically activated powder particles modified with high-melting nanoparticles.

It is a well-known fact [12] that coatings obtained by gas thermal (and also plasma) spraying are formed from individual splats, or flattened and solidified melt droplets, laid one by one onto the base. With the aim to examine the effect of mechanical activation of initial powder and its modification with high-melting ultra-fine particles on the treatment of particles in a plasma jet, and also on the formation of splats and coatings, we performed model experiments in which, as the initial powder, a standard CoNiCrAlY (Amdry-9951) powder was employed, normally used in spraying as bond layer of thermal barrier coatings, and, as the modifying additives, titanium carbide nanoparticles were used [13, 14].

Fig. 10. External appearance of the CoNiCrAlY powders: initial AMDRY-9951 powder (a), powder obtained by joint mechanical activation of the AMDRY-9951 powder with ultra-fine TiC particles in an AGO-2 planetary mill [15] (b).

Figure 10 shows SEM photographs illustrating the morphology of the initial and processed (MA+M) CoNiCrAlY powders. It was found that, during the high-energy mechanical pre-treatment of the initial powder in an AGO-2 centrifugal-planetary mill [15], disintegration of initial particles into fragments and subsequent adsorption of working-gas molecules (air, argon, etc.) on the newly formed chemically active surface of the fragments, occurred. During further processing, simultaneous volume mixing, disintegration, and aggregation of fragments proceeded; those processes led to the formation of gas-rich

particles with a large specific surface and high porosity. In combined mechanical activation (MA) of the initial powder with high-melting nanoparticles (MA+M), an additional factor acting to increase the gas content of obtained mechanocomposite particles was chemical activity of the nanoparticles.

Subsequent treatment of the MA/MA+M metal and alloy powders in plasma resulted in the formation of hollow spherical droplets, which then solidified into hollow microspheres (Fig. 11, a). The splats formed from the hollow droplets impinging onto substrate under plasma-spray conditions (Fig. 11, b) exhibited a more stable formation pattern in comparison with dense particles of the same mass; this ensured a more continuous coating/substrate interface and, hence, improved functional properties of sprayed coatings [16-18].

Fig. 11. Morphology of CoNiCrAlY particles processed in plasma and then quenched in a liquid (a) and that of CoNiCrAlY particles after their impingement onto a polished stainless-steel substrate (b). 1 – initial powder; 2 – after mechanical activation; 3 – after mechanical activation and modification with TiC nanoparticles.

3.3. Processing of gas-rich metal and alloy particles

As it was noted above, the major requirements for obtaining hollow microspheres are a sufficiently high gas content of the initial powder particles to be treated in plasma, and also a sufficient rate of the heat flux from plasma to particles providing for a gradient heating of particles till the moment the material starts melting at the surface, i.e., for the condition $L_{qm} / R_p = \lambda_p^{(s)} (T_{pm} - T_{p0}) / q R_p \ll 1$.

Fig. 12. External appearance of the initial PNE-1 nickel powder.

In conducting experiments, as the model metal powder, a PNE-1 nickel powder with a developed surface was used; this powder was formed by 1-3 μm sized microparticles (Fig. 12). Yet, in contrast to the agglomerated ZrO_2 powder, in the PNE-1 powder the metal microparticles forming individual agglomerates sized 45-50 μm (after sizing) with porosity $p = 0.05$ were tightly joined together. The specific surface area of the powder was $S_{\text{specific}} = 2.21 \text{ m}^2/\text{g}$; this value

provided for a high gas content of the particles.

As it was noted above, an effective method to increase the gas content of metal powders is mechanical activation; for instance, processing of the PNE-1 nickel powder in an AGO-3 planetary mill [15] (acceleration 80 g, process duration 15 seconds) ensured an absorbed gas-to-material mass ratio $m_g / m_p = 2 \cdot 10^{-3}$. Due to plasma treatment and subsequent quenching in water, the porosity of the powder was at a level of $p=0.05-0.08$.

In spite of the fact that the gas content of the initial and mechanically activated powders was one order of magnitude greater than that of the ZrO_2 agglomerates, we failed to obtain hollow particles from those powders in argon plasma; the particles obtained were spheres with a structured surface, sometimes with holes observed in it. Figure 13 shows SEM photos that illustrate the external appearance and cross-sectional view of PNE-1 powder particles treated in plasma. Examination of cross-sectional cuts of the particles showed that the particles contained, instead of a single gas cavity, a number of volume-distributed large pores (see Fig. 13, b). As a result of treatment in plasma, the porosity of the powder has increased by several times, to $p=0.44$. It is worth noting that, as it was shown in [19, 20], composite particles obtained by SHS and spheroidized in plasma displayed a similar morphology.

Fig. 13. The PNE-1 nickel powder treated in a plasma jet (argon plasma, thermal power $P_T = 21$ kW, processing capacity $G_{Ni} = 5$ kg/hour): (a) – external appearance, (b) – cross-sectional view.

The factors leading to that, as a result of processing of the metal powder in argon plasma jet, no hollow spheres were formed were: (i) a high thermal conductivity of nickel (Biot number $Bi \ll 1$) and (ii) a low rate q of the heat flux from argon plasma to particles. It can be shown that, in the latter case, the condition $t_a / t_{qm} = R_p q / \lambda_p^{(s)} (T_{pm} - T_{p0}) > 1$ was not met. As a result, a uniform (gradientless) heating of particles to the melting point took place, leading to that the particles melted uniformly throughout their volume; already before the melting, a considerable portion of the gas mass initially contained in the particles could escape into environment as a result of an intense thermal expansion of the gas and its leaving the agglomerates. As a result, in the volume-melted particles the initial pores formed, instead of a central gas cavity, a system of volume-distributed gas cavities.

On the contrary, in the case of processing of agglomerated ZrO_2 particles in a nitrogen or air plasma jet, due to a low thermal conductivity of the oxide and a greater rate of the heat flux from plasma to particles the particles underwent a gradient heating during which a melt surface film formed on the surface of the particles. As a result, a considerable gas mass remained arrested inside the particle, the melting front moved from the surface into depth, thus forcing the gas cavities towards the particle center and causing their merging there.

3.4. Processing of metal hydroxide particles

One more production process of hollow powders is exemplified by plasma treatment of aluminum hydroxide particles 70 to 120 micrometers in diameter with 12 to 17 wt.% of

chemically bound water. The treatment was performed in an air plasma jet flowing out in a quasi-laminar regime out of a 50-kW cascaded plasma gun.

Fig. 14. SEM photographs of the synthesized hollow powder of microspherical aluminum oxide taken at different magnifications.

As a result, a microspherical aluminum oxide was obtained, which, as SEM data show, consisted of particles 70 to 120 micrometers in diameter shaped as hollow spheres with a smooth or ribbed surface [4] (see Fig. 14).

Fig. 15. Solid-state NMR spectra of ^{27}Al in the powder made up by hollow corundum microspheres. Primary phase - $\alpha\text{-Al}_2\text{O}_3$ (1), $\gamma\text{-Al}_2\text{O}_3$ component (about 1 wt.%) (2).

Measured solid-state MNR spectra of ^{27}Al showed (see Fig. 15) that, in such a microspherical aluminum oxide powder, the aluminum atoms resided in the octahedral surrounding of oxygen atoms with a high degree of crystal ordering. According to derivatographic data, the obtained microspherical aluminum oxide contained 1% of low-temperature aluminum oxide phases and no physically bound water. Thus, the sample was 99 wt.% of $\alpha\text{-Al}_2\text{O}_3$ (corundum) having no developed surface.

3.5. Suspension plasma treatment

In several recent years an active interest has been shown to suspension plasma spraying (SPS), a process in which a liquid containing suspended nano- and submicrometer particles of spray material is injected under pressure into a plasma flow [22-25].

We were first to show that, under such conditions, formation of hollow particles was possible.

In [26] it was shown possible to obtain hollow microspheres several ten micrometers in diameter by processing an agglomerated SiO_2 powder in plasma.

The starting powder was a quartz glass powder that was mechanically treated in a high-energy AGO-2 planetary mill. The external appearance of the initial powder is shown in Fig. 16; here, the submicrometer particles form agglomerates sized predominantly 10 to 20 μm . On introduction of the powder into a liquid, the agglomerates disintegrated into separate submicrometer particles. BET measurements showed that the specific surface area of the powder was $S_{\text{specific}} = 22.72 \text{ m}^2/\text{g}$, this value yielding for the effective diameter of the spherical particles a value of 100 nm.

Here, the traditional method for injection such an agglomerated powder into a high-temperature, high-velocity zone of a plasma jet through an injector with the help of a transporting gas could not be implemented because the effective density of the particles was

low and the flowability of the powder, poor. An alternative was treatment in plasma of a atomized suspension comprising a liquid and nano- and submicrometer solid particles suspended in the liquid [26]. To this end, a special injector was designed (see Fig. 17), which was used to introduce a powder suspension in water, initially contained in a pressure vessel, into the plasma jet. On atomization, the liquid jet disintegrated into droplets several ten micrometers in size, which contained quartz glass ultra-fine particles suspended in the liquid. The adopted conditions allowed the formation, after evaporation of droplets, of agglomerates of initial particles, whose subsequent heating and melting led to the formation of hollow SiO_2 particles.

Fig. 16. External appearance of the initial SiO_2 powder.

Fig. 17. Diagram of the suspension injector: 1– suspension vessel, 2–high-pressure gas line, 3–injectors, 4–plasma gun.

A hollow microspherical SiO_2 powder was obtained with the help of a plasma torch operated at 76-kW electrical power, with the flow rate of plasma-forming air 1 g/s, water suspension discharge 1.1 g/s, and mass content of powder in water 25 g/l.

(a)

(b)

Fig18. External view (a) and size distribution (b) of SiO_2 particles processed in plasma jet.

As it is seen, the processed powder contained no particles smaller than 25 μm in diameter, and the majority of spheres in it had sizes 40 to 70 μm (see Fig. 18). Measurements of the effective density of the obtained powder showed that the powder porosity was 47%, yielding for the mean relative shell thickness of hollow particles a value $\bar{\delta}_p = 0.11$.

Thus, we have developed a combined process incorporating two production stages in obtaining hollow particles, the formation of agglomerates from fine material grains, and subsequent formation of hollow droplets. On atomization, the suspension jet formed droplets several ten micrometers in size, which comprised submicron SiO_2 particles. On evaporation of the liquid, there formed agglomerates of initial particles and, then, hollow SiO_2 droplets emerged according to the scenario described above. The presence of irregularly shaped particles sized 150-250 μm was indicative of the fact that, during plasma processing, large drops formed, which, as they underwent an intense evaporation, yielded agglomerates, which underwent sintering yet had not enough time to get melted.

4. Conclusions

In the present paper, we gave an overview of our studies aimed at development of plasma processes for obtaining hollow microspherical metal, alloy, and oxide ceramic powders. It was shown that thermal plasma can be used in production of such powder materials from initial powders whose particles present porous agglomerates obtained by (i) spray drying of materials, (ii) mechanical activation of powder materials in a high-energy planetary mill, (iii) electrolytic deposition, and (iv) spraying of suspensions with contained nano- and submicrometer-sized particles. Besides, with the example of aluminum oxide and hydroxide, we proved it possible to obtain hollow corundum microspheres. The main conditions for production of hollow particles were formulated: sufficient gas content in feedstock material and density of heat flux.

A simple theoretical grounds of involved processes are presented, allowing one (i) to formulate requirements to the plasma flow for guaranteed production of hollow microspheres from processed agglomerated particles (ii) and to predict the behavior of hollow droplets formed in the plasma flow with the aim of controlling the particle size and shell thickness.

The results of the present work may prove useful for specialists involved in the high-temperature synthesis, and application, of various-purpose powders, including plasma processing of powder materials.

The results overviewed in the present article were obtained in the framework of Program of Prezidium of Russian Academy of Sciences No. 11 on 2009-2011 (Project № 7).

References

1. M.F. Zhukov, O.P. Solonenko, High-temperature dusted jets in powder materials treatment processes, V.E. Nakoryakov Ed., Novosibirsk, ITP SB RAS, 1990, 516 P. (in Russian).
2. M.A. Maurakh, B.S. Mitin, Liquid refractory oxides, Moscow, Metallurgiya, 1979, 288 P. (in Russian).
3. N.B. Vargaftik, Handbook on thermophysical properties of gases and liquids, Moscow, Nauka, 1972, 720 P. (in Russian).
4. O.P. Solonenko, A.V. Smirnov, I.P. Gulyaev, Spreading and solidification of hollow molten droplet under its impact onto substrate: computer simulation and experiment, Proc. of 4th Int. Conf on Flow Dynamics, 26-28 September 2007, Sendai, Japan, P. 325-332.
5. O.P. Solonenko, A.V. Smirnov, I.P. Gulyaev, Hollow droplets microexplosive thermal spraying: fundamentals, Proc. of International Thermal Spray Conf., 2-4 June 2008, Maastricht, Netherlands.
6. O.P. Solonenko, I.P. Gulyaev, A.V. Smirnov, E.V. Kartaev, Plasma processing of spray-dried YSZ powder and formation of splats from hollow molten particles impinging onto substrate, Proc. of 18th Int. Symposium on Plasma Chemistry, 26-31 August 2007, Kyoto, Japan, P.637-640.
7. O.P. Solonenko, A.V. Smirnov, I.P. Gulyaev, Spreading and solidification of hollow molten droplet under its impact onto substrate: computer simulation and experiment, Complex Systems: The 5th Int. Workshop on Complex Systems (26-28 September 2007, Sendai, Japan), American Institute of Physics, Melville, New York, 2008, Vol. 982, P.561-568.
8. O.P. Solonenko, I.P. Gulyaev, A.V. Smirnov, Plasma technologies of production, treatment and spraying of powders consisting of hollow particles, Proc. of 9th Int. conf. "Films and Coatings", May 26-29 2009, St.-Petersburg, Russia, P. 206-210 (in Russian).
9. O.P. Solonenko, A.N. Cherepanov, V.N. Popov et al., Plasma spraying of resistant coatings of mechanically activated and modified with nano-particles powder materials, Surface layers and interface regions in heterogenous materials, V.E. Panin Ed., Novosibirsk, SB RAS Publ., 2006, P. 418-460(in Russian).
10. O.P. Solonenko, A.N. Cherepanov, V.F. Kosarev et al., Development of combined

- production technologies of promising powder materials, functional coatings and surface layers with regulated nano- and microstructure, Proc. of science session of Presidium of Siberian Branch of RAS, December 22 2006, Novosibirsk, SB RAS Publ., 2007, P. 186-198 (in Russian).
11. O.P. Solonenko, A.N. Cherepanov, V.V. Marusin, V.A. Poluboyarov, Combined technologies of promising powder materials production, coatings deposition and surface layers with regulated nano- and microstructure hardening, Heavy Engineering, 2007, Vol. 10, P. 10-13 (in Russian).
 12. V.V. Kudinov, Plasma coatings, Moscow, Nauka, 1976, 189 P. (in Russian).
 13. O.P. Solonenko, V.A. Poluboyarov, A.N. Cherepanov, I.P. Gulyaev, A.E. Lapin, Peculiarities of plasma treatment and spraying of mechanically activated metal and metal alloy powders modified with ultra-fine refractory particles, Proc. of 18th International Symposium on Plasma Chemistry, 26-31 August 2007, Kyoto, Japan, 4 P.
 14. O.P. Solonenko, V.A. Poluboyarov, A.N. Cherepanov, I.P. Gulyaev, A.E. Lapin, Peculiarities of plasma treatment and spraying of metal and alloy powders mechanically activated and modified with refractory nanoparticles, Proc. of 8th Int. Conf. "Films and Coatings", May 22-25 2007, St.-Petersburg, Russia, P. 18-21 (in Russian).
 15. E.G. Avakumov, A.R. Potkin, O.I. Samarin, Planetary-type mill, Patent of Russian Federation № 975068, 1982 №43.
 16. O.P. Solonenko, I.P. Gulyaev, A.V. Smirnov, Plasma processing and deposition of powdered metal oxides, consisting of hollow spherical particles, Technical Physics Letters, 2008, Vol. 34, No. 12, pp. 1050–1052.
 17. O.P. Solonenko, V.A. Poluboyarov, A.E. Lapin, Z.A. Korotaeva, A.N. Cherepanov, Potentials of powders mechanical activation for spraying of thermal coatings sublayers, Proc. of Russian Sci.-Tech. Conf. "Ultra-dispersed powders, nanostructures, materials: production, properties, application", September 28-29 2006, Krasnoyarsk, P. 266-269 (in Russian).
 18. O.P. Solonenko, V.A. Poluboyarov, A.E. Lapin et al., Mechanical chemical nano-dispersions for improvement of sprayed sublayers of thermal coatings on gas turbines blades made of nickel superalloy, Proc. of 4th Int. Technological Congress "Military hardware, armament and modern technologies in military and civil production", June 4-9 2007, Omsk, part 2, P. 399-405 (in Russian).
 19. V.E. Ovcharenko, V.A. Klimylenov, O.V. Lapshin et. Al., Plasma processing and spraying of composite powders having a microdispersed inner structure, Proc. of 3rd European Congress on Thermal plasma Processes, 19-21 September 1994, Aachen, Germany, P. 395 – 403.
 20. P.Yu. Gulyaev, I.V. Milyukova, O.P. Solonenko, I.P. Gulyaev, Phase-structural changes in powdered SHS-materials during plasma spraying, Izvestia VUZov, Physics, 2007, Vol. 9, appendix, P. 349-352.
 21. O.P. Solonenko, A.M. Leonchikov, F.V. Nedosedkin, E.V. Efimova, Powdered aluminium alpha-oxide, production method and product, Patent on invention of Russian Federation № 2386589, 17.09.2008.
 22. J. Fazilleau, et al., Phenomena involved in suspension plasma spraying. Part 1: Suspension injection and behavior, Plasma Chem. Plasma Process, 2006, №26, P. 371-391.
 23. J. Fazilleau, et al., Phenomena involved in suspension plasma spraying. Part 2: Zirconia particle treatment and coating formation, Plasma Chem. Plasma Process, 2006, №26, P. 393-414.
 24. O. Tingaud, A. Grimaud, A. Denoirjean, et al., Suspension plasma-sprayed alumina coating structure: operating parameters versus coating architecture, J. Therm. Spray Tech., 2008, Vol. 17(5-6), P.662-670.
 25. F. Tarasi, M. Medraj, A. Dalatabadi, et al., Effective parameters in axial injection suspension plasma spraying process of alumina-zirconia ceramics, J. Therm. Spray Tech., 2008, Vol. 17(5-6), P.685-691.
 26. O.P. Solonenko, A.V. Smirnov, A.M. Leonchikov, I.P. Gulyaev, Oxide powder processes based on dc and twin plasma torches, Proc. of 6th Intern. Symp. on the Basic and Application of Plasma Technology, 14-18 December 2009, Hsinchu, Taiwan, 4 p.