Production and modification of hollow powders in plasma under controlled pressure

Igor P Gulyaev
Institute of Theoretical and Applied Mechanics SB RAS
ul. Institutskaya 4/1, Novosibirsk, 630090, Russia
E-mail: gulyaev@itam.nsc.ru

Abstract. Conducting plasma processes under high or low pressure is an efficient way to affect the heat, mass and momentum exchange in a two-phase flow and this technique is widely used in such well-developed technologies as low-pressure plasma spraying (LPPS) and high pressure plasma-chemical processes. In addition operating pressure is a key parameter in novel plasma process for modification of hollow powders properties. Plasma processing of porous ceramic powders is an effective method of producing hollow spheres (HOSP) with predefined properties. Regardless the method hollow powders were produced their geometric and structural properties can be adjusted by re-melting in plasma of certain pressure: low pressure processing will expand hollow spheres and high pressure – contract it. Regulating the outer diameter of hollow sphere allows adjusting its shell thickness, apparent density, gas pressure in the cavity etc. Preliminary experiments with zirconia hollow powders demonstrated good agreement with theoretical estimations of HOSP properties. The same technique can be used for adjusting properties of ceramic hollow powders produced by different methods, including cost effective fly-ash particles (cenospheres).

1. Introduction

Hollow ceramic spheres are widely as filler in composite materials for weight reduction, improving its heat and sound isolating properties. Applications that do not request strict phase composition and geometric properties of spheres can utilize microspheres produced from coal ash – cenospheres [1]. On the contrary technologies demanding decisive chemical compound of hollow spheres, its size and shell thickness require specially produced powders. Hollow spheres were found to be used in systems for separation of light gases like helium and hydrogen [2]. Plasma sprayed zirconia thermal barrier coatings produced of hollow spherical (HOSP) powder demonstrate decreased heat conductivity compared to coatings produced of compact powders [3] which is essential for gas turbine and jet engine production. The reason for different coating microstructure is likely to be explained with peculiar fluid dynamics during spreading of hollow droplet which produces a counter-jet [4]. Aside from spreading process hollow powders undergo complete melting in thermal jet due to thinner wall which can broaden possibilities of spraying refractory materials using methods with relatively low gas temperature (HVOF, detonation spraying). Plasma processing of porous particles is an effective way of production of hollow spherical powders of various materials including ceramics [5]. Formation of hollow spheres takes place owing to surface melting of material and generation of liquid surface film which entraps the gas contained in pores. Further complete melting and heating of the particle heating doesn’t affect the mass (moles) of entrapped gas, however the size of the sphere can
change. Final dimensions of the sphere are defined by balance of inner gas pressure $P_g$, ambient pressure $P_{amb}$ and surface (Laplace) pressure $P_{surf}$ at material solidification temperature [6]. During traditional plasma treatment of powders (spheroidization) at atmospheric pressure $D_p$, shell thickness $\Delta_p$ and apparent density $\rho_{app}$ are predefined by the porosity $p$ of initial material. As shown below, the ambient pressure $P_{amb1}$ is a key parameter governing diameter and apparent density of produced hollow spheres. Further manipulation by these properties can be achieved by re-melting obtained HOSP at different pressure $P_{amb2}$. In the case that the hollow spheres need to be expanded, i.e. lower the shell thickness and apparent density, re-melting should be conducted under lowered pressure $P_{amb2} < P_{amb1}$. In the case that produced powder needs to be densified re-melting should be conducted at raised pressure $P_{amb2} > P_{amb1}$.

2. Experimental setup

Experiments on plasma processing of powders under controlled pressure were conducted using setup shown in fig. 1. DC plasma torch (ITAM SB RAS, Novosibirsk) with channel diameter 8 mm was used for generating plasma. It was connected to pressure-tight water-cooled plasma chamber of 30 L volume, provided with plasma gas line and powder transport line. Typical operating conditions were nitrogen plasma gas flow rate 20-60 slpm, arc current 200-250 A (electric power 30-60 kW), achieved pressure range 0.5 – 2.5 atm.

Working gas flowrate was measured using RMB series rotameters (Dwyer) and PFM series flowmeters (SMC). Pressure in the plasma chamber was measured using MPX5700 pressure sensors (Freescale Semiconductors). During operation of plasma torch there is a constant gas flow into the chamber therefore maintaining preselected pressure requires controlled evacuation of gas. This was implemented by special pressure regulator, which could be connected to a vacuum pump for operation under lowered pressure. The minimum operating pressure was limited by throughput of the vacuum pump, while maximum pressure – mainly by stable operation of plasma torch and durability of applied pneumatic lines.

3. Theoretical model of hollow sphere formation

The necessary condition for hollow powder formation in a plasma jet is presence of sufficient amount of gas inside a particle of initial material. This can be provided by a number of methods: microporosity of the particles, preliminary gas sorption, gas release due to thermal decomposition or chemical reaction. The proven method of ceramic hollow spheres production is plasma treatment of agglomerated powders obtained by spray drying technology [5]. Such particles present agglomerates of
diameter 20 – 200 μm, consisting of bound 3 -5 μm grains. The individual agglomerate contains $10^3 – 10^5$ grains and has volume porosity about 50%.

Consider the simplest scenario of hollow sphere formation from a porous particle with diameter $D_{p0}$ and open porosity $p$ (all the pores are interconnected), which is being uniformly heated. When the porous agglomerate enters plasma jet its material as well as the inner gas is being heated (fig. 2). While the gas expands it leaves the volume of the particle, however the volume of pores remains the same. In the moment when particle surface reaches the melting temperature the liquid shell is being formed. It captures and fixes the mass of the gas inside the particle. The trapped gas gathers into the single central cavity, the size of which depends on temperature and ambient pressure. The final outer diameter $D_p$ of produced hollow sphere is defined by pressure balance on the droplet surface at material solidification temperature.

Let’s define the outer diameter $D_p$ of produced hollow droplet and relative shell thickness $\delta_p = \Delta_p / D_p$ corresponding to the melting temperature of material $T_m$, i.e. final dimensions of the sphere after cooling and solidification. The total volume of the pores in initial agglomerate is $V_{g0} = \frac{\pi}{6} D_{p0}^3 \cdot p$, and the mass of trapped gas is $m_g = V_g \rho_g$, where $\rho_g$ - gas density at temperature $T_m$ and pressure being equal to ambient pressure $P_{amb}$. After complete melting and formation of single gas cavity the shrinkage of melted droplet takes place due to the action of additional surface (Laplace) pressure $P_{surf}$, so the final volume of the gas cavity will reduce to the value. The droplet diameter $D_p$ and relative shell thickness $\delta_p$ can be calculated with the pressure balance on the droplet surface at the given temperature $T_m$:

$$m_g \frac{RT_m}{M} V_g = P_{amb} + \frac{4\sigma}{D_p} \left(1 + \frac{1}{1 - 2\delta_p}\right),$$

(1)

where $M$ - molar mass of the gas and $\sigma$ - surface tension of melted material. The left-hand side of the equation is pressure in the gas cavity $P_g$ calculated by the ideal gas law. It is counterbalanced by the sum of the ambient atmosphere pressure $P_{amb}$ and the surface pressure $P_{surf}$ calculated considering both surfaces of the liquid shell. Equation (1) contains two unknown variables, namely $D_p$ and $\delta_p$. However one of them can be easily expressed through another using the mass balance $(1 - 2\delta_p) = \frac{1}{3} \left[1 - 6m_p / \pi D_p^3\right]$, where mass of the particle $m_p$ is defined by diameter and porosity of initial agglomerate $m_p = \frac{\pi}{6} \rho D_{p0}^3 (1 - p)$. Iterative solution of equation (1) (minutely discussed in [6]) provides equilibrium diameter $D_p$ and relative shell thickness $\delta_p$ of the hollow droplet as a function of initial powder porosity $p$, material melting temperature $T_m$ and ambient pressure $P_{amb}$. In practical operations it is more convenient to measure apparent density of the spheres $\rho_{app} = \rho_{ZrO2} \left[1 - (1 - 2\delta_p)^3\right]$. Properties of
zirconia used for calculations are as follows: density 5.6 g/cm$^3$, surface tension at melting point 0.43 N/m, melting temperature 3000 K.

**Figure 3.** Calculated dependence of zirconia hollow sphere diameter (a) and apparent density (b) on initial agglomerate powder diameter for various feedstock porosity.

Calculation results in fig. 3, a demonstrate that the diameter of formed zirconia sphere $D_p$ is only slightly (by 2-10%) less than initial agglomerate diameter $D_{p0}$ and almost independent of porosity in the range $p = 0.2 - 0.7$. This result is typical for ceramic materials like zirconia, alumina and silica. On the other hand the porosity $p$ is the key parameter governing the apparent density (or shell thickness $\delta_p$) of the formed sphere. Figure 3, b shows expected result: the less initial porosity of the feedstock – the higher is apparent density of produced spheres.

The influence of ambient pressure $P_{amb}$ on parameters of hollow zirconia spheres produced from 100 $\mu$m agglomerates with porosity $p=0.6$ is presented in table 1. Gas inside the pores of initial particle, which originally had pressure $P_{amb}$, is being compressed by additionally applied pressure $P_{surf}$, which reduces the droplet diameter to the value $D_p < D_{p0}$. The final pressure in the gas cavity is equal to the sum of ambient pressure $P_{amb}$ and surface pressure $P_{surf}$. As one can see $P_{surf} \sim 0.4$ atm, therefore formation of hollow spheres under comparable ambient pressure $P_{amb} = 0.5$ atm causes noticeable reduction of particle diameter down to 90 $\mu$m and corresponding rise of particle apparent density. However in case of $P_{amb} = 2.5$ atm the surface pressure is minor compared to ambient pressure, so the shrinkage of droplet is small enough and its diameter $D_p = 97.5$ $\mu$m is almost equal to initial $D_{p0}$.

**Table 1.** Calculated parameters of hollow zirconia spheres produced from initial particles with diameter $D_{p0}=100$ $\mu$m and porosity $p=0.6$ under various ambient pressures $P_{amb}$

| $P_{amb}$, atm | $D_p$, $\mu$m | $\rho_{app}$, g/cm$^3$ | $\delta_p$ | $P_{surf}$, atm | $P_g$, atm |
|---------------|---------------|-----------------|------------|----------------|------------|
| 0.5           | 90            | 3.1             | 0.118      | 0.44           | 0.94       |
| 1.0           | 94            | 2.7             | 0.098      | 0.41           | 1.41       |
| 2.5           | 97.5          | 2.4             | 0.086      | 0.4            | 2.90       |

The two-step method of production of hollow powder with specified properties becomes available under controlled pressure processing. Assume the hollow sphere of diameter $D_{p1}$ and shell thickness $\delta_{p1}$ was formed under ambient pressure $P_{amb1}$ and then re-melted under different ambient pressure $P_{amb2}$ which caused change of diameter to the value $D_{p2}$. Estimation of new sphere diameter should be carried out by the pressure balance equation (1), where new value of $P_{amb2}$ should be used.
and the mass of trapped gas should be calculated by expression

\[ m_g = (P_{ambi} + P_{surf}) \frac{M}{RT_m} \frac{\pi}{6} D_p^3(1-2\delta_p)^3, \]

where surface pressure \( P_{surf} = \frac{4\sigma}{D_p}(1+1/(1-2\delta_p)). \)

Figure 4 shows results of calculations for apparent density of zirconia spheres produced from 100 μm initial particles with porosity \( p=0.5 \). The white circles display density of the spheres after their formation at a given pressure.

![Figure 4](image)

**Figure 4.** Calculated change of apparent density of hollow zirconia spheres produced from 100 μm initial particles with porosity \( p=0.5 \)

As one can see, regulating formation ambient pressure from 0.2 to 5 atm provides change of powder density in wide range 4.3 - 2.9 g/cm\(^3\). Even more pronounced changes in density can be realized with second stage processing. For example, if the hollow powder produced at \( P_{ambi1} = 5 \) atm is re-melted at \( P_{ambi2} = 0.2 \) atm its density will drop down to 0.35 g/cm\(^3\).

4. Results and discussion

Firstly three types of zirconia agglomerated (spray-dried) powders were spheroidized under atmospheric pressure. These feedstock powders had wide-range size distribution 20-120 μm. Average porosity was measured for all 3 types of feedstock powder and was found to be \( p_{av} = 0.4, 0.5, 0.6 \). Figure 5 demonstrates apparent density measurements using fluid pyknometry method (accuracy \( \varepsilon =5\%) of various size fractions of produced hollow zirconia powders (figures with solid lines). Dash lines are calculated estimations for apparent density of zirconia hollow spheres produced from agglomerates with \( p = 0.4 \) and 0.6.

The measured apparent density is systematically higher than calculated one for the small size spheres which can be explained with presence of dense fragments of broken particles shell. Moreover, different fractions of initial agglomerated powders obtained by spray drying can have significantly diverse porosity \( p \) [7], and average value \( p_{av} \) doesn’t account this. This explains very steep curve of measured density for the initial porosity \( p_{av}=0.5 \).

In order to eliminate undesired effects of initial powder variable porosity and presence of broken fragments two-step experiments with variable pressure were conducted using narrow powder fraction. First, the hollow zirconia powder of wide size range 20 – 120 μm was produced under raised pressure of \( P_{ambi1} = 2.5 \) atm. The narrow fraction of 71-80 μm was separated using sieving machine and its apparent density was found to be 4.14 g/cm\(^3\). Second, the separated fraction was re-melted under atmospheric pressure \( P_{ambi2} = 1 \) atm, and its apparent density was found to be 3.3 g/cm\(^3\) (fig. 6).
In order to validate these experimental results calculations using proposed hollow sphere modification model were conducted. The solid line in fig. 6 demonstrates change in zirconia hollow sphere apparent density after processing (re-melting) under controlled pressure. In calculations was used measured value of formation gas pressure $P_{\text{ambi}}=2.5$ atm, sphere diameter $D_p=75$ μm (average over the fraction 71-80 μm) and shell thickness $\delta_p=0.18$ (corresponding to $P_{\text{app}}=4.14$ g/cm$^3$). As one can see model predicts decrease in apparent density (down to 3.23 g/cm$^3$) of hollow powder almost identical to the measured one. This is very promising result, although it is obvious that more broadened experiments are required to investigate limitations of this technique.

5. Conclusion

Formation of hollow spherical powders in plasma was analyzed and theoretical model described. Novel method of hollow powders modification using plasma under controlled pressure was introduced and first experiments described. The suggested method can be used for modification of hollow spheres obtained by various techniques, including cost-effective separation of fly-ash particles (cenospheres). Obviously clear understanding of capabilities of introduced method requires broadened experiments under controlled pressure as well as study of adjacent problems such as determination of thermal properties of plasmas and performance of plasma torch (power, efficiency) under non-atmospheric pressures.

Acknowledgements

The reported study was partially supported by RFBR, research project No. 12-08-31150.

References

[1] Drozhzhev V S, Danilin L D et al. 2005 Proc. World of Coal Ash Conf., 11-15 April, Lexington, USA 115-16
[2] Fomenko E V, Anshits N N et al. 2010 Doklady Physical Chemistry 435(2) 202-04
[3] Chi W, Sampath S, Wang H 2006 J. Thermal Spray Tech. 15(4) 773-78
[4] Gulyaev I P, Solonenko O P, Gulyaev P Yu, Smirnov AV 2009 Tech. Phys. Lett. 35(10) 885–888.
[5] Solonenko O P, Gulyaev I P and Smirnov A V 2011 J. Ther. Sci. Technol. 6(2) 219–34
[6] Gulyaev I P 2010 Ph. D. dissertation ITAM SB RAS, Novosibirsk (In Russian)
[7] Vehring R, Foss W R and Lechuga-Ballesteros D 2007 Aerosol Sci. 38 728–46