Physical and technical processes for preparing silicate melts and silicate-melt products using low-temperature plasma

V V Shekhovtsov, O G Volokitin, N K Skripnikova, G G Volokitin and V A Vlasov

Tomsk State University of Architecture and Building, 2 Solyanaya Sq., Tomsk, 634003, Russia

E-mail: nks2003@mail.ru

Abstract. The paper presents the experimental results of fabricating refractory oxide- and silicate-based microspheres of various density. In highly-concentrated thermal plasma with the specific bulk enthalpy ranging between 24131–35739 kJ kg\(^{-1}\), three types of microspheres can be formed, namely: dense microspheres with gas inclusions in the surface layer, hollow microspheres and vitrified agglomerates. The obtained experimental data are in good agreement with the calculated dependence between the wall thickness of a microsphere and the porosity of the agglomerated powder.

1. Introduction

Currently, hollow microspheres are widely used in the development of new technologies of constructional materials and coatings. Hollow microspheres possess high thermophysical and mechanical properties [1–3]. Aluminosilicate hollow particles are the most common type of microspheres in the industrial applications. They are coal combustion by-products remaining in boiler furnaces of thermal power plants (TPP) after 1500 K heating [4, 5]. In this case, the microsphere formation is chaotic and uncontrolled, with a large amount of ash residual. The microsphere concentration in it is not over 5–8% that does not meet the industrial requirements. It is important to note that the phase composition of aluminosilicate microspheres is comparable to that of ash residual. This type of material is a combination of refractory oxides and silicates having the high melting temperature (over 1850 K). Refractory oxides and silicates is an important source of raw materials in the microspheres production. The microspheres production from ash residual using the highly-concentrated thermal plasma provides the intensification of physical processes in condensed media that cannot be achieved by the traditional heating sources [6–8].

The analysis of the theoretical calculations and experimental data found in the literature shows that little attention has been paid to the formation mechanism of ash microspheres and associated physical processes. The aim of this work is a study of conditions and mechanisms for the formation of refractory oxide-based microspheres using the thermal plasma treatment.
2. Materials and methods

The theory of the formation of hollow microspheres from plasma treated agglomerated particles is based on such physical processes as heating, melting, gas encapsulation with the subsequent growth of the melt droplet [9, 10]. Encapsulated gas and further expansion of the gas phase which determine the outer diameter and the wall thickness of a condensed particle can be described by the dependence between the initial bulk porosity of agglomerate and the heating rate [11, 12].

The main raw material used in this experiment is a mixture of refractory oxides and silicates which are the coal combustion by-products remaining in boiler furnaces of the Belovo Thermal Power Plant (the Kemerovo region, Russia) [13]. These materials contain ~60 wt.% SiO₂ and >20 wt.% Al₂O₃. The raw materials under study comprise SiO₂ and Al₂O₃ single-component oxides and ≤1 wt.% allowable content of impurities [14]. Table 1 gives the chemical composition of these raw materials.

| Raw materials     | Parameters | Oxide content (wt.%) |
|-------------------|------------|----------------------|
|                   | ρ₁, λₚ, Tₘ | SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, Δm₁, Δm₂ |
| Ash from TPP      | 2.20       | 59.85, 5.65, 1.87, 0.8, 0.2, 5.1 |
| Silica sand       | 2.65       | 98.2, 0.68, 0.09, 0.07, trace, 0.9 |
| Boehmite          | 3.08       | 0.03, 99.0, 0.02, –, –, 0.3, 0.6 |

Note: ρ₁ – density, g·cm⁻³; λₚ – thermal conductivity, W·m⁻¹·K⁻¹; Tₘ – melting temperature Tₑ – evaporation temperature, K.

In order to obtain agglomerated powders, we used a method of granulation of ground materials to achieve a 2–5 µm grain size. An aqueous solution of polyvinyl alcohol (PVA) is used as a binder, the PVA/powder ratio being 1:7 [15]. The given agglomerate is a spherical object comprising heterodisperse grains (dₚ = 2–5 µm). It has a branched micropore structure. The grain-size composition of the agglomerated powder is Dₚ₀ = 20–200 µm and its average bulk closed porosity is P = 31±5 %. The agglomerate porosity P is determined as P = 1–ρ₁/ρ₂, where ρ₁ and ρ₂ are porosities of the material and the agglomerated powder, respectively. The density is measured by hydrostatic weighing.

The experiment utilizes a thermal plasma torch with non-transferred arc [13]. Table 2 summarizes thermophysical properties of plasma jet at a gas rate of Gₜ = 1 g·s⁻¹.

| Composition | I (A) | U (V) | P (kW) | η (%) | Hₑ (kJ·kg⁻¹) | Tₑ (K) | uₑ (m·s⁻¹) |
|-------------|-------|-------|--------|-------|--------------|--------|-------------|
| 1           | 200   | 97    | 19.4   | 61.4  | 24131.9      | 6100   | 424         |
| 2           | 250   | 94    | 23.5   | 63.1  | 29936.8      | 6700   | 515         |
| 3           | 300   | 90    | 27.0   | 65.6  | 35739.3      | 7300   | 627         |

The specific bulk enthalpy Hₑ of plasma jet at the nozzle exit of anode assembly ranges from 24131 to 35739 kJ·kg⁻¹ which corresponds to the bulk temperature Tₑ = 6000–7300 K. Figure 1 presents a photograph of the plasma treatment of the powder agglomeration at stationary operation conditions.

![Figure 1. Photograph of powder agglomeration plasma treatment.](image)
3. Assessment of thermal parameters of condensed phase in plasma

In our previous research [16] we proposed a model of selecting geometrical and operating parameters of the plasma generator to provide the required heating and melting dynamics. The gas temperature $T_p$, flow rate $u_p$, and molten mass $\varphi$ of the porous particle can be derived from a system of differential equations:

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\begin{align*}
\frac{dv}{dt} &= C_D \frac{\pi D_p^2 \rho_f (T_f - u_f)(u_f - u_p)}{4 m_p} ; \\
\frac{dT_p}{dt} &= \frac{\pi D_p \lambda_f}{c_p m_p} \text{Nu}(T_f - T_{melt}) ; \\
\frac{d\varphi}{dt} &= \frac{\pi D_p \lambda_f}{L_m} \text{Nu}(T_f - T_{melt}) 
\end{align*}
$$

where $T_f$ is the carrier gas temperature, $u_f$ is the carrier gas rate; $\rho_f$, $\lambda_f$ are respectively density and thermal conductivity of carrier gas with account for $T_f = 0.5(T_g + T_p)$; $\text{Nu}=2+0.16Re^{2/3}$ is the Nusselt number; $C_D$ is the resistance factor; $D_p$, $m_p$, $c_p$ are the particle diameter, mass and specific heat, respectively; $T_{melt}$ is the melting temperature of the crystalline modification.

Numerical calculations allow us to determine the heating dynamics for 50–150 µm agglomerated particles at thermal parameters given in table 1 for the experimental plasma generator. In particular, figure 2 presents the heating and melting dynamics of SiO$_2$ particles moving along $x$-axis of the plasma flow at the process parameters $N_2$, with and without a consideration for the phase transformation.

Let us assume that at the temperature of the phase transformation, parameters $\lambda_p$, $\rho_p$, and $c_p$ suddenly change and then keep constant within the stability region of the given crystalline modification. The highest melting heat of SiO$_2$ particles is accepted to be 186.6 kJ·kg$^{-1}$. This value is obtained by summing the melting heat near the triple point and summing the phase transformation heat during the change in the crystalline modification with the temperature increase within 390–1993 K range.

![Figure 2](image)

**Figure 2.** Dependences of motion, heating and melting dynamics of SiO$_2$ particles moving along $x$-axis: $a$ – molten mass; $b$ – temperature; $c$ – particle velocity. Particle size: 1 – 50 µm; 2 – 100 µm; 3 – 150 µm. Porosity: 0 and 0.4. Process parameter: $N_2$.

The surface temperature of the porous SiO$_2$ particle rapidly reaches the value of $T_{\text{sur}}>T_{\text{melt}}$ starting from the area of their introduction into the plasma flow. However, the opposite situation is observed during the formation of the molten mass. This effect is determined by the low conductivity of porous particles and indicates to a great temperature difference between the particle surface and its nucleus. Thus, it is important to pay attention to the initial porosity of particles when synthesizing hollow
particles from powder agglomerations. As expected, SiO$_2$ particles with lower porosity accelerate slower, and their velocity is proportional to their initial mass. The difference in the velocity of solid and hollow particles can vary between 20–120 %, depending on their size and porosity.

4. Results and discussion

The energy dispersive spectroscopy (EDS) on the scanning electron microscope (SEM) was used to study the surface morphology and the elemental composition of the obtained microspheres. A comparison between these microspheres and TPP-produced aluminosilicate microspheres obtained by the traditional technique are presented in figure 3.

![Figure 3. SEM images of obtained microspheres (a); EDS spectra (b) of the elemental composition; 1 – ash from the thermal power plant; 2 – silica sand; 3 – boehmite.](image)

According to the diagram [17], the sphericity of the fabricated microspheres is 0.9. If we compare the fabricated and aluminosilicate microspheres (see figure 3a), we see neither pores nor micron-sized fused particles of the initial raw material on the microsphere surface. According to the elemental composition measured by EDS (see figure 3b), there are no evaporation of the main elements contributing to the initial composition of agglomerates.

The main physical parameters of microspheres include the diameter $D_{p,m}$, density $\rho_p$ and relative wall thickness $\delta/D_{p,m}$. Figure 4 illustrates the optical images of the plasma treated agglomerated powders based on the ash residual. The particle size is 90–100 µm at different gas rates (0.5–1.5 g·s$^{-1}$).

![Figure 4. Optical images of the agglomerated powders after plasma treatment: a – dense microsphere with gas inclusions in the surface layer; b – hollow microsphere; c – vitrified agglomerate.](image)
At the lowest gas rate of 0.5 g·s⁻¹, the particles overheat with the subsequent formation of dense microspheres ($D_{p,m} = 65\pm3$ µm, $\rho_p = 1.98$ g·cm⁻³) in the surface layer. The rational heating is performed at a 1.0 g·s⁻¹ gas rate, resulting in the formation of hollow microspheres ($D_{p,m} = 110\pm2$ µm, $\rho_p = 0.83$ g·cm⁻³). Their wall thickness varies between 4–5 µm. With the increase in the gas rate up to 1.5 g·s⁻¹, the agglomerate surface vitrifies, thereby forming a thin film ≤1 µm thick. The particle diameter and density are in their initial state ($D_{p,m} = 95\pm2$ µm, $\rho_p = 1.36$ g·cm⁻³).

Figure 5 depicts the dependence between the relative wall thickness δ/$D_p = 0.5(1 – P^{1/3})$ of microspheres and the porosity of the agglomerated powder. The experimental data obtained during the plasma treatment of the agglomerated powder ($P = 31\pm5$) are marked by different figures.

The underestimated value of the relative wall thickness of ash microspheres can be explained by the dehydration and decarbonization processes. This is supported by the preliminary estimation of the ignition losses (5.1 wt.%) as well as the low dynamic viscosity of the melt. As compared to SiO₂, this value is $\eta_{SiO2}/\eta_{ash} = 5\times10^4$. The experimental data obtained for SiO₂ and Al₂O₃ are in good agreement with the calculated dependence, the standard deviation being respectively 8 and 6%.

5. Conclusion
Based on the results, it can be concluded that in highly-concentrated thermal plasma with the specific bulk enthalpy ranging between 24131–35739 kJ·kg⁻¹, three types of microspheres were formed, namely: dense microspheres with gas inclusions in the surface layer, hollow microspheres and vitrified agglomerates. The obtained experimental data were in good agreement with the calculated dependence between the wall thickness of microspheres and the porosity of the agglomerated powder. The proposed technological solutions demonstrated the suitability of natural and anthropogenic materials (silica sand, ash residual and boehmite) for use in the microspheres production from agglomerated powders with the melting temperature ranging from 1900 to 2300 K.

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