Analysis of interphase heat and mass transfer in suspension plasma spraying using air

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Abstract. A theoretical model of interphase interaction “suspension particle - plasma flow” is proposed. The model assumes several successive stages of the evolution of liquid material: 0) entry into the plasma stream and break-up of the liquid into droplets; 1) heating the droplet to the evaporation temperature of the carrier fluid; 2) evaporation of the liquid, accompanied by convective mixing of the material; 3) evaporation of the liquid with the formation of a dry crust; 4) heating the solid material to melting; and 5) evaporation. Based on the analysis of the intensity of the processes of interfacial heat transfer, evaporation, diffusion and filtration mass transfer, relations are obtained for evaluating at each stage of the process duration, particle size, speed and distance passed in the flow. Demonstration calculations were performed for an aqueous ZrO$_2$ suspension with a solid phase concentration of 20% injected into the air plasma stream at a flow velocity of 2000 m / s and a flow temperature of 5000 K.

1. Introduction

Methods using suspensions (Suspension Plasma Spraying) and precursor solutions (Liquid Precursor Plasma Spraying) of materials are actively developing in the family of thermal spraying technologies. Interest in them is caused by the possibility of forming coatings with thicknesses from units to hundreds of micrometers with a fine structure of submicron scale at a productivity of several grams per minute [1]. To date, there are a large number of works demonstrating the features and advantages of such coatings; on the other hand, the dynamics of heat and mass transfer of suspension droplets in a plasma jet remains poorly studied. The main feature of such methods is the process of mass transfer of liquid from the droplet volume (evaporation) under the action of high plasma temperatures.

In the present work, an attempt was made to outline the main stages of the interaction of suspension droplets with plasma, to obtain analytical estimates of the dynamics of the main processes of heat and mass transfer. The results of calculations of the dynamics of evaporation, heating, and acceleration of droplets of an aqueous suspension of ZrO$_2$ particles in an air plasma jet are presented.

2. The scenario of suspension droplets evolution in plasma

Let’s consider a single spherical drop of a suspension with a given initial concentration of solid phase $\phi_0$, which is instantly placed in a uniform plasma stream (figure 1). The flow of a particle around a particle with a high-speed gas stream causes tangential stresses on the particle surface, which lead to convective mixing of the material [2] and, as a result, the temperature profile and particle concentration in the volume become uniform. After the particle reaches the boiling point of the liquid, its evaporation begins and the volume concentration increases up to the value at which the increased
viscosity of the suspension stops mixing in the drop volume. Further evaporation of the liquid leads to the formation of a dry porous crust on the surface and the gradual spread of its internal boundary to the center of the particle. The porous crust presents a significant resistance to the diffusion mass transfer of liquid vapor, so there is an increase in pressure inside the particle. The decrease in internal pressure occurs due to the filtration flow of steam. Further heating of the solid phase leads to its melting and the formation of a drop of melt of the material.

![Figure 1. Schematic representation of the process of drying a suspension drop in a plasma stream.](image)

For quantitative estimates, we will consider an aqueous suspension of submicron particles of zirconium dioxide with a concentration \( \phi_0 = 0.2 \) injected into an air plasma with a temperature \( T_f = 5000 \) K and a velocity \( U_f = 2000 \) m/s. At all stages of particle motion in a plasma stream, the equations of one-dimensional particle motion and heat transfer are used [3].

The sizes (diameters) of droplets of suspension produced by injectors of various designs usually lie in the range of 10-30 microns [4]. After the droplet of the suspension enters the plasma stream, it breaks-up to a size \( R_0 = \text{We}_{cr} / 2 \rho U_f^2 \) that corresponds to the critical Weber number \( \text{We}_{cr} = 10 \). The duration of the droplet spheroidization process is short and amounts to \( D_f \mu / \sigma \). The concentration of the suspension at this stage does not change and remains equal to the initial value \( \phi_0 \).

2.1. Heating of droplets to a liquid evaporation temperature

After droplet breaks-up to an equilibrium size, mixing of the material begins, caused by the tangential forces on the surface from the outside gas flow. The temperature and concentration of solid phase are equalized in volume. The drop is evenly heated to the boiling point of the liquid. The diameter of the droplet and the concentration of the suspension remain unchanged.

2.2. Evaporation of material with convective mixing

The evaporation of free liquid from the surface begins, the solid phase concentration increases, and the radius of the droplet decreases. All the heat flux coming from the stream is spent on evaporating the liquid. The temperature of the material remains constant, the concentration of solid phase increases, but remains uniform in volume due to mixing.

Mixing stops when the concentration of solid particles reaches a critical value of \( \phi_{fix} = 0.61 \) [5], at which the viscosity becomes large enough to stop internal convection. The gel is formed. The radius of the drop decreases and is determined by the expression \( R_{cr} = R_0 \sqrt[3]{\phi_0 / \phi_{fix}} \). The total heat flux to the particle \( Q \) remains unchanged, the evaporation rate of the material is
\[
\frac{dm_{H_2O\_e\_v}}{dt} = \frac{Q}{L_{e\_v}} \approx 10^{-9} \text{ kg/s}.
\]

The throughput of the gas boundary layer by diffusive mass transfer is higher than the liquid evaporation rate, therefore, the duration of this drying stage is limited by the heat flux to the particle.

2.3. Evaporation without liquid mixing.
A solid (porous) crust of radius \( R_{cr} \) is formed on the surface, the bulk density of which is equal to \( \varphi_{cr} = (1 - \text{porosity}) = 0.74 \). The crust has its effective coefficient of thermal conductivity \( \lambda_{cr} = \lambda_{sol} \varphi_{cr} \) and diffusion coefficient of water vapor \( D_{cr} \sim 10^{-6} \text{ m}^2/\text{s} \) [6]. The particle size is fixed. The thickness of the dry crust is constantly growing. The “concentrated suspension - porous crust” interface moves toward the center of the particle. The speed of movement is determined by the rate of evaporation of the liquid from the suspension. Water vapor slowly passes through the forming crust, so their pressure rises sharply. The outer radius of the particle is already fixed and equal to \( R_{cr} \), the final inner radius of the crust is determined from the mass balance (volume) of solid particles and is equal to

\[
R_i = R_{cr} \sqrt{1 - \varphi_{fix} / \varphi_{cr}}.
\]

Due to the fact that the thermal conductivity of the gas and the porous crust relate as \( \lambda_g / \lambda_{cr} \sim 10^{-1} \) the surface temperature of the particle is much closer to the temperature of the evaporating liquid, but not to the temperature of the gas. Estimation shows that the particle surface temperature at a final crust thickness is approximately 400-500 K, which is quite far from the melting point of the solid phase.

Diffusive mass transfer of liquid vapor from the surface of the suspension through a dry crust and a boundary layer of gas into the free flow is determined by the expression:

\[
\frac{dm_{H_2O\_s\_f}}{dt} \bigg|_{\text{diff}} = \frac{2\pi (\rho_{e\_s\_surf} - \rho_{e\_s\_g})}{D_g R_{cr} \text{Sh}} + \frac{2\pi (\rho_{e\_s\_surf} - \rho_{e\_s\_g})}{MR_{film} + MR_{crust}} \approx 10^{-12} \frac{\text{kg}}{\text{s}},
\]

where \( \rho_{e\_s\_surf}, \rho_{e\_s\_g} \) are the vapor density of the liquid on the evaporation surface and in the gas stream, \( D_g \) and \( D_{e\_s} \) - the vapor diffusion coefficient in the gas and the porous crust. As can be seen, the vapor diffusion mass transfer rate is 3 orders of magnitude lower than the liquid evaporation rate. In this case, the diffusion resistance of the crust \( MR_{crust} \) is approximately 3 orders of magnitude higher than the resistance of the gas boundary layer at the particle surface \( MR_{film} \). The time for the evaporation of the entire liquid of 2 orders of magnitude is shorter than the time required for diffusion outflow of steam through the crust (at atmospheric pressure inside), therefore, an increase in gas pressure inside the cavity will occur very quickly, accompanied by a proportional increase in the rate of filtration mass transfer.

The rate of filtration flow of liquid vapor through a porous crust is proportional to the pressure gradient (differential) and is determined by Darcy's law: \( v_{filt} = -\frac{K}{\mu_{vap}} \frac{\Delta P}{\Delta r} \), in which \( K, \mu_{vap} \) are the crust permeability and the viscosity of the vapor. The mass transfer rate of vapor through the outer surface of a particle of a fixed radius \( R_{cr} \) calculated using the expression for the permeability of a porous medium [7] is equal to:

\[
\frac{dm_{H_2O\_s\_f}}{dt} \bigg|_{\text{filt}} = S_{surf} \rho_{vap} v_{filt} \approx 10^{-9} \text{ kg/s}.
\]
When water evaporates, its density decreases 2000 times: from 1000 to 0.560 kg/m³ (at atmospheric pressure). This leads to an instantaneous increase in pressure inside the pores of the particles and accelerates the filtration outflow of steam. Thus, the drying speed of the droplet is limited exclusively by the heat flux to the particle; all the liquid that has been evaporated will be removed from the particle due to the pressure gradient. Calculations show that the pressure value, which ensures the filtration mass transfer rate of vapors equal to the liquid evaporation rate, is approximately 3 atm.

The evaporation of free liquid from the surface begins, the solid phase concentration increases, and the radius of the droplet decreases. All the heat flux coming from the stream is spent on evaporating the liquid. The temperature of the material remains constant, the concentration of solid phase increases, but remains uniform in volume due to mixing.

2.4. Heating the dry material to the melting temperature.
The liquid is completely vaporized, the particle presents a porous frame. Further heating of the material leads to melting of the material (Tₘ = 3000K). The radius of the droplet somewhat decreases at this stage due to the fact that the solid skeleton of the main ZrO₂ material completely melts and takes the form of a dense sphere (without pores):

\[ R_p = \sqrt[3]{\frac{3m_{sol}}{4\pi \rho_s}}. \]

2.5. Heating the material to the boiling temperature.
The entire heat flow that enters the particle is spent on heating the material to a boiling point (Tₜ = 4573 K) and its evaporation.

3. The scenario of suspension droplets evolution in plasma
Figure 2 presents the dynamics of changes in the diameter and mass of the sprayed particle upon injection of a 20% wt ZrO₂ suspension into a one-dimensional plasma stream with a temperature of 5000 K and a velocity of 2000 m/s. As can be seen, the particle reaches a final diameter of 0.9 μm (melting of the material) at a distance of about 9 mm, while it has a velocity of 1800 m/s, close to the velocity of the gas stream. A comparison of the durations of the various stages shows that the processes of liquid evaporation during convective mixing of the suspension (stage 2) and the heating and melting of a dry particle take the longest time (stages 4 and 5).

**Figure 2.** Evolution dynamics of 20% wt ZrO₂ suspension droplet placed in a one-dimensional air plasma stream with a temperature of 5000 K and a speed of 2000 m/s: a change in the diameter, mass, and comparison of the duration of the various stages of drying the droplet.
The developed model was used to analyze the influence of air plasma flow conditions on the characteristics of the sprayed particles. Calculations were carried out for the values of the initial concentration of the suspension $\varphi_0 = 0.01 \div 0.4$, flow rate $U_f = 500 \div 2500 \text{m/s}$, and flow temperature $T_f = 3000 \div 5000 \text{K}$. Typical values of the vapor pressure during drying of the porous crust are 1.5–4.0 atm, and the pressure increases with increasing flow rate, flow temperature, and suspension concentration.

An increase in the plasma flow velocity is expected to reduce the diameter of the sprayed particles. The minimum particle size values of 0.1 - 0.2 $\mu$m (for $\varphi_0 = 0.01 \div 0.05$) are achieved at the highest speed and lowest flow temperature. Plasma flow rates of less than 1500 m/s are unsuitable for suspension plasma spraying, since the distance of the complete melting of the material exceeds 50 mm. The temperature of the plasma flow weakly affects the dynamic and dimensional characteristics of the sprayed particles. An increase in the initial concentration of the suspension in the range $\varphi_0 = 0.01 \div 0.4$ leads to an increase in the size of the sprayed particles and from 0.2–0.3 $\mu$m to 1–1.5 $\mu$m, the distance of complete melting of the material from 3 mm to 20 mm.

4. Conclusion
A theoretical model of the interfacial interaction “suspension particle - plasma flow” has been developed. Based on the analysis of the intensity of the processes of interfacial heat transfer, evaporation, diffusion and filtration mass transfer, relations are obtained to estimate the duration of the stages, particle size, speed and distance traveled.

It is shown that the diffusion mechanism of mass transfer is not able to provide the vapor release rate corresponding to the intensity of the liquid evaporation. At the same time, the filtration mechanism of mass transfer allows vapor to be removed from the particle with an increase in internal pressure to 1.5–4 atm. The developed model was used to analyze the influence of air plasma flow conditions on the characteristics of the sprayed particles. The minimum particle sizes of 0.1–0.2 $\mu$m (for concentrations of 1–5%) are achieved at a high flow velocities of 2000–2500 K. Plasma flow velocities of less than 1500 m/s are not suitable for suspension plasma spraying. The temperature of the plasma flow weakly affects the dynamic and dimensional characteristics of the sprayed particles.

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