Modeling of liquid ceramic precursor droplets in a high velocity oxy-fuel flame jet

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Abstract

Production of coatings by high velocity oxy-fuel (HVOF) flame jet processing of liquid precursor droplets can be an attractive alternative method to plasma processing. This article concerns modeling of the thermophysical processes in liquid ceramic precursor droplets injected into an HVOF flame jet. The model consists of several sub-models that include aerodynamic droplet break-up, heat and mass transfer within individual droplets exposed to the HVOF environment and precipitation of ceramic precursors. A parametric study is presented for the initial droplet size, concentration of the dissolved salts and the external temperature and velocity field of the HVOF jet to explore processing conditions and injection parameters that lead to different precipitate morphologies. It is found that the high velocity of the jet induces shear break-up into several μm diameter droplets. This leads to better entrainment and rapid heat-up in the HVOF jet. Upon processing, small droplets (<5 μm) are predicted to undergo volumetric precipitation and form solid particles prior to impact at the deposit location. Droplets larger than 5 μm are predicted to form hollow or precursor containing shells similar to those processed in a DC arc plasma. However, it is found that the lower temperature of the HVOF jet compared to plasma results in slower vaporization and solute mass diffusion time inside the droplet, leading to comparatively thicker shells. These shell-type morphologies may further experience internal pressurization, resulting in possibly shattering and secondary atomization of the trapped liquid. The consequences of these different particle states on the coating microstructure are also discussed in this article.

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1. Introduction

The solution precursor plasma spray (SPPS) process has been successfully developed to deposit high quality coatings on hardware components. In this process, liquid droplets containing dissolved salts of the coating material are injected into high temperature plasma where the droplets transform into molten or semi-molten particles deposited on a substrate surface through a series of thermophysical changes [1–3]. The ease of injecting and handling liquid precursors and the resulting favorable coating microstructures have made this process [4,5] attractive for many industrial applications. Similar to the plasma processing, liquid precursor droplets can be injected into a high velocity oxy-fuel (HVOF) flame jet to obtain either oxide powders of the injected precursor salts or thin oxide coatings.

In the HVOF thermal spray process, a high temperature jet is produced from the combustion of a hydrocarbon fuel. The combustion process typically takes place upon the pre-mixing of fuel with oxygen within the HVOF torch, from which the hot combustion products are ejected through a converging diverging nozzle. The flame jet at the nozzle exit is characterized by a centerline temperature of about 3000 K and high velocities exceeding 800 m s⁻¹. The jet is typically an underexpanded supersonic jet and it becomes subsonic downstream through a system of oblique shock waves, forming a classic shock diamond pattern. Liquid
droplets can be injected axially into the flame and are accelerated to very high velocities. In comparison to DC arc plasma processing, the HVOF flame has higher velocities (~800 vs. 400 m s\(^{-1}\)) but lower temperatures (3000 vs. 10,000 K). Thus, it provides processing conditions different to those provided in a plasma jet. For example, the initial high relative velocity between the injected droplets and the HVOF flame as well as the presence of shock diamonds create conditions conducive for droplet break-up and generation of smaller sized droplets, as explained later. Another attribute of the HVOF flame jet is the very high kinetic energies imparted into the formed particles with which they impact onto the substrate. The high velocity impact typically results in superior dense coatings [6]. However, the significantly lower temperature of the HVOF flame jet typically does not allow processing of high melting point ceramic materials, although some limited success has been achieved in HVOF processing of ceramics [7]. Additionally, significant work has been reported on flame synthesis of nanoparticles. Chen et al. [8] used a flat flame burner for the synthesis of oxide phases in the form of powders, films or coatings. Skandan et al. [9] reported that it is possible to produce oxides from metal organic precursors by carefully controlling the thermochemistry in low pressure flames. Limaye and Helble [10] sprayed droplets into a combustion flame to produce nanoscale crystalline particles in both agglomerated and unagglomerated forms. Similar results were reported by Mueller et al. [11], who produced zirconia nanoparticles by flame spray pyrolysis at high production rates. Baranwal et al. [12] showed a novel processing route in which a flame environment was used to synthesize alcohol-soluble precursors to produce nanopowders of mullite composition.

As in any thermal spray process, a detailed understanding of various thermophysical and thermochemical transformations of a liquid precursor droplet injected into the HVOF flame jet is needed to improve the design and control of the spray process parameters and conditions. Some of these processes include droplet shear break-up, evaporative shrinkage and precipitation of dissolved solute, with resulting changes in particle morphologies. The chemical, thermal and morphological states of the HVOF processed precursor droplets ultimately determine the coating microstructure and its macroscopic properties. Parameters such as droplet size, injection velocity, location and temperature zone of the HVOF flame jet where droplets are injected, precursor characteristics, HVOF temperature and velocity fields can all have varying degrees of influence on the final coating quality.

It has been suggested [13–16] that various possible processing paths exist for liquid precursor droplets, leading to different in-flight particle morphologies. Variations of droplet heating rate, initial droplet diameter and properties of the dissolved salts can lead to the formation of different particle morphologies from solid spheres to hollow, fragmented shells. Usually small droplets exhibit uniform solute concentration increases during the evaporation phase prior to precipitation and form solid spheres. Larger droplets require greater mass diffusion time to reach uniform solute concentration compared to the heating timescale and hence surface precipitation occurs, resulting in the formation of shells of varying thicknesses. The thickness of the shell is dependent on the supersaturation limit of the solute and the mass diffusivity of solute in the solvent. Higher mass diffusivity and higher supersaturation limits favor formation of thicker shells. The fate of particles upon surface precipitation of a shell depends on the physical characteristics of the shell, such as its elasticity and porosity. For low porosity shells, internal pressurization due to vaporization of the trapped liquid can result in shell fracture. Highly porous shells may vent out the internally formed vapor and remain as hollow shells. While it is difficult to observe these morphologies as they are formed in a flame or plasma environment, it is possible to observe their qualitative features in micrographs of deposits such as that shown in Fig. 1a–c [17,18], obtained from an HVOF experiment. Observed features include spherical particles (SP) of sizes of less than 1 μm, surface splats (SS), deformed shells, and cracked shells (CS) of sizes around 10 μm. It is evident that a multitude of particle morphologies from small spherical entities to deformed shells and shell fragments are omnipresent in all the images of single pass deposits obtained in HVOF and plasma spray systems. Because of the difficulties for quantitative experimental characterization of the in situ process and the lack of appropriate diagnostic methods in a high turbulence, high temperature and high velocity environment, modeling at the droplet scale currently appears to be the only viable approach to studying the underlying physics.

Modeling of thermophysical processes that the precursor droplets undergo has been reported in the literature [13–16]. They include computation of droplet temperature and solute concentration distributions as droplets are heated in a high temperature gas jet whose properties (temperature and velocity distributions) are either experimentally or computationally determined. Modeling of solute precipitation characteristics has typically relied on the homonucleation hypothesis [19]. This hypothesis suggests that, whenever the surface concentration of the solute reaches a certain supersaturation limit, precipitation is triggered instantaneously and all parts of the droplet exceeding the equilibrium solute concentration are precipitated. While some shortcomings of such a hypothesis can be pointed out, it is presently adopted due to the lack of a better model for solute precipitation.

Early studies by Fuchs [20] and Ranz and Marshall [21] included analytical studies of diffusion and evaporation in droplets. Due to the limitations of these studies, such as constant droplet diameter during evaporation, more detailed solutions of droplet vaporization and the resulting solute concentration fields were obtained from numerical solutions and qualitative experiments [19,22]. Most of these studies only considered droplets vaporizing in a surrounding high temperature stagnant gas environment.
The more realistic modeling of droplets in a convective gas environment has been reported by our group for plasma and subsonic flame processing conditions [13–16]. Some of these models included effects of shear-induced internal flow recirculation within the droplet and its effects on precipitate morphology based on the homonucleation hypothesis. The modeling work also encompassed the internal pressurization experienced by the droplets after precipitation. These computations, carried out for aqueous solutions of zirconium acetate, have revealed thin shell-type morphologies for large droplets and solid particle morphologies for droplets smaller than 5 μm under rapid plasma heating conditions [13–16]. The computations also included predictions of other possible processes that lead to morphological changes through a series of parametric studies on the porosity, initial solute loading and droplet size [16]. Qualitative evidence of these morphologies was found in single pass sample collection experiments from both DC arc plasma and HVOF experiments.

In this article, we present a modeling study for HVOF flame jet processing of liquid precursor droplets. First, the computational results for the HVOF flame jet velocity, temperature and pressure fields, produced by a Metco Diamond Jet torch, are presented. This is followed by presentation of three droplet sub-models that account for the thermophysical processes in precursor droplets from their point of injection into the HVOF flame jet until they reach the substrate. These models account for the aerodynamic droplet break-up, vaporization and solute precipitation as well as internal pressurization of the formed precipitate shell formations.

2. Modeling an HVOF flame jet

The first part of the model simulates temperature and velocity fields of an HVOF flame jet. The full governing (Navier–Stokes) equations are solved for a hot jet issuing out of a round nozzle, including the compressibility effects [23]. In this study, an HVOF flame jet flow field was modeled as a turbulent hot jet originating from a 8 mm diameter nozzle at a velocity, temperature and pressure of 825 m s⁻¹, 3000 K and 2.5 atm., respectively, to match the typical HVOF jet nozzle exit conditions for propylene combustion in a METCO Diamond Jet HVOF torch. The turbulence intensity was taken as 2% at the exit of the nozzle. In the present study, Fluent 6.2.16 commercial software was used to solve the governing equations of the jet composed of the products of a stoichiometric mixture of oxygen and propylene issuing into the ambient from the nozzle exit at the operating pressure and mass flow rate. Oxypropylene combustion physics was not modeled; instead the oxypropylene combustion products were assumed to eject from the nozzle at its chemical equilibrium composition. A two-dimensional axisymmetric geometry was employed for the computational domain. A standard \( k-\varepsilon \) model was used for modeling the turbulence in the jet. Thermophysical properties, such as viscosity, thermal conductivity, specific heat and mass diffusivity, were computed at different temperatures and supplied as user-defined input functions to the model. The length of the computation domain was chosen to be \( L = 0.75 \) m, to include the long tail of a typical HVOF jet.
3. Droplet processes in the HVOF flame jet

The droplets after being injected axially or transversely into the HVOF flame jet undergo several processes. The first is the aerodynamic break-up as the slow moving droplets are entrained into the high velocity jet as they accelerate in the high velocity gas stream. Depending on their size and the thermophysical properties of the liquid and the surrounding gas, droplets can undergo severe deformation and eventually break up into smaller droplets. The time-scale associated with this process is of the order of microseconds. The droplet break-up process in the HVOF jet can be important for obtaining high-density deposits, as will be discussed later.

The second process is the droplet heating and surface evaporation in the hot HVOF jet stream, leading to loss of solvent and concentration of the solute in the droplet near its surface. As the solute concentration increases within the droplet, precipitation is triggered at some critical supersaturation value of solute concentration. Depending on the droplet size and the mass transport characteristics within the droplet, different precipitate morphologies can be obtained. Spherical shell or solid particle type morphologies are possible based on the evolution of solute concentration within droplets. While a homonucleation hypothesis allows prediction of the precipitation onset time and the resulting shell thickness, the precipitation model is at best a highly simplified approximation of a much more complex process.

Beyond the shell formation, the next process is the further heating of the precipitates in the HVOF flame jet before their impact on the substrate surface. In addition to the chemical transformation of the precipitate into ceramics, the thermophysical processes include vaporization of the liquid in the core for a shell-type precipitate, vapor venting from porous shell, pressure build-up within the shell and possible shell rupture. These processes are dependent on the porosity and thickness of the formed shell and the heating rate in the HVOF flame jet. While the porosity of the produced shells is largely an uncertain quantity, a distributed porosity range of up to 20% has been inferred based on the porosity of the final coating [24,25].

3.1. Initial stage of aerodynamic break-up

The first possible process encountered by a droplet injected into an HVOF flame jet is shear break-up. The droplets injected transversely or axially into the jet experience a highly varying velocity field, which gives rise to droplet surface instabilities, depending on the droplet size and thermophysical properties of the droplet liquid and the surrounding gas flow field, leading to deformation and break-up. The key factors influencing the droplet break-up are the relative velocity between the droplet and the surrounding gas flow, viscous damping and surface tension. Other effects, like surface evaporation, are usually considered to be negligible at the timescale of the droplet break-up process. A droplet injected with a nominal velocity of around 12 m s\(^{-1}\) undergoes distortion from its spherical shape as it encounters the high oscillatory velocity field of the HVOF flame jet. Viscous damping and surface tension are the forces responsible for restoring the droplet to its initial spherical shape. In general, viscous damping is much smaller than the surface tension and, as such, inertia and surface tension effects determine the droplet break-up behavior. The ratio of these two forces is the relevant non-dimensional parameter called the Weber number, defined as

\[
We = \frac{\rho_d \Delta u d^2}{\sigma}
\] (1)

The Weber number indicates the relative importance of inertia over surface tension. Values of \(We > 1\) signify an inertia dominated regime wherein a droplet is likely to deform and eventually break-up. However, all droplets having \(We > 1\) may not undergo break-up since the degree of surface distortion may not be sufficient for break-up. A review of the literature [26,27] suggests that one acceptable measure of the onset of droplet break-up is \(We = 14\). Any value greater than this critical Weber number signifies large deformations, which may lead to droplet break-up.

For modeling the droplet break-up, the Taylor analogy break-up (TAB) model [28] can be used. The model assumes that the droplets behave like an oscillating spring–mass system, with the external force being mimicked by the aerodynamic drag and restoring forces being represented by surface tension and viscosity. The equation for the oscillating droplet analogous to a spring–mass system is [29] written as

\[
F_{\text{inertia}} - F_{\text{ST}} - F_{\text{viscous}} = m_d \frac{dx}{dt} = m_d \frac{d^2x}{dt^2}
\] (2)

where

\[
F_{\text{inertia}} = C_F \frac{2 \rho_d \Delta u^2}{\rho_d d^2}; \quad F_{\text{ST}} = \frac{8 C_d \sigma}{\rho_d d^2}; \quad F_{\text{viscous}} = \frac{4 C_d \mu_d}{\rho_d d^2}
\] (3)

and all the quantities are defined in the nomenclature. \(C_F\), \(C_d\) and \(C_d\) are constants having values of 1/3, 8 and 5, respectively [30,31]. Break-up is assumed to occur when the distortion \(x\) is [29] \(x \geq 0.5d\). Solution of Eq. (2) requires knowledge of the HVOF velocity and temperature fields. More details about the TAB model can be found in Refs. [28,29,31].

The process of droplet break-up occurs on a timescale of the order of microseconds and, as such, droplet heating and vaporization are not considered in detail at this stage.

3.2. Droplet heat-up, vaporization and internal precipitation

The short timescale of the aerodynamic break-up process facilitates its separation from the heating and vaporization phase of the model. In this phase, droplets injected into the HVOF flame jet undergo rapid heating, which
vaporizes the solvent and increases the solute concentration near the droplet surface. As soon as the surface concentration of the solute reaches a preset value of a critical mass fraction (0.95 for zirconium acetate), precipitation is triggered, leading to the formation of a precipitate shell around the liquid core. This part of the model follows from our earlier work [13], which is simplified here for spherically symmetric concentration and temperature distributions within the droplet and thus does not account for the fore-to-aft variations due to internal flow recirculation within the droplet. The droplets are assumed to be composed of zirconium acetate (solute) dissolved in liquid water (solvent). Droplet motion in the hot convective gas environment is governed by the droplet momentum equation, given by [13]
\[
\frac{\partial U}{\partial t} = \frac{3C_D}{8r_s} \frac{\rho_s}{\rho_L} (U_\infty - U) (U_\infty - U) \quad (4)
\]
\[
\frac{\partial V}{\partial t} = \frac{3C_D}{8r_s} \frac{\rho_s}{\rho_L} V^2 \quad (5)
\]
where \( U, V \) are the droplet velocities in \( x \) and \( y \) directions, and \( C_D \) is the drag coefficient due to the relative motion between the droplet and the surrounding hot gases, with \( U_\infty \) being the calculated free stream flow velocity, i.e. the local flame jet velocity. The change in the droplet radius is given by [13]
\[
\frac{dr_s}{dt} = -\frac{m}{4\pi \rho_L r_s^2} \quad (6)
\]
where \( m \) is the mass rate of vaporization, \( \rho_L \) is the liquid density and \( r_s \) is the radius of the droplet. The drag coefficient, \( C_D \), is modified for the surface blowing effects. Under these assumptions, the conservation of solute mass and energy equations can be written in simplified form as
\[
L e_L r_s^2 \frac{\partial \tilde{y}}{\partial t} - 0.5L e_L \frac{\partial r_s}{\partial t} \frac{\eta}{\eta} \frac{\partial r_s}{\partial \eta} = \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial \tilde{y}}{\partial \eta} \right) \quad (7)
\]
\[
L e_L r_s^2 \frac{\partial T}{\partial t} - 0.5 \frac{dr_s}{dt} \frac{\eta}{\eta} \frac{\partial T}{\partial \eta} = \frac{1}{\eta} \frac{\partial}{\partial \eta} \left( \eta \frac{\partial T}{\partial \eta} \right) \quad (8)
\]
where the following dimensionless quantities are employed,
\( \tilde{x} = r/r_s, \quad \tau = \frac{a_L T}{r_s^2}, \quad \eta = r/r_s, \quad \lambda = \frac{(\tilde{x} - \tilde{x}_0)}{\tilde{x}_0}, \quad \bar{T} = \frac{(T - T_0)}{T_0}, \) where \( r_0 \) is the initial radius, \( a_L \) is the liquid thermal diffusivity, \( t \) is time, \( r_s \) is the droplet radius and \( T \) is temperature, with \( T_0 \) being the initial value and correspondingly \( \tilde{x} \) being the solute mass fraction, with \( \tilde{x}_0 \) being its initial value. \( L e_L \) is the liquid phase Lewis number. The initial and boundary conditions within the droplet can be written as
\[
\begin{cases}
\tilde{x} = 0 & \text{and} & \frac{\partial}{\partial \eta} \tilde{x} \bigg|_{\eta=0} = 0 \\
\frac{\partial}{\partial \eta} \tilde{T} \bigg|_{\eta=1} = \frac{2\nu_m}{2\nu_m + D_x,0} \tilde{T} \bigg|_{\eta=0}
\end{cases}
\]
where \( \tilde{Q}_L \) is the heat flux to the droplet, \( k_L \) is the liquid conductivity, \( \rho_L \) is liquid density and \( D_x \) is the mass diffusivity of solute in solvent.

### 3.3. Internal vaporization and pressurization

The model described in the previous section predicts the heating and vaporization of the droplet until encapsulation of the droplet by a precipitate shell. Beyond this point, the droplet encapsulated by the precipitate shell continues to heat in the HVOF flame, forming a vapor annulus around the liquid core within the shell. This trapped vapor pressurizes the shell, which may lead to shell shattering. Subsequent to shell formation, further heating of the particle containing a liquid core is modeled as follows. The motion of the droplet is governed by Eqs. (5) and (6). However, droplet surface vaporization has ceased at this stage, and internal vaporization will lead to formation of vapor annulus around the liquid core. If the shell formed is porous, differential pressure gradient across the shell allows vapor formed from the liquid core to escape to the surroundings through these pores, creating a venting effect. The shell porosity is a parameter that depends on the morphology of the precipitate shell, and cannot be predicted. In this context, a parametric variation of porosity based on the final porosity of the resulting microstructure [24,25] is employed to identify the possible outcomes upon further heating in the HVOF flame jet. In this part of the model, the droplet is divided into three zones of a shrinking liquid core, a vapor annulus and a porous precipitate shell, as schematically shown in Fig. 2. For each of these regions, energy equation is the same as Eq. (9), with a moving boundary between the liquid and the vapor. The enthalpy carried away by the vapor escaping through the porous shell is also taken into consideration in this analysis. Depending on the shell porosity range [24], there may or may not be any venting effect. The vapor pressure rise within the shell is governed by [16]
\[
\frac{dp}{dr} = \frac{RT_v}{V_v} \left[ 4\pi r_1^2 \rho_v \frac{dr_1}{dr} - 4\pi r_1^2 \rho_l \frac{dr_1}{dr} - \rho_v A_{\text{pore}} V_{\text{pore}} \right]
\]

where \( V_{\text{pore}} \) is the velocity of the gas venting through the pores of the shell estimated from Karman–Cozeny equation, while \( A_{\text{pore}} \) is the total area of the pores. \( \rho_v \) and \( \rho_l \) denote the densities of the vapor and liquid phase, respectively, while \( r_1 \) is the radius of the liquid core. Internal pressurization of the shell is primarily responsible for shell fracture or inflation, depending on the morphology of the precipitate and the chemistry of the concerned binary system. It is difficult to prescribe the failure stress of a porous precipitate shell because of the lack of data in the literature. However, it is expected that the sharp internal pressurization will lead to shell fracture within microseconds of the formation of the shell.

4. Results and discussion

The results are first presented for the flow field of the HVOF jet that was simulated as described in the previous sections. Fig. 3 shows the temperature, velocity and static pressure profiles along the jet centerline. It is seen that the profiles exhibit spatial oscillations about their mean values in the potential core of the jet. However, farther downstream, the static pressure becomes constant at a nominal value of 1 atm. (or \( P/P_{\text{exit}} = 0.4 \)), while the temperature and the velocity show the characteristic decay in a jet. These profiles are quite different from plasma, where the temperature decay rate is steeper and the potential core is smaller.

In the following sections, we first present the droplet break-up results based on the TAB model described earlier. This is followed by results from droplets undergoing vaporization, precipitation, shell formation and possible disintegration due to internal pressurization. The guidelines obtained from this modeling effort are then discussed in the context of obtaining different types of deposit morphologies. The numerical method used has a truncation error of order \( O[(\Delta t)^2, (\Delta r)^2, (\Delta t/\Delta r)^2] \). For the employed time and spatial resolutions of \( \Delta t = 1 \times 10^{-10} \text{s} \) and \( \Delta r = 0.227-0.9 \times 10^{-6} \text{m} \), the incurred discretization error is much less than the typical uncertainties encountered in thermophysical properties and other model inputs (\( \leq 0.5\% \)).

4.1. Aerodynamic break-up results for axial injection

In the case of axial injection, droplets are injected into the HVOF flame jet at a velocity of 12 m s\(^{-1}\) along the nozzle axis. The initial droplet temperature was assumed to be 300 K. Fig. 4 shows the droplet diameter distribution with a downstream axial distance for an initial droplet diameter of 5 \( \mu m \). It is found that the droplets injected into the HVOF jet undergo vigorous shear break-up due to the extremely high relative velocity they experience upon injection. It is seen clearly that a 5 \( \mu m \) droplet which is normally stable to shear break-up in the DC arc plasma flow field breaks up in this high velocity jet. The resulting droplets range in diameter from 0.5 to 1 \( \mu m \), which are stable with respect to shear instability. Similar results were obtained for a 30 \( \mu m \) diameter droplet, which experiences break-up into small 0.5–2 \( \mu m \) diameter droplets.

The timescale of droplet break-up is typically microseconds, which is almost instantaneous compared to the timescale of vaporization up to the point of precipitation onset. These findings are consistent with our earlier estimates of droplet break-up in a plasma jet and the limiting Weber numbers for break-up. For example, the 5 \( \mu m \) diameter droplet with a surface tension value of 0.06 has an estimated Weber number of 33, which is significantly greater than the critical value of 14 suggested in the literature [27]. On the other hand, the maximum Weber number for a 1 \( \mu m \) diameter droplet is around 7 and hence the droplet is not expected to break up in the HVOF jet based on the limiting Weber number criterion. Based on the presented results from the TAB model and the Weber number regimes, it appears that droplets larger than 1 \( \mu m \) diameter will experience break-up upon injection into the HVOF jet. The aerodynamic simulations also show that the presence of shock diamonds promotes the break-up process. This

![Fig. 3. Centerline velocity, temperature and static pressure profiles of the HVOF jet.](image1)

![Fig. 4. Diameter distribution of 5 \( \mu m \) axially injected droplets after shear break-up.](image2)
is because the axial velocity undergoes rapid change across a shock diamond.

4.2. Aerodynamic break-up results for transverse injection

In this external injection scheme, the droplets are injected radially inward at some distance downstream from the nozzle exit. This type of injection mimics the external injection typically employed in DC arc plasmas or in situations where internal injection is not feasible. In the present case, droplets were injected at 12 m s\(^{-1}\) and 300 K at 8 mm downstream of the nozzle exit and 12 mm away from the nozzle centerline. These droplets initially pass through the cooler, lower velocity edges of the HVOF jet and, due to the axial offset of 8 mm, they do not experience as high a relative velocity as that encountered in the axial injection case. Fig. 5 shows the diameter distribution of 30 µm droplets injected into the HVOF jet as a function of axial distance. It should be noted that, since the droplet traverses some distance vertically towards the HVOF jet axis, the axial distance traversed is small initially, but slowly increases as the droplet is axially accelerated by the HVOF jet. It is seen in Fig. 5 that the 30 µm droplets injected transversely into the HVOF jet undergo break-up resulting in a range of droplet sizes from 2 to 15 µm. The 30 µm droplets, which normally do not break up in plasma, may do so in the HVOF jet.

It is inferred from both axial and radial injection simulations that a significant reduction in droplet diameter occurs as a result of droplet break-up due to the high relative velocities experienced by the droplets in an HVOF jet. However, it must be noted that these results are only valid for a single stream of uniform diameter droplets injected axially or transversely into the HVOF jet. In practice, droplets are injected in a spray cone with a wide range of droplet sizes. This, coupled with the velocity oscillations of the unsteady HVOF jet, may produce droplets anywhere from submicrons to tens of microns in diameter. The larger droplets may be driven towards the low velocity jet periphery due to the fluctuations of jet velocity field and may not undergo aerodynamic break-up. Also some population of the larger droplets may not be broken up as efficiently as others, leading to presence of larger droplets tens of microns in size.

4.3. Results on precipitate formation

From the aerodynamic droplet break-up analysis, the average droplet diameter ranges between 0.5 and 5 µm for the injection methodologies studied here. However, some larger droplets are still present in HVOF spraying. Smaller droplets (<5 µm) normally result in dense coatings, but it is the small percentage of larger droplets and their heat and mass transport characteristics that may significantly influence the coating quality in terms of microstructure and density. Furthermore, Phase Doppler Anemometry measurements of droplet sizes suggest the presence of larger droplets (as large as 20 µm) which contribute a significant portion of the injected droplet volume fraction. For parametric studies, droplets of three different initial diameters (5, 10 and 20 µm) were studied for the thermophysical transformations in the HVOF field. The behavior of droplets smaller than 5 µm were found to be similar in that they undergo uniform increase in solute concentration and ultimately produce solid particles upon precipitation.

Droplets injected into the HVOF jet are heated by the convective flow field, resulting in rapid vaporization of the solvent. Vaporization increases the concentration of the dissolved solute near the droplet surface and decreases the droplet radius. Precipitation is modeled based on the homonuclear precipitation hypothesis. In the case of zirconium acetate precursor, the critical supersaturation mass fraction is taken as 0.95 based on the values available in the literature [22]. The shell thickness formed around the liquid core is calculated based on the equilibrium saturation mass fraction of zirconium acetate in water of 0.56. All parts of the droplet exceeding this equilibrium value are assumed to precipitate when the critical supersaturation level is achieved at the droplet surface. Fig. 6 shows the variation of temperature and solute mass fraction in a 5 µm diameter droplet injected axially into the HVOF flame jet with an initial solute mass fraction of 0.2. The temperature varies by only 0.5 K within the droplet, with the highest temperature of 355 K being at the droplet surface. The solute concentration shows a steeper gradient due to the low mass diffusivity of the solute compared to its thermal diffusivity. The solute mass fraction is lowest near the droplet center and increases to 0.95 at the droplet surface. However, at the time of precipitation, the equilibrium concentration of 0.56 is exceeded everywhere in the droplet. The entire precipitation process takes about 0.5 ms, which is slower than in the plasma, where the precipitation time for same size droplets is 0.37 ms. Similar profiles were obtained for a 10 µm diameter droplet with an initial solute mass fraction of 0.2 (not shown). When compared with the 5 µm droplet, it was found that the precipitation of a thick
shell (about 3 μm) is expected in this case. Fig. 7 shows the temperature and solute concentration distribution inside a 20 μm diameter droplet. It is found that the solute mass fraction profile exhibits a sharp gradient near the surface, although the temperature varies little inside the droplet. In fact, the solute concentration remains at its initial value in the core of the droplet, indicating that mass diffusion into the droplet core takes significantly longer. The shells formed around these large droplets are thin, with a predicted thickness of about 0.6 μm.

The results shown in Figs. 6 and 7 suggest that the smaller droplets tend to form solid precipitates while the larger ones form shell-type morphologies. Since axial droplet injection into the HVOF flame jet results in aerodynamic break-up and production of droplets smaller than 5 μm in diameter, HVOF processed droplets are more likely to form smaller solid particle morphologies as compared to plasma jet injection. Lower temperatures of the HVOF jet facilitate slower vaporization and consequently more time for mass diffusion resulting in more uniform solute concentration profiles inside droplets. As demonstrated in our previous studies [13–16], smaller droplet size, longer precipitation time, high solute diffusivity and less difference between the equilibrium and critical supersaturation limits favor precipitation of solid particles.

In the context of solute precipitation, it is also pertinent to explore the effect of higher initial solute loadings on the precipitation characteristics of a droplet. The 5 μm initial diameter droplet was found to undergo volume precipitation for the initial solute mass fraction of 0.2. For this reason, simulation of higher solute loading was only considered for larger droplets. Fig. 8 shows the temperature and solute mass fraction profiles for a 10 μm droplet for initial solute loadings of 0.2 and 0.4. It is seen that the droplet with a higher solute loading of 0.4 reaches the supersaturation concentration in 1.0 ms, which is faster than a droplet with a solute loading of 0.2 precipitating in about 1.5 ms. Similar results were found for a 20 μm droplet as well, with precipitation times of 1.85 and 1.23 ms for initial solute loadings of 0.2 and 0.4, respectively. The temperature rise for a 20 μm droplet with an initial solute mass fraction of 0.2 is 5 K higher than a droplet with an initial mass fraction of 0.4. Usually, in all droplets, the higher initial solute concentration leads to faster precipitation, but the shorter heating time does not allow the temperature to rise as much. The solute concentration profiles are similar, although the droplets with a solute mass fraction of 0.2 exhibit a steeper concentration gradient near the droplet surface. However, the processed droplets develop similar shell thicknesses irrespective of the initial solute loading. This is because irrespective of mass diffusion, for a large droplet it still takes much longer to dissipate the steep concentration gradients near the droplet surface even though a higher initial solute loading tends to favor volume precipitation.
4.4. Internal pressurization of precipitates

The modeling of droplet vaporization and precipitation presented above suggests that 5 μm droplets precipitate into solid particles while larger droplets form precipitate shells. The post-precipitation processes upon continual heating in the HVOF jet is presented below for 10 and 20 μm diameter droplets. The results from the precipitation model are provided as inputs into the thermal model to predict internal pressurization. The HVOF velocity and temperature fields are sampled as the particle continues along its trajectory to calculate the heat transfer into the particle. Here, the post-precipitation study is different from the plasma in that the high velocity of the HVOF jet and the longer precipitation timescale takes the droplet to the colder region of the HVOF jet. In the plasma, the droplets still experience intense heating due to the comparatively lower velocity and higher temperature of the jet. The reduced heating rate of the precipitates in the HVOF jet implies a longer time for the internal pressure rise as well as the lower temperature rise of the shell. Fig. 9 shows the internal pressure rise for 10 and 20 μm droplets after precipitation for two levels of porosity. As expected, the internal pressure rise is fastest for the impervious shell since the shell does not allow the escape of vapor formed within it. An initial rapid pressure rise occurs due to formation of the vapor layer between the liquid core and the shell. This is followed by a continuous rise of pressure due to vaporization within the shell. The rate of pressure rise in a shell with 20% porosity is significantly reduced compared to an impervious shell due to venting of the formed vapor from the shell. Similar results are seen for a 20 μm droplet. In all cases, the internal pressure rise occurs over a period of microseconds as compared to the timescale of precipitate formation of milliseconds, indicating time separation of three orders of magnitude between the two processes. Once the precipitate shell forms, the subsequent internal pressurization is almost instantaneous. Rupture of the precipitate shell may occur as a result of this internal pressurization, depending on the fracture strength of the precipitate shell and the developed internal pressures.

5. Concluding remarks

A detailed modeling and analysis of liquid ceramic precursor droplets processed in an HVOF flame jet has been presented in this article. The presented model includes the processes of aerodynamic break-up, vaporization and solute precipitation, as well as internal pressurization of the formed precipitate shell. It is predicted that droplets injected into an HVOF flame jet experience vigorous shear break-up and produce smaller droplets. The smaller droplet sizes ensure superior entrainment and rapid heating, resulting in solid particles. Large droplets experience surface precipitation, to form shells with a liquid core. Depending on the porosity of the formed precipitate shell, precipitates may undergo internal pressurization and secondary break-up of the liquid inside. It is found that the lower temperatures of the HVOF jet compared to those in a DC arc plasma allows slower vaporization of the droplets, allowing for longer solute diffusion times prior to precipitation. This leads to more uniform solute concentration profiles within the droplets and promotes solid particle and thick shell morphologies. The implications of HVOF processing of atomized liquid precursors is the possibility of forming dense coatings as a result of (i) the higher likelihood of solid particle morphologies and (ii) the high impact velocities in an HVOF jet.

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