Morphology of ceramic particulates formed in a premixed oxygen/acetylene flame from liquid precursor droplets

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Abstract

This study concerns high temperature flame synthesis of ceramic deposits utilizing a mono-disperse stream of droplets composed of an aqueous precursor. The droplets were injected into an oxy-acetylene flame. Mono-disperse droplets were generated with an electrostatic spray technique. High-speed droplet images suggest evidence of shedding of small particulates from the droplet surface as they enter the flame. Flame temperatures were measured by a spectroscopic technique utilizing chemiluminescence from the $Q_1$ branch of hydroxyl (OH) radical $\Delta^2 \Sigma^+ \rightarrow \chi^2 \Pi(0,0)$ rotational band. Scanning electron microscopic analysis of the extracted samples was performed to identify the types of deposits. The thermophoretically obtained samples show a morphology transition at flame equivalence ratios between 1.1 and 1.5. Large droplets in cooler flames impact onto the substrate as gelated material or liquid, whereas, smaller droplets traversing higher temperatures yield sintered poly-crystalline particulates. Raman analysis of multi-pass deposits indicates presence of tetragonal phase of the yttria-stabilized zirconia.

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1. Introduction

Hardware components used in the power generation industry and similar fields, such as gas turbine blades, combustor liners, etc., operate under elevated temperatures and harsh environment for metallic components. These components are protected against high temperatures and high heat fluxes by applying thermal barrier coatings (TBCs) on the surfaces exposed to these harsh conditions. The service life of TBCs often depends on the thermal cycling conditions that these coatings are subjected to. Presence of a mismatch between the thermal expansion coefficient of the coating and the substrate often causes premature failure of the coating. Some of the important properties of a good TBC are, then, low thermal conductivity, good thermal expansion characteristics and high spallation resistance.

Conventional ceramic TBCs are usually applied by spraying a powder of ceramic material into a plasma jet, where the powder particles are melted and accelerated toward the substrate. This process has been used extensively in industry and matured over the years [1,2]. Persisting demand for coatings with better properties has generated significant interest in nano-structured ceramic coatings. The nano-structured coatings have been shown to have superior properties and such coatings have been successfully produced by using modified nano-structured ceramic powder in the conventional air-plasma spray process [3,4]. While these efforts have yielded quite promising results, there are certain difficulties inherent to coating of the nano-structured powder [4]. First of all, as the powder particles are entrained into a plasma or a high temperature jet, depending on the local temperature field, they may undergo melting.
Without melting, powder particles are not well bonded in the coating. On the other hand, molten ceramic particles lose their nano-structure content, and thus do not contribute to superior properties of its coating. Second, splat boundaries present in the coating are detrimental to the service life of the coating. Interpass boundaries that result from the individual splats form surfaces which are not resistant to fracture in the coating and decrease the damage threshold of the coating. In order to obtain a good coating structure, one has to carefully adjust the processing parameters so that partial melting is obtained and a good bonding between the ceramic material and substrate is formed without compromising the nano-structure. In order to eliminate the deficiencies of the described process, a new method of coating generation has been pioneered by the materials research group at the University of Connecticut and the Inframat Corporation.

This new method utilizes liquid precursors sprayed into a DC-arc plasma jet to obtain ceramic coatings. Generation of ceramic particulates using liquid precursor solutions has been extensively employed in spray pyrolysis field in the past. The literature on this process has been reviewed by Messing et al. [5] and extensive work has been undertaken by researchers [6,7]. Using the spray pyrolysis technique, different particle morphologies can be obtained (such as solid or hollow spheres) depending on the initial size of the droplets, temperature and velocity of the high temperature jet and the chemical composition of the droplets. This technique can produce powders as small as tens of nanometers in size [5]. While powders produced by the spray pyrolysis process have been used in conventional plasma spray processes, the process described above which we refer to as solution precursor plasma spray (SPPS) process generates coatings [8,9].

Solution precursor plasma spray process is similar to the conventional thermal spray process in the hardware setup of the plasma jet except that the powder feed system used in the conventional thermal spray is replaced by a pressure atomizer for the atomization of the precursor which is an aqueous solution of zirconium acetate, yttrium nitride with some additives. This process simplifies the conventional plasma spray process in that powder handling is completely removed. The process relies on the chemical transformations of the solutes in the solution and subsequent deposition process, and thus, the coatings generated by this technique are devoid of any splat boundaries that exist in the conventional thermal spray deposits. Initial studies of the SPPS process showed that the yttria-stabilized zirconia TBCs contain vertical cracks for strain tolerance, have lower thermal conductivity at high temperatures and better thermal cyclic life when compared to the conventional coatings of the same material system [8]. These superior characteristics of the SPPS coatings combined with the potential advantages (such as circumvention of costly powder preparation step in the conventional spray process, ability to spray compositionally graded as well as multi-layered microstructures with ease) have generated interest in studying the particle formation and deposition mechanisms associated with this process.

Schematics of the SPPS process setup is shown in Fig. 1, where liquid precursor is atomized into the plasma with the aid of pressurized nitrogen gas to obtain 20–100 μm droplets. These droplets injected into the plasma jet undergo subsequent vaporization, precipitation and decomposition which ultimately results in a composition of 93 wt% zirconia and 7 wt% yttria (7YSZ) in the coatings. The characterization of this process is made difficult due to the very high temperature, luminous plasma environment as well as dispersion of the liquid
Fig. 2. A typical image taken during the actual process by illuminating the spray plume and the plasma by a pulsed Nd-YAG laser, using a 532 nm bandpass filter centered at laser wavelength and gating to 50 ns exposure by a microchannel plate.

Fig. 3. Schematics of the designed model experiment.
spray in the plasma as depicted in Fig. 2. This image taken by Mie scattering from the spray indicates that only a cloud of droplets can be observed, which would be virtually impossible to analyze due to the complex nature of the process. Hence, the study presented here was conducted in the spirit of studying a simpler process configuration wherein a monodisperse stream of precursor droplets are injected to a high temperature combustion jet as shown schematically in Fig. 3.

The main objective of this study is to experimentally determine the morphologies of the particles formed in the high temperature flame environment and characterize them as a function of temperature of the gas medium as well as the residence time (location) in the flame. To this end, experiments were performed to (i) image the droplet motion in the flame, and, (ii) extract samples from an oxygen–acetylene premixed flame that were subsequently investigated using the scanning electron microscope (SEM) and Raman spectroscopy.

The oxygen/acetylene flame that replaced the plasma flame in this study is measured to have peak flame temperatures of about 4500 K. Actual peak temperatures at the core of the argon–hydrogen plasma have been measured to be in the order of 10,000 K [10]. However, modeling of droplets injected transversely into the plasma indicate that the plasma temperatures to which the droplets are exposed are significantly lower than this peak temperature and remain typically below 3000 K due to the aerodynamic deflection of droplets away from the plasma core [11]. Therefore, the oxygen–acetylene flame was considered as a viable alternative to plasma jet in these experiments.

2. Experimental systems

The oxygen–acetylene flame used in the experimental setup is obtained by using a standard oxy-acetylene cutting torch assembly (Victor Firepower, 250-510-DS DLX). The torch nozzle is positioned horizontally on a rigid mount and the commercially available assembly is modified with the introduction of two mass flow controllers (Porter Instruments, Models 201-DKASVCAA and 251-DKASVCAA) to control the gas flow rates precisely. Flow rates of the oxygen and acetylene are controlled to obtain flames with different stoichiometries and consequently different peak flame temperatures. The flow rate of the oxygen was set at a constant value of 0.116 L/s while the acetylene flow rate was varied between 0.8 and 1.5. Here, \( m_0 \) is the oxygen mass flowrate, \( m_f \) is the acetylene mass flowrate and subscript “st” refers to the stoichiometric value, \( \frac{m_f}{m_0} \) at = 0.325.

The liquid feedstock is introduced into the hot flame environment in the transverse direction similar to the actual process as shown in Fig. 3. The liquid feedstock is pumped into a stainless steel capillary nozzle which has an internal diameter of 102μm utilizing a syringe pump. The syringe pump provides flow rates between 0.278 and 2.78 μL/s. The liquid nozzle also serves as the positive electrode of the electrospray setup. The negative electrode is a thin copper plate with a 9.5 mm diameter circular hole whose center is aligned with the nozzle, so that the generated droplets can pass through. Upon application of an electric potential difference between the two electrodes, mono-sized droplets are generated. Electrostatic generation of droplets involves application of a strong electric field around an electrically conductive liquid stream that is deformed into the Taylor cone as it leaves the nozzle exit. Depending on the strength of the electric field, electrical properties of the liquid, liquid flow rates and the electrode configuration, different droplet generation modes are obtained. In this case, when the potential difference is set to 6 kV, droplets are obtained in the so-called drop mode. The liquid flow rates in this mode varied between 1.39 and 2.78 μL/s. When the applied voltage was increased to 11 kV, droplet generation changed into a variant of the cone-jet mode. The liquid feed rate was typically reduced to a value between 0.833 and 1.39 μL/s in order to stabilize the droplet stream. In this mode, carbon dioxide co-flow is introduced to overcome the corona discharge through the ambient air, the details of which are discussed in the literature [12,13]. A more common mode is the cone jet mode that produces a conical spray of very small droplets. This mode was not employed in this study.

The electrospray setup is mounted on a two-axis micrometer stage that allows fine-tuning of the droplet stream-flame alignment so that the droplets traverse into the centerline of the flame. Insofar as to achieve the imaging of the droplets in the flame, an Argon-ion laser (Coherent, Innova 90-6) was used. The laser beam was formed into a light sheet using cylindrical lenses and this light sheet was positioned on the centerline of the flame jet and the droplet generator. A high speed camera (Redlake, Model PCI 8000S) was used in conjunction with a long distance microscope lens (Questar, QM100). As the process was initiated, high speed movies were recorded at 2000 frames per second rate with a shutter speed of 1/4000 s and they were digitally stored on a computer.

Formation of zirconia in the droplets is highly affected by the flame temperature to which the droplets are exposed. Higher temperatures would result in a higher degree of pyrolyzation and therefore, in this analysis characterization of the temperature field in the flame was deemed essential. One method to relate the flame stoichiometry to the temperature is to calculate the adiabatic flame temperature for a given fuel-oxidant composition. Calculations using the STANJIAN Chemical Equilibrium Code [14] indicate that flame temperatures vary in the range of 4250–5500 K for equivalence ratios.
from 0.8 to 1.5, which can be attained experimentally by changing the acetylene flow rate. However, these are theoretical temperatures and they do not necessarily reflect the actual temperatures in the experiments due to heat losses through radiation and/or incomplete combustion. Therefore, an experimental measurement of the flame temperatures was performed.

Among different measurement techniques, spectroscopic measurement of the temperature is most suitable since it is non-intrusive and high temperatures in the flame can be measured with such a technique. For example, thermocouple probes would not survive at the high temperatures of oxy-acetylene flame. In this study, temperatures were measured using the chemiluminescence from the OH radical naturally present in the flame by analyzing several emission lines from the $Q_1$ branch of the $A^2\Sigma^+ \rightarrow X^2\Pi(0,0)$ rotational transition band [15]. Here, one should note that only the rotational transitions of the OH radical is considered. Vibrational and electronic transitions are not significant at the flame conditions and the rotational temperature is close to the actual flame temperature for the atmospheric-pressure flames of oxygen and acetylene [16].

Theory of the spectroscopic temperature measurement relies on the intensity of the several emission lines. The intensity of a spectral emission line of a rotational transition for a molecular species that occurs for a particular transition ($j \rightarrow j'$) is given as

$$I_{jj'} = \frac{A_{jj'} S_{jj'} k^4}{\lambda_{jj'}^4} e^{-E_j/kT}.$$  

(1)

In this equation, $I_{jj'}$ is the intensity of the wavelength under consideration, $\lambda_{jj'}$ is the wavelength of emitted light, $S_{jj'}$ is the HönL–London coefficient, $E_j$ is the transition energy and $k$ is the Boltzmann constant. The constant, $A$, on the right side of this equation does not have an effect on the rotational temperature. A plot of $\ln \left( \frac{I_{jj'}}{S_{jj'}} \right)$ as a function of $E_j / T$ would yield a linear relationship and the slope would be $-1/T$. This plot is usually referred to as Boltzmann plot. Wavelength, $\lambda_{jj'}$, HönL–London coefficient, $S_{jj'}$, and transition energy, $E_j$, are available in the literature and values for several $Q_1$ branch transitions are tabulated in Table 1 [16].

Characterization of the flame temperature field was performed by the experimental setup depicted in Fig. 4. Using a 0.5 m focal length imaging spectrometer (Acton Research, SpectraPro 500i), spectral images of the flame were taken and data were collected at different downstream locations to obtain the temperature field. Spectral resolution was $\Delta \lambda = 0.03$ nm with 1800 gr/mm grating and 30 µm slit size. Since emission intensities are collected as line-of-sight integrated quantities, the local radial variations of the intensities were first obtained by Abel's inversion [17]. Abel inverted spectral line intensities were then used in constructing the Boltzmann plots for temperature determination.

Sampling of the droplets and/or particulates was accomplished using a pneumatic sampler, driven by a double-acting solenoid valve which was controlled by an electronic delay generator. The electric pulse generated by the delay generator enabled insertion of the substrates into the flame with a residence time of 100 ms during which samples were collected onto small copper substrates (32 mm $\times$ 25.4 mm $\times$ 1.6 mm). The samples were obtained with two different techniques. First one was the impact sampling technique in which the substrate was inserted perpendicular to the flow. In this mode, droplets and/or particulates impacted onto the

Table 1

<table>
<thead>
<tr>
<th>$Q_1$</th>
<th>$\lambda$ (nm)</th>
<th>$E_j$ (cm$^{-1}$)</th>
<th>$S_{jj'}$</th>
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<td>32779.49</td>
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<td>(15)</td>
<td>312.057</td>
<td>36396.66</td>
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substrate as they were convected in the flame. These samples were collected at 3 and 8 cm downstream of the flame nozzle. In the other sampling mode, the substrate was inserted parallel to the flame axis. As such, the droplets and smaller particulates were attracted towards the substrate by a combination of thermophoretic and electrostatic attraction as well as the turbulent convection, resulting in a more gentle collection scheme. Samples were extracted at 3 cm downstream of the flame nozzle using this technique. Collected samples were then analyzed using the environmental scanning electron microscope (Philips Electron Inc 2020 ESEM).

3. Results and discussion

In this section, the experimental results are presented and discussed. First, the droplets injected into the flame are imaged to determine their sizes and trajectories. Second, the temperature field of the flame is characterized by emission spectroscopy to determine the thermal environment the droplets traverse. Third, the results obtained from the SEM images of droplets and/or particulates are presented and discussed.

3.1. Droplet size measurements and trajectories

While the electrostatic spray apparatus was operated in the drip mode, high speed images were taken in order to determine the size of the droplets. A typical image of a droplet ejected from the liquid nozzle is shown in Fig. 5. The image was taken with the Questar long distance microscope coupled with the high speed camera. Size of the generated droplets is consistently 100 μm in this mode and they are initially ejected at a velocity of 0.18 m/s. These droplets were not only accelerated by gravity, but also due to the charge they carry. The electrostatic forces between the droplet and the ground

Fig. 5. Two consecutive images of the droplet generated by the electrostatic spray in the drip mode. The nozzle location is aligned with the bottom edge of the image. The droplet movement direction is upwards.

Fig. 6. Images of two droplets generated by the electrostatic spray in the variant of the cone-jet mode. Nozzle location is aligned with the bottom edge of the image. Notice that the droplets move from the bottom of the image to the top. Droplet in (a) is about 50 μm, whereas in (b) droplet size is 25 μm. Also a cloud of very fine droplets is apparent in both images.
electrode enables the droplets to reach velocities of 1.5–1.8 m/s as they enter into the flame.

Fig. 6 shows images of two typical droplets for the variant cone-jet mode operation of the electrospray. Of these two droplets, in Fig. 6(a), 50 μm droplet is ejected from the nozzle, whereas, the droplet in Fig. 6(b) is 25 μm in size and moves somewhat diagonally. That diagonal movement is due to the charge repulsion of droplets. It is found that the sizes of the droplets in this mode were not as consistent as those in the drip mode but they typically varied from 25 to 60 μm. Also, presence of a cloud of much finer droplets is evident in these images around the larger droplets.

In Fig. 7, a combined image of droplet trajectory is given. This image was obtained by superimposing multiple frames in the recorded movie. The camera was shifted in steps to downstream positions to track the droplet trajectory since the field of view of the camera was not sufficiently large for the whole field of view. The solid curved line in the figure is the position of the flame core that is not visible in this image. The hot gas jet extends beyond the indicated flame core and the droplets traverse the flame core and stay in the hot

Fig. 9. Boltzmann plots of the sample cases showing 3318, 3609 and 3909 K temperatures.
gas region as observed by the orange glow of the formed particulates in the flame.

An interesting observation was made when the high speed movies were analyzed without the spectral filter for the Argon-ion laser wavelength. The images shown in Fig. 8 suggest that as the droplets are entrained into the hot flame core, a luminous plume is shed off. This plume emanates from the droplet as it is seen clearly in the third picture of the series. This indicates that the process may contain some heterogeneous precipitates that are accompanied by shedding of particles off the droplet surface. The evidence of the orange glow in the plasma jet also suggests that a similar behavior is observed in the actual SPPS process.

3.2. Spectroscopic temperature measurements

The spectroscopic measurement setup was arranged to collect spectral distributions of the emitted light for various flame equivalence ratios and at different downstream locations. The collected data contain information on the spectral distribution as well as the radial distribution of the intensities. The recorded intensity distributions are in the form of line-of-sight integrated intensities. These intensities were first deconvoluted in order to get the localized radial distributions. Two different techniques, two-point Abel’s inversion and “onion-peeling”, were employed and compared in order to confirm the validity of the deconvolution, details of which are described in the literature [17]. It was seen that the two-point Abel’s inversion and the onion-peeling version, produced almost identical results.

The deconvoluted intensities were then processed and plotted in Boltzmann plots. Three example cases are given in Fig. 9. It is seen that the data points at given transitions fit well into Boltzmann plots without much scatter from which the temperature can be determined unambiguously. The uncertainty associated with these measurements was determined to be around 25 K. The measured temperature fields are shown in Fig. 10 for three different equivalence ratios of the flame. It is seen that the temperatures for $\phi = 1.1$ case, which is the closest to the stoichiometric composition result in the highest temperatures. The highest temperatures are observed at the centerline of the flame, however, there is a small

![Fig. 10. Temperature distributions in the flame for (a) $\phi = 0.8$, (b) $\phi = 1.1$, and (c) $\phi = 1.5$. The axial direction of the flame is denoted by 'x' and radial direction is denoted by 'r' (see Fig. 3).](image)

![Fig. 11. Temperature distributions along the centerline of the flame nozzle. Temperatures of the lean flame ($\phi = 0.8$) are significantly lower than the $\phi = 1.1$ case, especially further downstream of the flame.](image)
high temperature region close to the flame nozzle exit at about 1–2 mm in the radial direction. This is due to the remnants of one of the flamelets emanating from the torch assembly. Centerline temperatures indicate that the equivalence ratio which is closest to the stoichiometric composition ($\phi = 1.1$) has the highest temperatures and the lean mixture ($\phi = 0.8$) has the lowest temperatures as depicted in Fig. 11. As the droplets travel further downstream, the temperatures are significantly lower in $\phi = 0.8$ case than the flame temperatures of the other two cases, which is also consistent with the shortened flame length for this case.

![ESEM images of the droplet "foot-print"s from impact samples for: (a) $\phi = 0.8$, (b) $\phi = 1.1$ and (c) $\phi = 1.5$ at 3 cm downstream of the flame nozzle; and, (d) $\phi = 0.8$, (e) $\phi = 1.1$ and (f) $\phi = 1.5$ at 8 cm downstream of the flame nozzle. These samples were collected in the drip mode operation of the electrospray.](image-url)
3.3. Sampling results

The variation of the flame equivalence ratio was employed to study changes in the overall temperature levels in the combustion jet. The effect of the temperature changes on the morphology of the flame synthesized particles was studied subsequently. While the flame temperature was varied, sampling of the droplets generated by two modes of the electrospray were attained by impact sampling technique at 3 and 8 cm downstream of the flame nozzle, and by thermophoretic sampling technique at 3 cm downstream of the flame nozzle.

3.3.1. Drip mode

In Fig. 12(a)–(c), typical images of the droplet formations sampled with the impact sampling technique at 3 cm downstream of the flame nozzle are shown for equivalence ratios (\(\phi\)) 0.8, 1.1 and 1.5. In these images, one can observe that the droplet foot-prints for the three equivalence ratios show mostly gel-type formations. One large lump of gelated material is typically observed in the center of a droplet splat, which points to the presence of some liquid in the droplet prior to impact. Even the equivalence ratios that will give rise to higher temperatures do exhibit presence of liquid. One should keep in mind that, the droplets generated in the drip mode are 100 \(\mu\)m in size. Therefore, their momentum in the flame is much higher than smaller droplets/particulates. In the impact sampling, only these larger droplets are collected. The images of the samples collected further downstream, i.e. 8 cm downstream of the flame nozzle, in Fig. 12(d)–(f) reveals a similar pattern. These samples still have certain resemblances to those at 3 cm location with a similar gel-type formation occurring at \(\phi = 1.1\).

In contrast to impact sampling, thermophoretic sampling technique collects smaller samples as the attraction of the samples onto the substrate surface is more gentle. As shown in Fig. 13, features associated with these samples are typically smaller and the characteristic lengths are in the order of 50–80 \(\mu\)m. Similar to the impact samples, the cooler flame (\(\phi = 0.8\)) gives more gel-like structures, whereas the samples from the hotter flames (\(\phi = 1.1\) and 1.5) exhibit characteristics that indicate a higher degree of solidity based on the jagged edges of these samples.

3.3.2. Cone-jet variant mode

Impact samples in the cone-jet variant mode collected at 3 cm downstream of the flame nozzle show similar behavior to that in the drip mode. The cooler flame image given in Fig. 14(a) shows similar characteristics, with gel-like structures present. However, the samples extracted from the hotter flames shown in Fig. 14(b) and (c), exhibit some interesting structure. Here, there is less evidence of gel-like structures, however, presence of the smaller features are seen as bubble-like formations with small “black-dot”s. These indicate some nucleation sites for the precipitates of zirconium acetate. Samples extracted at farther downstream shows a similar behavior where cooler flames exhibit gel-like structures and hotter flames show images with smaller features as shown in Fig. 14(d)–(f). Even though the images of the samples shown in Fig. 14(d) and (f) are containing gel-like structures of a large droplet, Fig. 14(e) shows remnants of a much smaller droplet. The remnants shown in this figure are not similar to gel formations but featured a thin crust. This crust is probably formed from a smaller droplet. The presence of these smaller droplets in the cone-jet variant mode was shown in Fig. 6(b). Since the droplet size is smaller than those in the other images, gel formation is not present in this case.

Since the cone-jet mode contains a cloud of very fine droplets, one might think that the non-existence of these small particles is surprising. Nevertheless, these smaller entities follow the flow, and upon encountering the substrate, these smaller droplets would be deflected by the

![Fig. 13. Images of the thermophoretically collected samples for: (a) \(\phi = 0.8\), (b) \(\phi = 1.1\) and (c) \(\phi = 1.5\) at 3 cm downstream of the flame nozzle. These samples were collected in the drip mode operation of the electrospray.](image-url)
flow, whereas larger droplets would impact the substrate due to their larger momentum. The relevant non-dimensional group which determines whether a droplet will impact the surface or not is the Stokes number defined as

$$St = \frac{\rho d^2 V_o}{18 \mu_l l}.$$

In this non-dimensional group, $\rho$ is the density of the droplet, $d$ is the diameter of the droplet, $V_o$ is the droplet velocity, $\mu_l$ is the dynamic viscosity of the gas field and $l$ is a characteristic length on the impact surface. When the Stokes number is larger than unity, the momentum of the droplet is sufficiently larger than the effects of the flow, therefore, the droplet will most likely impact on the surface. However, if the Stokes number is smaller than 1, the aerodynamic drag force will overcome the inertia of the droplet and the
droplet will be swept away from the substrate. For a typical droplet velocity of 20 m/s, the critical droplet diameter for water is calculated to be 32 μm to impact on the substrate.

As mentioned earlier, very fine droplets of the cone-jet mode cannot be sampled using the impact sampling technique. Since the momenta of these droplets are not large enough to overcome the momentum of the flow field, they are diverted as they encounter the substrate. However, the thermophoretic sampling technique is based on the attraction of the droplets towards a substrate which is inserted parallel to the streamlines. Since there is no force acting in that direction to divert the flow, very small attraction forces between the droplet and the substrate will allow the sampling of the small droplets. In Fig. 15(a), a particle formation on a copper substrate is shown for an equivalence ratio of 0.8, which is the coolest of the three flame compositions studied here. The formations observed are about 10 μm in size and these formations appear to be in transition from a gel structure to the dried gel phase. Nevertheless, samples observed in Fig. 15(b) and (c) indicate very interesting structures. These formations are in perfect spherical shape with surface features of the order of 100 nm size. The sizes of the spheres are about 8–15 μm. These structures are indicative of sintered poly-crystalline zirconia. Also, some smaller formations (about 2–3 μm) with spherical shapes are observed.

3.4. Coatings

After the sampling experiments were performed, attempts were made to produce coatings in the oxygen–acetylene environment using the same setup. If possible, production of ceramic coatings in oxy-acetylene environment has certain advantages such as circumvention of need for a costly plasma setup, possibility of on-site repairs, etc. Thus, an extension of this study was undertaken by continuous insertion of the substrate into jet at a certain distance from the nozzle exit. The continuous deposition procedure should be performed with an equivalence ratio low enough to avoid soot contamination from the acetylene flame. On the other hand, high temperatures must be sustained by increasing the equivalence ratio. Therefore, an equivalence ratio of φ = 1.1 was selected since this is close to the stoichiometric composition and has the highest temperatures. Deposits were then collected by repetitive insertion of a grit blasted stainless steel substrate for 1000 times at a stand-off distance of 5 cm. Each insertion had 100 ms residence time in the flame and the substrate was aggressively cooled with nitrogen on the back surface for a period of 100 ms in between insertions. The top surface micrograph of the sample is given in Fig. 16(a). In this picture, fine structure of the deposit can be clearly seen with features of few micron size. These images are consistent with the spray trials done under the plasma conditions as shown in Fig. 16(b) [9,18].

To verify the different phases in the deposits, they were analyzed by Raman scattering. The Raman spectra is shown in Fig. 17. It is seen that the peaks for the tetragonal 7YSZ are present. Also, peaks for the CH₃ and COO are present which is an indication of the presence of the unpyrolyzed material. One reason for this is the repetitive insertion process which results in the flame heating the same location at each insertion. In a real spray process, the plasma flame traces a raster pattern, so that the substrate is more evenly heated and the amount of unpyrolyzed material would typically be less. However, in this repetitive insertion process, cooler regions of the substrate is expected to contain more unpyrolyzed material. Even though these deposits cover the surface, the deposit is not adherent and it is powdery.

Fig. 15. Images of the thermophoretically collected samples for: (a) φ = 0.8, (b) φ = 1.1 and (c) φ = 1.5 at 3 cm downstream of the flame nozzle. These samples were collected in the cone-jet variant mode operation of the electrospray.
4. Conclusions

In this study, experiments were conducted to investigate the formation of zirconia particulates from liquid precursor containing zirconium acetate. An experimental setup was utilized to study the SPPS process under controlled conditions. The results of this study indicate that the formation of the zirconia from liquid precursors is a complex phenomenon. As the droplets enter into the hot gas region, a plume was observed in the high speed images in which small particulates are shed off the surface of the droplets. This plume might result from the zirconium acetate precipitates which are torn off the droplet surface due to shear.

Larger droplets impact onto the surface as liquid or in gel phase. Pyrolysis of these droplets is probably completed upon arrival onto the high temperature substrate surface and glazing of the flame in the actual SPPS process. Examination of the thermophoretic samples of the cone-jet mode indicate that flame samples produce sintered poly-crystalline spheres above equivalence ratios of 1.1 of the flame. As the droplet sizes get smaller and flame temperatures are higher, more sintered poly-crystalline particles are collected onto the substrate. One can hypothesize that these fine particles arriving onto the surface are actually bonded by the liquid or gel phase material so that an adherent coating can be obtained.

The repetitive insertion of the substrate into the flame resulted in deposits covering the surface of the substrate. These deposits are not fully adherent and contain some acetate groups from the precursor which was not pyrolyzed fully due to uneven heating of the substrate. Raman analysis of the coatings clearly indicate the presence of the CH$_3$ and COO groups, which are the remnants of the liquid or gel phase material which did not have enough time to pyrolyze on the surface. However, Raman analysis also indicates the presence of the tetragonal yttria-stabilized zirconia. Future efforts will seek to obtain adherent coating using smaller precursor droplets and different combustion jet conditions.

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