Combustion-aided suspension plasma spraying of $Y_2O_3$ nanoparticles: Synthesis and modeling

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Combustion-aided suspension plasma spraying (SPS) was developed for the synthesis of $Y_2O_3$ nanoparticles. Numerical models for Ar, Ar/O2, and combustion-aided plasma fields were built using FLUENT V6.3.2© to compare their different plasma thermophysical properties. Modeling and experimental results both indicate that the plasma field was substantially altered by combustion-aided SPS. The plasma exhibited an elevated volume average temperature and reduced velocity as well as a broadened plasma plume, which resulted in an enhanced vapor supersaturation degree and a faster quenching rate in the radial direction. These can be attributed to the dual effects of oxygen dissociation/recombination and acetone solvent combustion. Consequently, productivity of the obtained nanoparticles increased remarkably and the particles’ morphology was improved, with a smaller mean particle size and a narrower size distribution in comparison with those of powder feeding spraying. Furthermore, plasma-induced cubic—monoclinic phase transformation in the as-sprayed $Y_2O_3$ particles was restrained by combustion-aided SPS to some extent. © 2008 American Institute of Physics. [DOI: 10.1063/1.2841524]

I. INTRODUCTION

Since nanoparticles have shown their superior properties in electronic, chemical, and mechanical industries, various techniques have been developed or tailored for their synthesis. Among these techniques, inductively coupled radio frequency plasma (rf-ICP) spraying has been widely used over the past two decades in a number of material processing applications involving in-flight melting and deposition of metals, ceramics, and composites, plasma reactive deposition, and plasma synthesis of nanoparticles.1 The heat source of common rf-ICP, using Ar as a medium and generated by inductively coupled radio frequency ac power, creates plasma field with a temperature over 8000 K, allowing the melting of any material. In comparison with dc plasma and capacitive rf plasma sprayings, the main advantages of rf-ICP spraying are the relatively large plume volume, low plasma velocity, axial material injection, and high throughput. More importantly, the absence of electrodes offers the added advantage of ease of operation with a wide range of inert, oxidizing, or reducing gases at atmospheric and low pressure conditions.2

However, conventional power feeding method in rf-ICP spraying has its limitations in dealing with fine powders. In our previous research,3 serious clogging problem occurred in the synthesis of rare earth oxide nanoparticles by powder feeding rf-ICP spraying, which resulted from the small particle size ($< 20 \ \mu m$) and large molecular weight of rare earth oxides. This cannot be solved by increasing the carrier gas flow rate because it will drastically disturb the stability of the plasma jet, thereby affecting the constancy of the heat treatment.4 Neither can rare earth salt solution feedstock be used because the corrosive by-products from inorganic salts could seriously damage the plasma spraying system. Organic salts are less corrosive but much more expensive than rare earth oxide raw materials. Therefore, suspension plasma spraying (SPS) technique was adopted instead of the commonly used powder feeding spraying to solve the clogging problem.5 The SPS process was developed by Bouyer et al.6 in 1997 and has been proven to be a very effective way for fine particle feeding in plasma spraying. The suspension, using water as solvent, is pumped into the plasma plume through an atomization probe to create micron-sized droplets comprising raw material particles. The droplets are flash dried, and the remaining particles are melted, vaporized, and condensed into nanoparticles. The material flowability of SPS is excellent; however, the quenching effect caused by vaporization of water solvent deteriorates the particle heat treatment greatly, thus leading to a low productivity of nanoparticles. In addition, inhomogeneous heat treatment arising from the characteristically nonuniform heating of the plasma plume was appreciable. These are severe problems that impede the generalization of SPS in plasma spraying engineering.

In this study, combustion-aided SPS technique was developed aiming at improving the heat treatment and homogeneity in SPS synthesis of rare earth oxide nanoparticles. In this process, water solvent was replaced by organic solvent acetone which has a much lower heat of vaporization. Additionally, oxygen was introduced as secondary plasma gas in

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order to facilitate the complete combustion of acetone as well as to further elevate the plasma enthalpy. To elucidate the effects of different processing mechanisms, numerical models of combustion-aided SPS and powder feeding spraying were constructed using the computational fluid dynamics (CFD) analysis program FLUENT V6.3.2©. Modeling results were then related to the properties of the as-sprayed particles, such as morphology, productivity, and crystal structure.

II. EXPERIMENTAL

The raw material for spraying was commercial \( \text{Y}_2\text{O}_3 \) powder with particles in irregular shape and size range from 1 to 20 \( \mu \text{m} \) (AMR Technologies Inc., purity of 99.5 wt %). The spraying was carried out on a TEKNA plasma system with PL-35 induction rf plasma torch operating at 3 MHz. Three spraying schemes were performed: powder spraying by Ar plasma, powder spraying by Ar/O\(_2\) plasma, and combustion-aided SPS (Ar/O\(_2\)+acetone). Their operating conditions are listed in Table I. Ar was used as plasma central and sheath gas in all cases. Oxygen was introduced as secondary gas in the last two schemes with different proportions which were determined by the system stability. For powder sprayings, \( \text{Y}_2\text{O}_3 \) powder was carried by Ar gas and injected axially into the center of the plasma plume through a water-cooled injector. For suspension spraying, \( \text{Y}_2\text{O}_3 \) powder was first dispersed in acetone to form a 10 wt % concentration suspension and then fed by a peristaltic pump with Ar gas through an atomization injector. After plasma treatment, the material was quenched at extremely high rate and collected by a cyclone into two chambers (C1 and C2) which enabled the classification of particles according to their sizes.

The size distributions of the as-sprayed nanoparticles were measured using Brookhaven dynamic light scattering (DLS). The morphology of the particles was studied using scanning electron microscopy (SEM) (JEOL JSM 6340F) and transmission electron microscopy (TEM) (JEOL JEM 2010). For phase analysis, x-ray diffraction (XRD) experiments were conducted in Bragg–Brentano geometry employing a Shimadzu 6000 diffractometer with Cu \( K\alpha \) radiation (\( \lambda = 1.5418 \) Å). To determine the lattice parameters as well as the quantitative phase compositions, further analysis of the diffraction patterns by means of Rietveld refinement method was carried out using TOPAS.

III. NUMERICAL MODEL

Numerical models of the three spraying schemes were constructed with the CFD analysis program FLUENT V6.3.2©. The approach for modeling the plasma heat generation in FLUENT© was by means of the conventional constant volumetric heat source model. The simulation of rf-ICP spraying process involved two stages. In the first stage, a steady state thermal fluid solution for plasma and carrier gas flows without particle injection was obtained. In the second stage, \( \text{Y}_2\text{O}_3 \) particles were introduced in the plasma model as solid entities, and the heat and momentum transferred from the plasma to the particles were calculated so as to obtain the in-flight particle properties, e.g., temperature, velocity, size, and number concentration. The plasma and particle interaction was considered as one directional, i.e., the process of energy and momentum transfers only proceeded from the plasma to the particles but not in reverse. Although it greatly simplifies the computational task, the assumption may result in deviation from the realistic conditions since the particles act as a local heat sink and reduce the local plasma temperature and velocity. Nevertheless, in our spraying trials, the particle flow was set to a very dilute level (1 g/min) aiming to minimize the influence from the particles on the plasma. Thus, the energy and momentum the plasma received from or transferred to the particles would not be high enough to significantly alter the plasma temperature and velocity.

A. Plasma heat generation

The geometry of the models was developed using the commercial software GAMBIT V2.3.16©. The cylindrical computational domain included the rf-ICP torch and the free space of the upper part of the chamber is illustrated in Fig. 1. The mathematical model in FLUENT V6.3.2© was based on the Navier–Stokes equations and Reynolds method of averaging the time dependent equations, coupled with the standard \( k-\varepsilon \) model for turbulence representation.
To account for the heating from the inductively coupled rf power, the volumetric heat source was included in the governing energy equation and defined as

$$p_{in}^v = \frac{\eta EI}{V},$$

where $p_{in}^v$ is the volume-averaged heat source, $EI$ the input plasma power, and $V$ the volume of the torch. Torch efficiency $\eta$, which results mainly from the heat loss through cooling water in the plasma torch and injector, was set to 67% based on the TEKNA technical report.

In the energy differential equation, there is another source term, $S_r$, which represents the heat of chemical reaction. In the case of Ar plasma, no reaction takes place and therefore $S_r=0$. In the Ar/O$_2$ plasma case, the heat released from oxygen recombination was accounted for by the source term $S_r$. Lastly, the third case, i.e., the combustion-aided SPS, in addition to the oxygen recombination, the heat from the acetone solvent combustion was also included in the source term $S_r$ of the energy equation.

In the species conservation equation, the source term $R_s$ represents the net rate of production of each species component and $S_s$ is the rate of creation by addition from the dispersed phase plus any other sources. In this study, eddy dissipation model is applied to calculate the source term $R_s$ due to the reactions of oxygen recombination and acetone solvent combustion. The eddy dissipation model is a turbulence-chemistry interaction model based on the work of Magnussen and Hjertager. The model assumes that reaction rates are controlled by the turbulence so that the computationally expensive Arrhenius chemical kinetic calculations can be avoided. This is reasonable for oxygen recombination and acetone combustion as these processes are instantaneous and the overall rate of the reaction is controlled by the relatively slow turbulent mixing. The net rate of production $R_s$ can be modeled by taking the minimum of the following two expressions:

$$R_{s,r} = v_{l,r} M_{w,j} A \rho \frac{\varepsilon}{k} \min \left( \frac{Y_R}{v_{R,R} M_{w,R}} \right),$$

$$R_{s,r} = v_{l,r} M_{w,j} A B \rho \frac{\varepsilon}{k} \left( \sum \frac{Y_P}{\sum v_{l,j} M_{w,j}} \right),$$

where $Y_P$ is the mass fraction of any product species $P$, $Y_R$ is the mass fraction of a particular reactant $R$, and $A$ and $B$ are empirical constants equal to 4.0 and 0.5, respectively.

The process of dissociation of O$_2$ to O was represented by volumetric O$_2$ sink and volumetric O source. These O$_2$ sink and O source were calculated from the O$_2$ gas flow rate and based on the assumption that O$_2$ was completely dissociated once fed into the torch. Both sink and source were included as $S_s$ of species conservation equation and assigned to the torch domain only.

### 1. Modeling assumptions

The modeling of the free turbulent steady state rf-ICP flow was based on the following assumptions:

(i) The plasma was in local thermodynamic equilibrium condition.

(ii) The plasma heat was generated by volumetric heat source dependent on power input and torch efficiency. The plasma characteristics were not considered; thereby Lorentz flow (flow induced due to the potential differences in electric and magnetic fields) was neglected.

(iii) When spraying with oxygen addition, oxygen molecules were assumed to be completely dissociated in the torch and recombined in chamber. Ionization effect of O atom has a much higher ionization energy compared with that of O$_2$ dissociation; thus only a small amount of O atoms was ionized. The number density of O$^+$ in the plasma was two orders lower than O, thus, the influence of ionization was negligible. Second, it was hard to determine the ionization rate as it varies with plasma conditions.

(iv) Inertia was the dominant force for flow acceleration because the calculated value of Gr/Re$^{-2}$ (ratio of Grashof number to Reynolds number squared) was approximately $10^{-5}$. Thus, operation of the torch was assumed to be in steady state with negligible buoyancy and gravity force.

### 2. Governing equations

Based on the assumptions, there are five governing equations of fluid flow representing mathematical statements of the conservation laws of physics, conservation of chemical species, and turbulence. These governing differential equations can be generalized in the following form:

$$\nabla \cdot (\rho u \phi) = \nabla \cdot (\Gamma \phi \nabla \phi) + S_{\phi}, \quad (1)$$

where $\phi$ is the process variable and $u$ the velocity vector. The diffusion coefficients $\Gamma_{\phi}$ and the source terms $S_{\phi}$ for the different conservation equations are given in Table II.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Variable ($\phi$)</th>
<th>Diffusion coefficient ($\Gamma_{\phi}$)</th>
<th>Source term ($S_{\phi}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$u, v, w$</td>
<td>$\mu_1 + \mu_2$</td>
<td>$-\nabla p$</td>
</tr>
<tr>
<td>Momentum</td>
<td>$h$</td>
<td>$k_1 + k_2$</td>
<td>$P_{in} + S_r$</td>
</tr>
<tr>
<td>Energy</td>
<td>$Y_s$</td>
<td>$D_1 + D_2$</td>
<td>$R_s + S_s$</td>
</tr>
<tr>
<td>Species</td>
<td>$\kappa, e$</td>
<td>$\mu_1 \frac{Pr_{\kappa}}{\mu_2} \frac{Pr_{e}}{\mu_2}$</td>
<td>$G_{\kappa} - \rho \varepsilon C_{\kappa} \frac{e^2}{k}$</td>
</tr>
<tr>
<td>Turbulence</td>
<td>$\kappa, e$</td>
<td>$\mu_1 \frac{Pr_{\kappa}}{\mu_2} \frac{Pr_{e}}{\mu_2}$</td>
<td>$G_{\kappa} - \rho \varepsilon C_{\kappa} \frac{e^2}{k}$</td>
</tr>
</tbody>
</table>

$S_s$ and $R_s + S_s$ equal to zero when simulating the case with Ar plasma.

$\Sigma$, and $S_s + R_s$, equal to zero when simulating the case with Ar plasma.
TABLE III. Boundary conditions of spraying schemes.

<table>
<thead>
<tr>
<th>Operating condition</th>
<th>Ar</th>
<th>Ar/O₂</th>
<th>Combustion-aided SPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torza diameter (mm)</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Nozzle diameter (mm)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Torch exit diameter (mm)</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Powder size (μm)</td>
<td>1 20</td>
<td>1-20</td>
<td>1 20</td>
</tr>
<tr>
<td>Power (kW)</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Torch efficiency (%)</td>
<td>67</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>Heat source (W/m³)</td>
<td>4.164 901 × 10⁸</td>
<td>4.164 901 × 10⁸</td>
<td>4.164 901 × 10⁸</td>
</tr>
<tr>
<td>Turbulence intensity, central gas (%)</td>
<td>5.70</td>
<td>6.06</td>
<td>6.21</td>
</tr>
<tr>
<td>Turbulence intensity, sheath gas (%)</td>
<td>5.74</td>
<td>5.74</td>
<td>8.07</td>
</tr>
<tr>
<td>Turbulence intensity, carrier gas (%)</td>
<td>0</td>
<td>51.441 4</td>
<td>−14.310 8</td>
</tr>
<tr>
<td>O₂ sink (kg/m³ s)</td>
<td></td>
<td>102.882 9</td>
<td>28.621 5</td>
</tr>
<tr>
<td>O source (kg/m³ s)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3. Numerical operating and boundary conditions

The numerical operating conditions and boundary conditions are listed in Table III. The torch efficiency was fixed at 67% for all three cases, since the additional energy from oxygen recombination and acetone combustion was represented by the source term of the energy governing equation. The axial exit boundaries were selected a distance far away from the exit of the torch so that atmospheric boundary conditions were applicable there. The boundary conditions for the turbulence model at the inlets of the torch and injector were turbulence intensity and characteristic length. The turbulence intensities at the central, sheath, and carrier gas inlets were calculated based on

\[
T_i = 0.16(R_{e, \text{HD}})^{-0.125},
\]

where \(R_{e, \text{HD}}\) is the Reynolds number calculated for the gas flowing through the respective inlets, on the basis of the hydraulic diameter as the characteristic length.

### 4. Solution scheme

The governing equations were solved by the FLUENT V6.3.2© package using the control volume technique. This technique converts governing equations into algebraic equations that can be solved numerically. The numerical approach stores scalar variables at the center of the control volume. The face values of scalar variables that are required for the convection terms are obtained from interpolation. First order upwind scheme was used to calculate the face values of the scalar variables as the problem was convection-dominated flow. The segregated solver was selected as solution algorithm. The strategy is to solve each single variable field by considering all control volumes at the same time, followed by solving the next field variables in the same way, and so on.

### B. Particle dynamics and heat transfer formulation

After attaining converged solution for the plasma models, \(\text{Y}_2\text{O}_3\) particles were introduced in the models and their motion and thermal evolution were calculated. The particles were modeled in FLUENT© as discrete Lagrangian entities that received momentum and energy from the plasma in one-directional coupling. Particle in-flight behavior, e.g., particle velocities and particle temperatures, were predicted based on the Newton second law of motion and the energy balance equation, respectively.

In the particle dynamics formulation, it was assumed that the dominant driving force for particle acceleration was viscous drag force generated by the high speed plasma flow. In contrast, other forces acting on a particle such as buoyancy force, gravity, or thermophoresis force are insignificant and thereby neglected. As for particle heating or cooling, convective heat transfer from plasma to particle and vice versa was considered, whereas gas radiation heating was ignored as it was trivial compared to convective heating. The particle was assumed to have uniform temperature distribution, i.e., it has perfect thermal conductance or zero thermal resistance. Particle vaporization, nucleation, and subsequently the formation of nanoparticles were not modeled because of the software limitation.

In this study, the powder feed rate used is dilute, i.e., 1 g/min, which provides mean distance between two particles approximately ten times of their mean diameter. This distance is sufficiently far apart for the avoidance of particle to particle interaction.

### 1. Governing equations

The momentum transport equation coupled with stochastic tracking determines the particle motion and trajectory. Particle heating, cooling, melting, and solidification are governed by the energy transport equation.

\((i)\) Momentum transport. Based on the Newton second law of motion, the force balance equation in Lagrangian ref-
bridge frame that equates particle inertia with viscous drag force acting on the particle is as follows:

$$\frac{du}{dt} = F_D$$

(6)

where $F_D$ is the drag force per unit mass and is defined as

$$F_D = \frac{3\mu C_D (u - u_p) Re}{4 \rho_D D_p^2}.$$  

(7)

Re, is the relative Reynolds number and $C_D$ is the drag coefficient which are defined as

$$Re = \frac{\rho D_p (u - u_p)}{\mu},$$  

(8)

$$C_D = a_1 + \frac{a_2}{Re_r} + \frac{a_3}{Re_r^2},$$  

(9)

where $a_1$, $a_2$, and $a_3$ are constants applicable for smooth spherical particles for a range of Reynolds number.

(ii) Stochastic tracking. When a particle interacts with continuous turbulence eddies, random variations in the instantaneous drag force acting on the particle need to be considered. To account for the turbulence effect on particle trajectories, the “random walk model” was utilized. In this model, the instantaneous value of fluctuating gas flow velocity was used and assumed to be isotropic and obey the Gaussian probability distribution, so that

$$u' = \psi \sqrt{u'^2},$$  

(10)

where $\psi$ is a normally distributed random number and $\sqrt{u'^2}$ is local root mean square value of the velocity fluctuations. Hence, in Eqs. (7) and (8), instead of $u = \bar{u}$, the velocity fluctuation was included as $u = \bar{u} + u'$.

(iii) Energy transport. The concept of energy balance was adopted for convective and latent heat transfer from the surrounding plasma to the particle or vice versa. For particle heating or cooling phase, the energy equation is

$$h A_p (T_\infty - T_p) = m_p C_p \frac{dT_p}{dt} \quad \text{for } T_p < T_m \text{ or } T_m.$$  

(11)

$T_p$ is the particle temperature. The heat transfer coefficient $h$ in Eq. (11) is based on Ref. 14 and given as

$$h = \frac{k}{D_p} (2.0 + 0.6 \text{Re}_r^{0.5} \text{Pr}^{0.33}).$$  

(12)

As for particle melting or solidification, energy balance is defined as

$$h A_p (T_\infty - T_p) = m_p H_l \frac{d\zeta}{dt} \quad \text{for } T_p = T_m,$$  

(13)

where $\zeta$ is the liquid fraction.

2. Particle size distribution and properties

To introduce $Y_2O_3$ particles in the model, the particle size distribution (Fig. 2) in terms of diameter versus percentage weight was curve fitted via a Rosin–Rammler distribution and numerically introduced to the plasma field. The thermodynamic and transport properties of $Y_2O_3$ particles required in the simulation are shown in Table IV. As for the specific heat capacity, its value is strongly dependent on temperature. For particle temperature between 273 and 873 K, the $C_p$ is calculated as in Eq. (14). Above 873 K, the $C_p$ remains constant, which is 674.5 J/kg K.

$$C_p = 3.6273 \times 10^{-8} T_p^3 - 2.02475 \times 10^{-4} T_p^2 + 0.38864 T_p + 362.26349.$$  

(14)

IV. RESULTS AND DISCUSSION

A. Modeling results of plasma properties and particle behavior

1. Plasma temperature and velocity

The simulated temperature and velocity contours of Ar, Ar/O2, and combustion-aided plasma fields are illustrated in Fig. 3. It can be seen that the temperature apex was always located in the torch zone which is surrounded by the coils. Once released to the free space beneath the torch exit in the chamber, the plasma temperature dropped at a certain gradient which varied with plasma conditions. The temperature apaxes were 10,613, 9,560, and 11,453 K, and the volume average temperatures of the chamber were 617, 2,410, and 2,627 K for Ar, Ar/O2, and combustion-aided plasmas, respectively. The value of the temperature apex only describes the condition inside the torch. However, particle heat treatment was mainly conducted in the chamber area because of the particles’ longer residence time therein. Therefore, it is the volume average temperature of the chamber that is crucial for the plasma enthalpy and heat treatment degree evaluation. Obviously, the combustion-aided plasma had the highest volume average temperature and enthalpy level, followed by Ar/O2 plasma. Moreover, the shape of the plasma plume

TABLE IV. Thermodynamic and transport properties of $Y_2O_3$ particles.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $\rho_p$ (kg/m$^3$)</td>
<td>5030</td>
</tr>
<tr>
<td>Specific heat capacity $C_p$ (J/kg K)</td>
<td>Eq. (14)</td>
</tr>
<tr>
<td>Latent heat of fusion $H_l$ (J/kg)</td>
<td>3.71 $\times$ 10$^5$</td>
</tr>
<tr>
<td>Thermal conductivity $k_p$ (W/m K)</td>
<td>12</td>
</tr>
<tr>
<td>Kinematic viscosity $\nu_p$ (m$^2$/s)</td>
<td>5.8 $\times$ 10$^{-6}$</td>
</tr>
<tr>
<td>Melting point $T_m$ (K)</td>
<td>2703</td>
</tr>
<tr>
<td>Boiling point $T_b$ (K)</td>
<td>4573</td>
</tr>
</tbody>
</table>
was altered by the introduction of O_{2} secondary gas. As shown in the temperature contour in Figs. 3(a) and 3(b), Ar plasma had a thin and short, shuttle-shaped plume around the chamber centerline, whereas the plume of Ar/O_{2} plasma was about two times broader and longer. For combustion-aided plasma in Fig. 3(c), the plume was even broader but shorter than that of Ar/O_{2} plasma. In the last two cases, the temperature field that had a value above the Y_{2}O_{3} melting point spread to nearly the whole computational domain. To examine the temperature distributions along the axial and radial directions would be useful for understanding the temperature diversity. The axial temperature distribution in Fig. 4(a) indicates that although Ar plasma had the highest peak among the three cases, its temperature decreased much faster than the other two after the peak. In the radial views at 0.2 m standoff position in Fig. 4(b), it can be clearly seen that the temperature distribution of Ar plasma was quite narrow, and the plume field concentrated around the chamber centerline. In contrast, temperature distributions of Ar/O_{2} and combustion-aided plasmas were much broader, suggesting that their plume fields diffused both radially and axially.

Plasma velocity reaches its maximum inside the torch and drops quickly downstream. The plasma velocity variation among cases was large as shown in Fig. 3. Ar plasma had the highest starting velocity value at around 420 m/s and decreased to around 5 m/s at the end of the computational domain. Ar/O_{2} plasma had a similar contour pattern to that of Ar plasma, except that the starting velocity was much lower, about 250 m/s. The reason could be that the oxygen addition and its dissociation disturbed and retarded the normal plasma flow. The velocity was extraordinarily low for combustion-aided plasma, with a starting value of 20 m/s, and decreased to less than 1 m/s within the computational domain. Axial and radial velocity distributions in Fig. 5 give better understanding of the velocity diversity. The axial velocity distributions in Fig. 5(a) indicate that the Ar and Ar/O_{2} plasmas had velocity peaks inside the torch, whereas the curve of the combustion-aided plasma along the centerline was nearly flat. The radial direction velocity distributions in Fig. 5(b) show that the deviation of the radial velocity of the combustion-aided plasma was much smaller than those of other cases.

2. Particle behavior

As the particles were entrained in plasma flow, their in-flight behaviors were dependent on two factors: temperature and velocity distributions of the plasma field which transfer energy and momentum to the particles and particle characters such as size and thermodynamic properties. The in-flight behaviors of the particles including temperature, velocity, number concentration, and size were simulated and the contours are shown in Figs. 6–9, respectively. All the graphs are radial cross section view of the plume at 0.3 m standoff distance from the top of the torch. The contours were plotted by pro-
cessing the FLUENT® output data through the FORTRAN® program.

The particle temperature distribution contours in Fig. 6 are strongly related to the plasma temperature distributions. As can be seen in Fig. 6(a), the particles in Ar plasma with a high temperature were all at the chamber cross section center, on account of the concentrated Ar plasma plume. In contrast, the temperature distributions of the particles in Ar/O2 and combustion-aided plasmas [Figs. 6(b) and 6(c)] were much more divergent, which means that the particles were heated more homogeneously. In comparison with the particle temperature maximum of Ar plasma (3000 K), the particles in Ar/O2 and combustion-aided plasmas had a maximum at about 4500 K, which evidently resulted from the higher plasma enthalpy and longer residence time.

The particle velocity and number distribution are relative to the plasma plume shape and velocity. As shown in Fig. 7, the particle diffusivities increased in the order of Ar → Ar/O2 → combustion-aided plasma, in accord with the plasma plume diffusivities. Figure 8 shows that the particle velocities were proportional to the plasma velocities in Fig. 1. Since plasma flow transferred momentum to the entrained particles, their velocity vectors determined the particles’ trajectories. Ar plasma had higher velocity vector converged along the centerline, so did the particles it entrained [Figs. 7(a) and 8(a)]. Ar/O2 and combustion-aided plasmas, in contrast, had lower and diffusive velocity vectors; thus the particles entrained were slower and dispersed to a larger area [Figs. 7(b) and 7(c), Figs. 8(b) and 8(c)]. In other words, the plasma momentum was distributed more uniformly to more particles, with more divergent velocity directions.

The simulated particle size distributions describe only the micron-sized in-flight particles. The results are determined jointly by the three particle behaviors mentioned above, particle thermodynamic properties, and the initial particle size distribution. The pictures in Fig. 9 show qualitatively that the average particle sizes decrease in the order of Ar → Ar/O2 → combustion-aided plasma. In addition, the small particles in Ar plasma were mainly produced at the core of the plume where the high-temperature zone existed, whereas they spread to almost the whole cross section in combustion-aided plasma case due to the homogeneous heating favored by diffusive plasma plume and longer residence time.

B. Influence on micron-sized particle formation

1. Effects of O2 addition on plasma properties

Generally, the working fluid in rf-ICP spraying is pure Ar. However, in some cases, e.g., oxidization atmosphere spraying or chemical reactive spraying, it is often necessary or advantageous to use a secondary molecular gas such as H2, O2, or N2. In our spraying, O2 was chosen because rare earth oxide requires an oxidation atmosphere. There are six species including Ar, Ar+, O, O2, O+, and e− that are considered as the dominant reactants in Ar/O2 plasma. The dissociation and ionization rates of oxygen can be calculated by Eq. (15). The constants in Eq. (15) are taken from Refs. 15–17:
The ionization rate of Ar can be calculated by Eq. (16), which is taken from Ref. 18:

$$k_f = a_1 T^{b_1} \exp(-c/T).$$

The ionization rate of Ar can be calculated by Eq. (16), which is taken from Ref. 18:

$$k_f = 1.68 \times 10^{-20} T^{1.5} \left(\frac{135 \ 300}{T} + 2\right) \exp\left(-\frac{135 \ 300}{T}\right).$$

In this research, only the O₂ dissociation effect is discussed.

The strong effects of O₂ addition on the plasma properties can be visually observed. In comparison with Ar plasma, Ar/O₂ plasma plume was broader and longer and its brightness increased dramatically, which are in accord with the modeling results. These extraordinary phenomena can be explained by the thermodynamic properties of oxygen. Oxygen molecules have dissociation temperature between 3500 and 4000 K and low dissociation energy of 5.1 eV. Inside the torch, the high-temperature plasma field provided enough kinetics for oxygen dissociation; thus oxygen molecules absorbed a large amount of energy through collision and dissociated into O atoms. It has been demonstrated by Hsu et al.¹⁹ that electron impact dissociation of the O₂ molecules is the dominant reaction that produces O radicals in O₂-containing plasmas. The oxygen atoms moved downstream into the chamber where the temperature was relatively low, recombined into oxygen molecules, and released the additional energy in the form of heat. Hence, the oxygen dissociation and recombination processes literally increased the torch efficiency by carrying additional energy from the torch to the chamber. This additional part of energy, which would otherwise be dissipated through water cooling of the torch and injector, elevated the plasma enthalpy in the chamber remarkably. The effect was represented by an increase of volume average temperature of the chamber (Ar: 617 K → Ar/O₂: 2410 K) according to modeling results. In addition, the temperature apex in the torch decreased from 10 613 to 9560 K after oxygen addition. This is because the large energy consumption by oxygen dissociation resulted in a significant temperature drop in the torch. The temperature drop induced a more moderate temperature gradient near the torch wall in comparison with Ar plasma, thereby reducing the heat loss at the wall and increased the torch energy efficiency.

Plasma velocity was also affected by O₂ introduction as revealed by modeling results in Fig. 3(b). The starting velocity of Ar/O₂ plasma was almost halved in comparison with the Ar plasma, and the value dropped at a lower rate. This can be attributed to the oxygen dissociation and recombination processes, too. In Ar/O₂ plasma, the electrons from Ar ionization were accelerated by the electrical field in the torch and transferred energy to the oxygen molecules through collision. The electrons lost their kinetic energy and slowed down during the collision. Since the oxygen molecules are much larger and heavier than electrons and most of the energy they obtained from collision was spent on their dissociation, the acceleration of oxygen was limited and the overall plasma velocity was much lower than that of Ar plasma. Moreover, oxygen recombination process elevated the

FIG. 7. Contours of particle number distribution in (a) Ar, (b) Ar/O₂, and (c) combustion-aided plasmas.

FIG. 8. Contours of particle velocity distribution in (a) Ar, (b) Ar/O₂, and (c) combustion-aided plasmas.
plasma volume average temperature by almost four times, which increased the kinematic viscosity of the plasma species. This could also reduce the plasma velocity to some extent.

2. Effects of combustion-aided SPS on plasma properties

According to modeling results, combustion-aided SPS, i.e., (Ar/O₂+acetone) plasma spraying, created the highest chamber volume average temperature and plasma enthalpy. This can be attributed to the dual effects of oxygen dissociation and recombination and acetone combustion. The oxygen effects on plasma properties have been discussed in Sec. IV B 1. Besides oxygen effects, combustion of acetone solvent also contributed a lot to plasma enthalpy. When fed into plasma field, acetone solvent vaporized and combusted instantly. The combustion reaction is formulated as

$$C_3H_6O + 4O_2 \rightarrow 3CO_2 + 3H_2O + 29\,000 \text{ kJ/kg}.$$  (17)

Acetone’s heat of combustion (29 000 kJ/kg) is two orders higher than its heat of vaporization (525 kJ/kg); therefore, the energy consumed by acetone vaporization was negligible. Owing to the additional contribution of combustion reaction, the chamber volume average temperature increased to 2627 K, as against 2410 K of Ar/O₂ plasma, and the plasma plume became broader and shorter. Furthermore, the plasma velocity decreased dramatically in combustion-aided SPS. The reason is twofold. First, the atomization gas in this case was set to zero deliberately, aiming at prolonging particle residence time in plasma. Although this impaired suspension atomization slightly, it was very favorable for particle heat treatment. Second, the momentum transfer of plasma species was interfered by the oxygen dissociation and recombination as well as the combustion reaction. As a combination of the above effects, combustion-aided SPS offered a further elevated plasma enthalpy, a more dispersive plume, and a longer residence time in comparison with Ar/O₂ plasma.

3. Effects of plasma properties on micron-sized particle morphology

Rare earth oxides are highly thermodynamically stable, and thus require an enhanced plasma field for melting and vaporization. In the scheme of Y₂O₃ powder sprayed by Ar plasma, a large proportion of the micron-sized particles remained irregular shape like the raw material after spraying, suggesting an insufficient heat treatment [Fig. 10(a)]. To elevate the plasma enthalpy, O₂ was introduced as a secondary plasma gas in powder spraying. As a result, the morphology of the particles changed substantially. The obtained micron-sized particles comprised a large amount of spherical particles [Fig. 10(b)], indicating a melting history. Although the heat treatment was improved by O₂ introduction, the flowability of the feedstock in powder spraying was still bad. It resulted in discontinuous feeding and thereby an inhomogeneous heat treatment of the particles. In view of this, combustion-aided SPS technique was developed. In this process, the feedstock was carried by acetone solvent and injected into the plasma at a steady feed rate with no clogging issue. Moreover, the plasma enthalpy was further elevated due to the dual effects of O₂ introduction and acetone combustion. The product from combustion-aided SPS had much smaller micron-sized spherical particles than powder spraying by Ar [Fig. 10(c)]. The particle heat treatment degree in plasma spraying depends on two factors: plasma enthalpy and residence time. Either higher plasma enthalpy or longer residence time favors the particle heat treatment. Oxygen introduction satisfies both requirements simultaneously by offering a larger plume volume with higher enthalpy and a lower plasma velocity. Consequently, the micron-sized particles from Ar/O₂ plasma spraying comprised less irregular-shaped particles. However, because of clogging problem and particle spray trajectory cone, the heat treatment degrees for particles were not uniform, and the particles had a wide size distribution [Fig. 10(b)]. Combustion-aided SPS, with a suspension form feedstock, solved the clogging problem effectively and im-

![FIG. 9. Contours of particle diameter distribution in (a) Ar, (b) Ar/O₂, and (c) combustion-aided plasmas.]( Image 50x36 to 338x112 )

![FIG. 10. SEM micrographs of Y₂O₃ micron-sized particles synthesized from (a) powder feeding spraying by Ar, (b) powder feeding spraying by Ar/O₂, and (c) combustion-aided SPS.]( Image 113x629 to 497x742 )
proved the heating uniformity. The plasma plume broadening effect contributed to the uniform heating, too. Furthermore, combustion-aided SPS elevated the plasma enthalpy further and prolonged the particle residence time on account of its low velocity; thus, particle heat treatment was promoted to a higher level. As a result, the micron-sized particles from combustion-aided SPS in Fig. 10(c) exhibited a smaller size and a more uniform size distribution than those of other schemes.

Undoubtedly, increasing plasma enthalpy promotes further melting and evaporation and changes particle size. Moreover, in principle, the size distribution of the micron-sized particles after spraying is largely related to their initial size distribution of the raw material. However, under constant processing conditions, the heat treatment degree for each particle can still be different. This idea is justified by the modeling results in Sec. IV A 2, where the particle trajectory and velocity diversity are shown in Figs. 7 and 8, and the consequent particle temperature and size diversity are shown in Figs. 6 and 9. The detailed discussion on the mechanism of micron-sized particle formation can be found in our earlier work.3,5

C. Influence on nanoparticle formation

1. Mechanism of nanoparticle formation

The mechanism of nanoparticle formation in plasma spraying is different from that of micron-sized particles because nanoparticles are formed through vapor phase condensation. The procedure of nanoparticle formation is shown schematically in Fig. 11 and described as follows. In SPS, the droplets that carry particles are flash dried and the remaining micron-sized particles are melted and vaporized. Upstream of the plasma plume, the vapor partial pressure is higher than the saturation point because of the high temperature. The vapor saturation point will decrease with plasma temperature when the vapor is moving downstream until it becomes lower than the vapor pressure, where supersaturation occurs. At the supersaturation state and if the condensation kinetics permit, homogeneous nucleation will initiate and numerous tiny primary nuclei will emerge instantaneously. Once the nucleation occurs, the remaining supersaturation will be relieved by condensation on the surface of the primary nuclei, and nucleus growth will proceed rather than create more nuclei. With the vapor pressure quickly being depleted and nucleation tapering off, coalescence process begins to prevail, through which the nuclei collide due to Brownian motion and unite to form clusters, i.e., nanoparticles. The particle size is largely determined by the collision and coalescence rate in this stage. With the temperature decreasing further, coagulation process arises, in which the ultrafine nanoparticles combine and form agglomerates. If the quenching is slow and the temperature is high enough, nanoparticles will form hard agglomerates which cannot be fully dispersed by ultrasonic vibration. Otherwise, nanoparticles will be bound together by van der Waals forces and form loose agglomerates which can be dispersed into individual nanoparticles.20

The nucleus diameter \( d_p \) in nucleation process can be estimated from the Gibbs–Kelvin equation \(^{21}\)

\[
d_p = \frac{4\sigma v_1}{kT \ln S}
\]

where \( \sigma \) is the surface tension, \( k \) the Boltzmann constant, \( S \) the saturation ratio defined as the ratio of the partial pressure of the corresponding species to its saturation vapor pressure, and \( v_1 \) the volume of the monomer in the condensed phase. It can be seen that the higher the plasma temperature \( T \) and supersaturation ratio \( S \), the smaller the nucleus size. Therefore, to synthesize ultrafine nanoparticles with uniform size, first of all, a high plasma temperature and a high supersaturation degree are needed. Higher supersaturation degree leads to higher initial nucleus density during the nucleation burst, so that the succeeding vapor condensation can be distributed homogeneously to more nuclei. Thus, the individual nucleus growth is restricted and the particle size deviation will be small. To achieve a high supersaturation degree, firstly, an enhanced plasma enthalpy or a low plasma velocity is required to increase the heat treatment level and material vaporization. Secondly, a sharp quenching rate is indispensable. Quenching rate is also crucial for controlling the particle size as it affects both nucleation and the succeeding in-flight particle growth. Having reached sufficient partial pressure, the vapor phase still requires a sharp quenching rate to rapidly decrease its saturation point and create a high supersaturation degree before nucleation burst can occur, so as
to achieve ultrafine nuclei. Once nuclei are formed, they collide and coalesce at a rate that is proportional to the square of their number concentration which is only weakly dependent on particle size. A high quenching rate can shorten the coalescence time and lower the coalescence possibility, thereby restraining the nucleus growth. This is also applicable in the coagulation stage. During coagulation, according to Swihart’s study, if the quenching rate is low and the temperature is high enough, the particles sinter faster than they can coagulate and spherical nanoparticles, i.e., hard agglomerates, are produced. If the quenching rate is very high and the temperature is not high enough for sintering, loose agglomerates with open structure are formed. At intermediate conditions, partially sintered nonspherical nanoparticles are produced. In our research, loose agglomerates were formed due to fast quenching. Indeed, there are some other factors that may affect the size of the nanoparticles, such as chamber pressure and injector position. However, in the present research, these parameters were fixed and not discussed here.

2. Effects of plasma properties on nanoparticle productivity and morphology

The nanoparticle productivity, defined as the weight ratio of the obtained nanoparticles to the feedstock, increased considerably in combustion-aided SPS. As shown in Table V, the value was 7.1% for combustion-aided SPS, in contrast to 2.6% and 5.9% for powder spraying by Ar and Ar/O₂, respectively. For the same material, the productivity of the nanoparticles depends on the plasma enthalpy and degree at which the material vaporizes, while the size of the nanoparticles depends on the supersaturation degree and quenching rate of the vapor phase. In view of the plasma enthalpy levels of the three schemes, the trend in Table V is reasonable. In addition to increasing the productivity, the processing also altered the size distribution of Y₂O₃ nanoparticles. The results of DLS analysis illustrated in Fig. 12 indicate that the mean particle size decreased remarkably by O₂ addition in powder spraying and was further reduced by combustion-aided SPS. Furthermore, the size distribution was narrowed in the same sequence. The TEM micrographs in Fig. 13 show that the nanoparticles were in various shapes and loosely agglomerated.

In the case of Ar/O₂ plasma spraying, O₂ addition elevated the volume average temperature and the plasma enthalpy significantly. Besides, the plasma plume became broader and longer and the starting plasma velocity almost halved, both of which literally prolonged the particle residence time and promoted the vaporization. Hence a high supersaturation degree was achieved. Moreover, the quenching rate was also increased due to the plasma enthalpy elevation. When the chamber volume average temperature increased, the temperature contour curve at which nucleation occurred moved closer to the chamber wall in both radial and axial directions. The chamber wall was maintained at room temperature constantly because of the water-cooling system. Hence, a steeper temperature gradient was generated in the proximity of the wall; thereby the cooling rate was increased. This phenomenon has been reported in the modeling work of Desilets et al. in 1997. They found that higher plasma power induced greater temperature gradient, especially for the radial quenching of the vapor flow which is more important for a uniform particle size. Although the lower plasma velocity had negative effect on quenching rate, it could be counteracted by other positive effects. Therefore, since O₂ addition increased both supersaturation degree and quenching rate, the mean size of the nanoparticles decreased and the distribution narrowed (Fig. 12).

As for combustion-aided SPS, modeling results reveal that the volume average temperature (2627 K) was even higher than that of Ar/O₂ plasma (2410 K) and the plasma starting velocity decreased dramatically (20 m/s). Besides, the shape of the plasma plume became shorter and broader. Although a short plume might reduce residence time slightly, it could be safely compensated by the very low plasma velocity. However, lower plasma velocity in turn would cause a lower quenching rate. Fortunately it mainly affected the quenching rate in the axial direction. It was the radial quenching rate that really mattered for vapor cooling, which was greatly increased by the elevated enthalpy and broad plume. Hence, combustion-aided plasma created an even higher supersaturation degree and faster quenching rate than Ar/O₂ plasma did. This explains the further size decreasing and narrowing in Fig. 12.

D. Influence on crystal structure

As reported in our earlier work, rare earth oxides after plasma spraying showed a cubic (C-type) to monoclinic (B-type) phase transformation. The C → B transformation was induced by high-temperature treatment during spraying and retained at room temperature due to fast quenching. In this research, the C → B phase transformation happened, too, and its degree varied with spraying schemes. Determined by
the XRD pattern in Fig. 14(a), Y2O3 raw material had only cubic phase reflections. After being sprayed by various schemes, besides the cubic phase, the particles contained a monoclinic phase, which can be represented by the reflections between diffraction angles of 29.8° and 33.3° [Figs. 14(b) and 14(d)]. As shown in the patterns, Y2O3 monoclinic reflections from Ar/O2 plasma spraying had the strongest intensity among the three schemes, indicating that O2 introduction caused the highest C→B phase transformation degree. Quantitative phase analysis results obtained from XRD pattern refinement in Fig. 15 reveal that the cubic phase proportion in as-sprayed Y2O3 particles was 94, 90, and 99 wt % for Ar spraying, Ar/O2 spraying, and combustion-aided SPS, respectively. Another effect of plasma spraying on crystallography was the unit cell volume change. As shown in Fig. 15, the unit cell volume of Y2O3 cubic phase shrunk after spraying, with the value decreasing in the order of Ar→Ar/O2→combustion-aided SPS.

Y2O3 C-type structure is of cubic bixbyite type in space group Ia3̅, containing 32 metal atoms and 48 oxygen atoms per unit cell, described as a doubled-edge fluorite structure with one-fourth of the oxygen sites vacant and regularly ordered. All metal atoms are coordinated by heavily distorted octahedral of oxygen atoms, i.e., the coordination number of the cation is 6. The cubic structure is stable at room temperature for most rare earth oxides. When the temperature increases above the transformation point, the C-type structure starts to transform to B type. The B-type structure is of monoclinic phase in space group C2/m, with 12 metal atoms and 18 oxygen atoms per unit cell. Some of the cations become 7 coordinated by oxygen atoms while others are still in distorted octahedral environment. From C type to B type, the distance between cations gets shorter and the unit cell volume gets smaller. Therefore, being treated by plasma at very high temperature, Y2O3 cubic unit cells tended to lose oxygen and reconstruct the coordination bonds, with the cations moving closer to each other to form smaller monoclinic unit cells. When Y2O3 left the plume and quenched at a high rate, all the movements at high temperature were frozen and retained at room temperature. Since plasma treatment time was very short, not all the unit cells could finish the transformation. Those cubic unit cells that finished the transformation process exhibited B-type monoclinic phase, whereas those cubic unit cells frozen in the middle of the transformation were still identified as of cubic phase but with a unit cell contraction and distortion.

![FIG. 13. TEM micrographs of Y2O3 nanoparticles synthesized from (a) powder feeding spraying by Ar/O2 and (b) combustion-aided SPS.](image)

![FIG. 14. XRD patterns of Y2O3 particles from raw material and various spraying schemes.](image)
As discussed in our earlier work, for rare earth oxides, enhanced heat treatment leads to an increasing $C \rightarrow B$ phase transformation degree. In Ar/O$_2$ plasma, the elevated plasma enthalpy, broad plume, and long residence time enhanced both reaction kinetics and reaction time; therefore the $C \rightarrow B$ phase transformation degree increased. However, combustion-aided SPS showed a lower phase transformation degree than the others. This is unusual because modeling results show that combustion-aided SPS had higher enthalpy and longer residence time than powder spraying by Ar and Ar/O$_2$, which has been confirmed by the comparison of productivity and size of nanoparticles. Hence, it can be deduced that the phase transformation in spraying was not dependent only on heat treatment but also on other factors. Combustion-aided SPS somehow restricted the $C \rightarrow B$ transformation. The CO$_2$ and H$_2$O produced by acetone combustion reaction might be the main reason. As rare earth sesquioxides are thermodynamically unstable against hydration and carbonation at room temperature, they would be much more correlated with heat treatment than phase transformation. The cubic unit cell volume decreased with increasing heat treatment level, and the relationship was nonlinear because of the same reasons that affected phase transformation degree. It has to be noted that unit cell contraction degree is not correlated with phase transformation degree though it also arises from the crystal structure change. If we compare the cubic unit cell contraction degree with the volume difference between the cubic and monoclinic unit cells, the contraction value was quite small. This signifies that the unit cell contraction only represented the beginning of the phase transformation. Anyway, the unit cell contraction degree can still be used as a qualitative indicator of the plasma heat treatment level.

V. CONCLUSIONS

In the present study, combustion-aided SPS method was developed to synthesize Y$_2$O$_3$ nanoparticles which proved to be a more effective way for plasma processing of refractory materials. The spraying showed superior flowability over powder feeding spraying and better results. Modeling and experimental results reveal that, on account of the dual effects of oxygen dissociation/recombination and solvent combustion, combustion-aided SPS offered a higher plasma enthalpy, lower plasma velocity, and broader plasma plume in comparison with Ar and Ar/O$_2$ plasmas. Hence, particle heat treatment was elevated and radial quenching rate increased significantly. As a consequence, the nanoparticles’ productivity increased and the particle morphology improved remarkably, with mean size being smaller and size distribution being narrower. In addition, combustion-aided SPS also restrained the plasma-induced cubic$\rightarrow$monoclinic phase transformation of the as-sprayed Y$_2$O$_3$ particles to some extent. Finally, Y$_2$O$_3$ nanoparticles with a mean size of 14 nm and a standard deviation of 3.5 nm were synthesized at a productivity of 7.1%.

2. J. R. Roth, Industrial Plasma Engineering (Institute of Physics, Bristol, 1995).