Process map for plasma sprayed aluminum oxide–carbon nanotube nanocomposite coatings

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Abstract

Process map has been developed for plasma sprayed aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) ceramic nanocomposite coatings with carbon nanotube (CNT) reinforcement in varying content and spatial distribution. The process map was constructed using the temperature and velocity data of the in-flight powder particles exiting from the plasma plume. Process map elucidates the interdependence of powder feedstock pre-treatment, CNT content and dispersion behavior on the in-flight particle thermal history and subsequently evolving microstructure and coating properties. High thermal conductivity of CNTs alters the heat transfer characteristic during the splat formation. Microstructure of the coatings consists of fully melted zone (FM), partially melted or solid-state sintered zone (PM) and porosity. Process map provides a processing control tool for plasma spraying of Al\textsubscript{2}O\textsubscript{3}–CNT nanocomposite coatings.

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Keywords: Plasma spraying; Aluminum oxide; Scanning electron microscopy (SEM); In-flight powder diagnosis; Process-map generation

1. Introduction

Plasma sprayed Al\textsubscript{2}O\textsubscript{3} coatings have been used for liners, heat exchangers, crucibles, and thermal heaters [1,2]. However, the processing has been carried out in a relatively empirical manner to serve the specific application. Absence of processing maps and lack of quantifiable parameters in coating fabrication has limited control on the reproducibility of coatings [3]. Although a few researchers have conducted factorial experimental designs for optimization of microstructure, reproducibility of coating still remains a concern due to plethora of variables in plasma spraying that includes equipment, process and powder feedstock [4,5]. It is well known to thermal spray community that “temperature” and “velocity” of the exiting particles from the plasma plume are two important parameters that largely define the microstructure and property of the coating. Temperature controls the degree of melting/heating whereas velocity is an indicator of the degree of the flattening of the splat and subsequent coating structure formation. The advent of the in-flight diagnostic sensors that measure “temperature” and “velocity” of the in-flight particles brings a better control on the plasma spray process and the resultant coating structure [6,7].

In the current work, Al\textsubscript{2}O\textsubscript{3}–carbon nanotube (CNT) powder feedstock has been plasma sprayed to obtain the nanocomposite coating with improved fracture toughness. Owing to exceptional mechanical properties of CNTs (E~1 TPa and fracture strength of ~200 GPa) [8–10], CNTs are ideal reinforcement for toughening ceramics [11–14]. However, there exists a major challenge of dispersing undamaged CNTs in the Al\textsubscript{2}O\textsubscript{3} matrix during plasma spraying. Our research group has shown that CNTs reinforced nanocomposites can be successfully synthesized by plasma spraying [15,16]. Powder pre-treatment of spray drying is a critical step to obtain CNT nanocomposite powder [17]. Spray dried powders are porous spherical agglomerates containing dispersed CNTs and matrix which can easily flow through the powder feeder and plasma gun. In-flight diagnostic sensor has been utilized to develop process map for plasma sprayed Al\textsubscript{2}O\textsubscript{3}–CNT nanocomposite coating. Effect of thermal parameters on the resulting coating is represented in terms of CNT content, dispersion and heat transfer in the spray dried composite powder.
2. Experimental details

2.1. Spray drying of powder feedstock

Nano Al₂O₃ (150 nm particle size) and CNT (95% purity, OD 40–70 nm, 0.5–2.0 μm in length) have been used as powder feedstock for plasma spraying [17]. Owing to high surface friction (because of high surface area), nanoparticles tend to clog the plasma gun nozzle. Hence to improve the flowability of the powder and successfully plasma spray the nanosized particles, it becomes necessary to incorporate powder treatment [17,18]. Following powder treatments have been utilized:

(i) spray drying of nano Al₂O₃ (A-SD powder), size of 35.0±16.8 μm.
(ii) spray drying of nano Al₂O₃ followed by blending with 4 wt. % CNT for 24 hrs (A4C-B powder), size of 21.6±6.5 μm.
(iii) composite spray drying of nano Al₂O₃- 4 wt. % CNT (A4C-SD powder), size of 35.8±16.3 μm.
(iv) composite spray drying of nano Al₂O₃- 8 wt. % CNT (A8C-SD powder), size of 29.1±12.6 μm.

Size of powder agglomerate ranges between 15 and 60 μm. A schematic of the powder pre-treatment along with the nomenclature of the powders is shown in Fig. 1.

2.2. Plasma spraying of spray dried Al₂O₃-CNT nanocomposite

Different powder feedstock (A-SD, A4C-B, A4C-SD and A8C-SD) were plasma sprayed onto AISI 1020 steel substrate with plasma parameters listed in Table 1. Plasma spraying was carried out at a feed rate of 3.0 rpm of Praxair powder feeder, model #1264 that is equivalent to mass flow rate of 9.5–10.5 g/min for above listed powders. Higher power plasma was required to deposit coatings containing CNT.

2.3. In-flight particle diagnostics

Temperature and velocity of the powder particles exiting from the plasma plume were measured using AccuraSpray™ in-flight diagnostic sensor (Tecnar Automation Liée, QC, Canada). The configuration of the plasma gun and in-flight sensor is shown schematically in Fig. 2. The particle velocity is measured based on a time of flight technique, where two optical fibers sense and gather light, which is transmitted to photomultiplier. This in turn generates electronic pulse identifying the particle and triggering a pulse in calculating its time in traveling a certain distance. Cross-correlation factor (CCF) of >0.9 ensures the precision of 0.5% and higher for measuring velocity.

On the other hand, Plank’s law is utilized in measuring temperature by radiation pyrometry. Emissive power of a radiating body is described as a function of wavelength, emissivity and temperature. Dual-wavelength (ratio or two color) pyrometry measures spectral energy in two different wavelength bands (785±20 and 995±20 nm), and using Wein’s

Table 1 Plasma parameters for spraying A-SD, A4C-B, A4C-SD and A8C-SD coatings

<table>
<thead>
<tr>
<th>Coatings</th>
<th>A-SD coating</th>
<th>A4C-B coating</th>
<th>A4C-SD coating</th>
<th>A8C-SD coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>24.0</td>
<td>25.7</td>
<td>30.8</td>
<td>32.3</td>
</tr>
<tr>
<td>Primary, Ar (slm*)</td>
<td>32.1</td>
<td>32.1</td>
<td>32.1</td>
<td>32.1</td>
</tr>
<tr>
<td>Secondary, He (slm)</td>
<td>59.5</td>
<td>59.5</td>
<td>59.5</td>
<td>59.5</td>
</tr>
<tr>
<td>Carrier, Ar (slm)</td>
<td>19.8</td>
<td>19.8</td>
<td>19.8</td>
<td>19.8</td>
</tr>
<tr>
<td>Standoff distance (mm)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Coating thickness (μm)</td>
<td>400</td>
<td>350</td>
<td>450</td>
<td>500</td>
</tr>
</tbody>
</table>

⁎slm: standard liters per minute.
approximation, surface temperature ($T$) of radiating body can be calculated as:

$$\frac{1}{T} = \ln \left( \frac{I_{T_2}}{I_{T_1}} \right) \left( \frac{\lambda_2}{\lambda_1} \right)$$

Where $\lambda_1$ and $\lambda_2$ are two different wavelength bands, $c_2$ is a constant (1.4388 cm K), and $\varepsilon(\lambda, T)$ is the spectral emissivity.

AccuraSpray in-flight sensor utilizes a CCD camera in capturing the plume intensity ($I$) of plasma plume. Temperature is measured with an accuracy of $<0.5\%$ plume intensity (at CCF $>0.9$), when it is higher than 1573 K. Measurement in a volume of 75 mm$^3$ (and not an individual particle) makes temperature and velocity values an ensemble average.

2.4. Characterization of plasma sprayed Al$_2$O$_3$-CNT nanocomposite

Field emission-scanning electron microscope JEOL JSM 6330 F was utilized for imaging the cross-sectional images of plasma sprayed coatings. Archimedes water immersion technique is utilized to calculate the density of plasma sprayed coatings. Image-Pro % Plus, Version 5.1 imaging software (2004 Media Cybernetics Inc.) has been used for quantitative image analysis of the microstructural features. Mechanical characterization was done using Shanghai Taiming Optical Instruments, Zhongguo, HXD-100 TMC microhardness tester at a load of 200 g load and dwell time of 15 s. Vickers indentation technique was utilized to estimate the fracture toughness via impediment of radial-cracks using Antis equation [19]. Statistical analysis demonstrated more than 95% confidence level in the mean value measurement of fracture toughness for the plasma sprayed coatings.

3. Results

3.1. Powder morphology and CNT dispersion

Fig. 3a shows that CNTs are dispersed only on the surface of A4C-B powder, whereas CNTs are dispersed throughout the A4C-SD (Fig. 3b) and A8C-SD (Fig. 3c) powder agglomerate. This contrasting dispersion behavior of same CNT content (4 wt.%) is achieved by composite spray drying in A4C-SD powder (explained in detail in our earlier publication) [17]. A8C-SD powder feedstock has higher CNT content which are well dispersed in the Al$_2$O$_3$ matrix. The role of CNT content and dispersion behavior in altering the thermal and kinetic profile of in-flight powder particles is observed and discussed later in this paper. A-SD powder feedstock was selected as the baseline sample without CNT addition.

3.2. Plasma sprayed Al$_2$O$_3$-CNT nanocomposite coatings

Microstructure of the plasma sprayed A-SD, A4C-B, A4C-SD, and A8C-SD coatings is shown in the cross-sectional
images, Fig. 4a–d and quantified as: fully melted and resolidified structure (FM), partially melted/solid-state sintered region (PM), and porosity using Image-Pro imaging software. Fully melted region is obtained from the melting and resolidification of the outer zone of the spray dried powder whereas partially melted region (PM) is formed via solid-state sintering of the core of the spray dried powder. The quantitative image analysis (Fig. 5) of microstructural features of A-SD coating is adopted as a baseline to compare the other microstructures. As observed from Fig. 5, A4C-B coating exhibited slight increase in the FM content (to 82.1%) whereas reduction of FM content to 71.4% and 52.6% was observed in the A4C-SD and A8C-SD coating shows FM content of 80.9%, PM content of 15.9% and 3.2% porosity A-SD coatings respectively. Higher power plasma (Table 1) was used for A4C-SD and A8C-SD powder which intuitively should infer higher degree of fully melted (FM) region in corresponding coatings. Analysis of this anomaly requires an insight into the thermal and kinetic history experienced by the in-flight powder particles, which is explained later.

It is interesting to note that the combination of FM, PM and porosity regions combined with CNT addition and dispersion exhibited contrasting fracture toughness values. A-SD coating has fracture toughness of $3.22 \pm 0.22$ MPa m$^{1/2}$, which increased to $3.86 \pm 0.16$ MPa m$^{1/2}$ with the addition of 4 wt.% CNT in A4C-B coating [17]. Fracture toughness increased to $4.60 \pm$
0.27 MPa m\(^{1/2}\) in A4C-SD coating due to improved CNT dispersion [17]. Increasing CNT content to 8 wt.% increased the fracture toughness to 5.04±0.58 MPa m\(^{1/2}\) for A8C-SD coating, which is an increase of 57% percent in comparison with A-SD coating [20]. Toughening of the nanocomposite coatings is a function of the generated microstructure, which consequently depends on the thermal and kinetic history experienced by in-flight powders.

### 3.3. In-flight particle characteristics

Temperature and velocity variation of in-flight particles for different powders is evinced in Table 2. The difference in the temperature and velocity is attributed to several factors: (i) CNT content (ii) CNT dispersion (iii) and morphology of spray dried composite agglomerate. Due to the presence of CNTs which have high thermal conductivity and their spatial configuration in porous spray dried agglomerate, heat transfer becomes a complex phenomenon that affects the microstructure evolution and densification in plasma sprayed nanocomposite coatings.

### 4. Discussion

#### 4.1. Parameters affecting microstructure evolution and coating properties

The properties of plasma sprayed coatings are dependent on several parameters that include degree of melting (dictated by particle temperature), impact and flattening of splat (dictated by particle velocity), CNT content and its degree of dispersion in spray dried particles. Furthermore, there is interdependence of thermal and kinetic history with CNT content and dispersion that complicates the processing. Strong influence of CNT content and distribution in imparting thermal exposure to the blended and spray dried powder particles can be envisaged from the in-flight particle diagnostic data in Table 2 [21]. A flow diagram showing interdependence of several variables that affect coating microstructure and properties is presented in Fig. 6.

#### 4.2. Heat transfer in splat formed by spray dried powder

Microstructure of the plasma sprayed coating depends on the splat formation mechanism. Cooling rate defines the manner in which a molten particle solidifies to form a splat. Owing to flattening (given by splat thickness, \(S\)) of molten/semi-molten particles upon impact, overall cooling rate of the splat is controlled by the interfacial heat transfer coefficient (\(h\)). Isolation of overall splat cooling rate from the localized thermal gradient occurring with in nanosized Al\(_2\)O\(_3\) particles in spray...
dried agglomerate can be confirmed by a lower (<0.1) Biot’s number \((B)\) \([22]\) as:

\[
B = \frac{hS}{k}
\]

(2)

Where \(h\) and \(k\) are coefficient of heat transfer and thermal conductivity, and splat thickness \((S)\) is given as \([22]\):

\[
S = \left(\frac{2\eta d^3}{33\rho v}\right)^{0.25}
\]

(3)

Where \(\eta\) is viscosity, \(d\) is diameter, \(\rho\) is density, and \(v\) is velocity of the molten splat. The average value of heat transfer coefficient for splat thickness less than 10 \(\mu\)m is approximately \(10^5\) W/mK \([22]\). In our earlier work on the thermal conductivity of the CNT reinforced plasma sprayed coatings, a typical value of 5 W/mK was obtained \([21]\). Since the spray dried agglomerates range between 15 and 60 \(\mu\)m, the average particle diameter \((d)\) is assumed to be 35 \(\mu\)m. Viscosity of molten \(Al_2O_3\) is taken as 0.15 poise (at \(\sim 2800\) K), with a density of 3.99 g/cc for the calculation purpose \([22]\). From the observed thermal history of the powders, Table 2, in-flight particle velocity of \(\sim 250\) m/s is taken as a representative value for calculation purpose. Using the aforementioned data as the input in the Eq. (2), the Biot number \((B)\) is evaluated to be 0.085. The Biot number is further reduced with the creation of new interfaces that increases thermal resistance. Thermal resistance increases due to creation of (i) CNT–\(Al_2O_3\) interfaces, and (ii) inherent porosity \((\sim 30–40\%)\) in the spray dried agglomerate. Though low Biot’s number (0.085) confirms the independence of thermal gradient existing within the splats to the overall cooling rate of coating, existence of PM region defies the existence of uniform temperature within splats. Disparity of Biot’s number arises because plasma parameters are controlled in a way to melt the surface and allow solid-state sintering of the core of powder. Each splat forming from the spray dried powder can, therefore, be considered as multiple splats attaining heat from surrounding particle temperature. Thermal gradients occur within in the splat because of the nano particle–particle (\(Al_2O_3–Al_2O_3\), and \(Al_2O_3–CNT\)) interfacial thermal resistance \([21]\). An interlinked dependence of Biot’s number (<0.1) and porosity on the thermal resistance, therefore, is substantiated by the role of powder treatment towards describing thermal history of in-flight powder particles.

4.3. Process map

Excellent thermal conductivity of CNTs can dramatically alter the thermal exposure observed by in-flight particles. Owing to higher thermal conductivity of CNTs \((\sim 3000\) W/mK\) \([16]\) when compared to dense \(Al_2O_3\) \((\sim 36\) W/mK\) \([16,23]\), high heat is absorbed on the surface leading to enhanced thermal exposure and higher attained temperatures by A4C-B in-flight powder \((\Delta T=+376\) K\), Fig. 7, when compared to that of A-SD powder. Contrastingly, the reduction of thermal exposure in A4C-SD spray dried coating \((2332\) K\) is attributed to uniform CNT dispersion both on the surface and inside of the powder particles \((Fig. 3b)\). Reduced number of CNTs are present on the surface of A4C-SD spray dried powder (since content is same and CNTs are distributed uniformly also at inside of powder), thereby superheating of surface by CNTs is reduced \((\Delta T=-566\) K\), Fig. 7, when compared to that of A4C-B powder. Additionally, CNT content in the inside of the A4C-SD powder now ‘soak up’ the heat acquired by the surface CNTs towards reducing the temperature attained by powder particles.

![Fig. 7. Process map of plasma sprayed coatings indicating change in temperature and velocity of in-flight particles with CNT addition and dispersion.](image-url)
addition of CNTs (in A8C-SD powder) should marginally increase the surface temperature, but uniform CNT distribution inside the particle also increases and hence, heat extraction rate also increases. Owing to the rapid kinetics inherent to the process, short residence times of $\sim 4 \times 10^{-4}$ s in the plasma plume do not suffice superheating of surface CNTs. This phenomenon further lowers the temperature (to 2241 K) acquired by the A8C-SD powder particles in the plasma plume ($\Delta T = -91$ K), Fig. 7, when compared to A4C-SD powder. This explains the anomaly why A4C-SD and A8C-SD displayed reduced degree of fully melted (FM) region even though higher power plasma was used. Reduced thermal exposure resulting from increasing CNT content and dispersion suggest that higher plasma power is required to heat/melt Al$_2$O$_3$ particles and get thick coatings from A4C-SD and A8C-SD powders.

CNT spatial distribution also results a difference in the velocities observed by in-flight particles. Due to lower density of CNTs (~2.1 g/cc when compared to Al$_2$O$_3$ ~3.99 g/cc) inherent kinetic energy of particles is reduced. Reduced carrying capability of particles in carrier gas is elicited by reduced velocity (~271 m/s) of A4C-B particles ($\Delta v = -18$ m/s) when compared to that of A-SD powder (~289 m/s) as observed in Fig. 7. This difference is narrowed owing to agglomeration tendency of surface CNTs. Further CNT dispersion in A4C-SD and A8C-SD powders create interface mismatches between CNTs and Al$_2$O$_3$ powder particles, which inherently increase powder porosity. Reduced mass of the uniform porous cake with CNT addition (as in A8C-SD powder) thereby experiences enhanced air resistance at the interfacial surfaces. Thereby friction from the air resistance result reduced velocity of the A4C-SD (244 m/s, $\Delta v = -45$ m/s) and A8C-SD (232 m/s, $\Delta v = -57$ m/s) powder agglomerates when compared to that of A-SD in-flight particles. Poor densification of A4C-B coating was observed in spite of highest temperature (2898 K) and high velocity (271 m/s). This is attributed to the poor dispersion of CNTs in A4C-B powder. Hence, agglomerated CNTs lack the reorientation ability and are not available throughout the aluminum oxide matrix to fill the voids in A4C-B coating, which consequently results lower density [17]. Whereas in A4C-SD and A8C-SD coatings, improved CNT dispersion assists access to inter-splat voids more effectively and produces denser coatings [17]. Preference of CNT entrapment at the splat interface is presented in Fig. 8.

It becomes clear now that plasma parameters, CNT content and CNT dispersion are critical in defining the thermal exposure experienced by the powder particles. Thereby, it can be implied from the measurements that CNT dispersion offers two advantages: (i) damage to CNTs is reduced due to reduced thermal exposure, and (ii) solid-state sintered region can successfully retain CNTs and enhance the densification of the plasma sprayed coatings. Subsequently, thermal history assists evolution of FM and PM in the generated microstructure. Retention of nanocrystalline solid-state sintered region (FM region) in enhancing the fracture toughness is already stressed by many researchers [17, 24–26]. Therefore, enhanced control on the processing is offered by the in-situ monitoring of in-flight powder particles towards enunciating microstructural generation and mechanical property evaluation of Al$_2$O$_3$–CNT nanocomposite ceramic.

5. Conclusions

Process map of plasma sprayed Al$_2$O$_3$ coatings with varying content of CNT addition and degree of dispersion was successfully developed in terms of thermal and kinetic characteristic of in-flight particles. CNT agglomeration (in A4C-B powder) evinced enhanced thermal exposure ($\Delta T = +376$ K), and reduced velocity ($\Delta v = -18$ m/s) of the in-flight powder particles as compared with A-SD particles. Composite spray drying (of A4C-SD and A8C-SD powders) has resulted reduced thermal exposure because of uniform CNT dispersion inside the core and surface of spray dried agglomerate. CNTs residing in core act as heat sinks to reduce average particle temperature. Microstructure evolution in terms of fully molten region, partially molten region and porosity is reasoned to the thermal history experienced by the in-flight particles. The interdependence of particle morphology, CNT content and dispersion, and heat transfer on microstructural evolution is established.

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