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Splat morphology of plasma sprayed aluminum oxide reinforced with carbon nanotubes: A comparison between experiments and simulation

Anup Kumar Keshri [a,b], Arvind Agarwal [a,*]

[a] Plasma Forming Laboratory, Mechanical and Materials Engineering, Florida International University, Miami, FL 33174, USA
[b] Manufacturing Division, School of Mechanical and Building Sciences, Vellore Institute of Technology University, Vellore 632 014, Tamil Nadu, India

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ABSTRACT

This study elucidates the effect of carbon nanotube (CNT) addition on the splat formation in plasma sprayed aluminum oxide (Al_2O_3) composite coating using experimental and computational methods. CNT content was varied as 0, 4 and 8 wt.% in Al_2O_3 matrix. With an increasing CNT content, splat morphology became more circular and disk-shaped. The average diameter of disk-shaped splats increased from 28.6 ± 1.4 μm for Al_2O_3 to 43.2 ± 1.3 μm for Al_2O_3–8 wt.% CNT. The population density of splats with fingers, fragments, and voids was the lowest for the highest (8 wt.%) CNT content. The addition of CNTs resulted in two simultaneously competing phenomena *viz.* increased thermal capacity and increased viscosity of the melt. Increased thermal capacity delayed the localized solidification resulting in higher splat diameter while agglomeration of CNTs at the periphery of the splat results in higher viscosity of the melt which suppresses the splat fragmentation that leads to increased population density of disk shaped splats. Splat morphology of three compositions was also simulated using SIMDROP software, which showed a good agreement with the experimentally collected splats.

1. Introduction

Splat is the smallest unit of the microstructure of plasma sprayed coatings. The properties of the coatings are largely dependent on the splat morphology and their stacking [1–4]. Incomplete melting and improper stacking of splats can result in globular voids, poor adhesion at the inter-splat boundary which can have adverse effect on the mechanical, thermal and electrical properties of the coatings [5–7]. Hence splat formation and its morphology play a significant role in tailoring the coating properties. Several studies have been reported on the morphological aspect of splats [1,3,4,8–10] which suggest that splat morphology is largely dependent on (i) feedstock material properties [8], (ii) thermal and kinetic state of the in-flight particle [8,10] and (iii) substrate chemical state, roughness and temperature [3,4,11].

Elsebaei et al. [8] performed a study on the morphology of individual splats for different sets of plasma operating parameters (arc current: 700, 870 A, stand-off distance: 80, 100 mm) for the regular yttria stabilized zirconia (YSZ) (particle size: 45–100 μm) and the spherical agglomerate of YSZ (agglomerate size: 20–40 μm) synthesized from the nano-YSZ powder particle. Spherical agglomerate of nano-YSZ was used with the intent to melt the periphery of the agglomerate and to retain the nano-features in the core. Such coating resulted in bimodal microstructure. Lima et al. [12] studied thermal spray coatings synthesized from the nanostructured ceramic agglomerated powder and concluded that it was necessary to avoid the full melting of the agglomerates to preserve nanostructure in the coating. Elsebaei et al. [8] concluded that circularity (degree of roundness) and flattening degree (ratio of the diameter of splat to starting droplet) of YSZ splats synthesized from the spherical agglomerate were larger than the regular-YSZ splats. This was attributed to the smaller particle size, higher particle temperature and velocity of agglomerated-YSZ particles [8]. Splats synthesized using spherical agglomerates of YSZ were more disk shaped (*i.e.* better circularity) as compared to regular-YSZ splats at a higher stand-off distance [8]. This was due to the higher particle velocity of agglomerated-YSZ compared to regular-YSZ particle [8].

Bianchi et al. [13] deposited single splats by spraying micron-size zirconia on "cold" 304L stainless steel substrate (~100 °C) and observed a highly fragmented morphology. Perfect disk shaped splats were obtained for the substrate heated to 300 °C [13]. Fukumoto et al. [14,15] studied the relationship between the splat morphology (from the micron-sized feedstock particles) and the substrate temperature and observed distinct changes in the splat morphology. Threshold transition temperature for the substrate was first identified by Fukumoto et al. [15], beyond which splat morphology changes from fragmented to disk shaped. Sampath et al. [3,4] carried out a study on the effect of substrate temperature on the splat formation for partially stabilized micron-sized zirconia particles. The threshold transition temperature was found in the range of 250–300 °C [3]. In the case of "cold" substrates, initiation or localized solidification is responsible for

* Corresponding author. Tel.: +1 305 348 1701; fax: +1 305 348 1932.
E-mail address: agarwala@fiu.edu (A. Agarwal).

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spreading instability which leads to flattening splashing [3,4]. Preheated substrate above the transition temperature provides better contact and uniform heat conduction which minimizes the localized solidification [3,4]. The substrate heating also allows condensate and adsorbate desorption. Li et al. [16] studied the effect of substrate preheating temperature and surface organic covering on splat formation. Splats (aluminum, nickel, copper, Al_2O_3 and molybdenum) were deposited on polished stainless steel substrate surface covered with different organic substances (xylene, glycol and glycerol). It was found that when the preheating temperature exceeded 50 °C over the boiling point of organic substance, the regular disk type splats were formed [16]. An optimum substrate preheating is required to strike a balance between better splat formation and minimal residual stress. These studies indicate that powder feedstock, processing conditions and substrate conditions have significant effect on the splat formation.

Our research group has worked extensively on the synthesis of CNT reinforced aluminum oxide coatings by plasma spray technique [17–27]. Comprehensive process maps have been successfully developed to synthesize “lowest porosity” plasma sprayed Al_2O_3 composite coatings with 0, 4 and 8 wt.% CNT reinforcement [26]. Balani et al. obtained ~200% improvement in the elastic modulus [19], 57% improvement in the fracture toughness [17] and 49 times enhancement in dry sliding wear resistance [21] by adding 8 wt.% CNTs in Al_2O_3 coatings. Improved elastic modulus, fracture toughness and wear resistance were mainly attributed to excellent dispersion of CNTs in the Al_2O_3 matrix that promotes toughening mechanisms such as CNT bridging, and crack deflection at CNT/Al_2O_3 interface [17–21]. A majority of our past work on Al_2O_3–CNT coatings was focused on studying the material property as function of process, microstructure and CNT content. However, the role of CNT in the splat formation was never addressed. Bakshi et al. [27] did a preliminary study on the role of CNT in metallic Al–Si splat formation and concluded that splat shape is governed by the viscosity and thermal conductivity of the droplet which are dependent on the CNT content. Higher CNT content (10 wt.%) leads to disk shaped Al–Si splat as compared to lower CNT content (5 wt.%), which was attributed to increase in the viscosity of the melt due to increased CNT content [27].

Motivated by this scenario, the objective of this study is to understand the role of CNT in the Al_2O_3 splat formation. The effect of varying CNT content on the splat morphologies has been investigated. Splat formation can be optimized by experimentation but it requires extensive and time consuming experiments due to a large number of processing variables involved in plasma spraying. Splat morphology simulation for the given processing variables can save considerable amount of time. In this study, splat morphology simulation has also been performed using SIMDROP (Simulent Drop 3.0, Simulent Inc., Toronto, Canada) and comparison has been made with experimentally deposited splats.

2. Experimental

2.1. Powder feedstock

Sub-micron sized Al_2O_3 (~150 nm, average diameter) powder and multiwall carbon nanotubes (95%+ purity, 40–70 nm outer diameter, 0.5–2.0 μm in length) were used as starting materials. Since sub-micron sized fine powder and CNTs cannot be fed in the plasma flow using conventional carrier gas due to their high interparticle friction and resulting inconsistent flow, spray drying was implemented to manufacture micron-sized agglomerates. Spray drying also allows homogeneous dispersion of CNTs in Al_2O_3 matrix. Sub-micron Al_2O_3 powder was spray dried (referred as A-SD) to obtain spherical agglomerates of 30 ± 10 μm in diameter. The diameter of the spherical agglomerates was measured from 5 to 6 different SEM images. From each image, 15–20 measurements of agglomerate diameter were taken. Powder size distribution of A-SD, A4C-SD and A8C-SD is shown in Fig. 1(a)–(c) respectively. Spray drying of sub-micron Al_2O_3 with 4 wt.% CNTs (referred as A4C-SD) and 8 wt.% CNTs (referred as A8C-SD) resulted in spherical agglomerates of 26 ± 7 μm and 24 ± 5 μm respectively. A-SD powder served as the control sample to investigate the effect of CNT addition.

2.2. Synthesis of single splat

A-SD, A4C-SD, and A8C-SD powders were plasma sprayed using SG 100 gun (Praxair Surface Technology, Danbury, CT, USA) on polished (R_a = 0.03 μm, R_Z = 0.098 μm) AISI 1020 steel substrate (22 mm × 19 mm × 3.2 mm) to collect splats. Diameters of the splats were measured using Image J software (http://rsbweb.nih.gov/ij/index.html). A total of ~100 splats were taken into consideration from 5 to 6 different SEM images. Splats were deposited at optimized plasma process parameters which showed lowest porosity in the coating [26]. Details of the optimization of plasma process parameters can be found elsewhere [26]. Substrate preheat temperature was maintained at 453 K which was the same as in the optimization study for the lowest porosity coating [26]. Table 1 summarizes the plasma spray operating parameters for splat experiments. Carrier gas flow rate was adjusted for three different powder feedstock to maintain a constant powder feed rate of 3 g/min. Fig. 2(a) shows the set-up for plasma spraying of single splats. Temperature and velocity of the in-flight powder

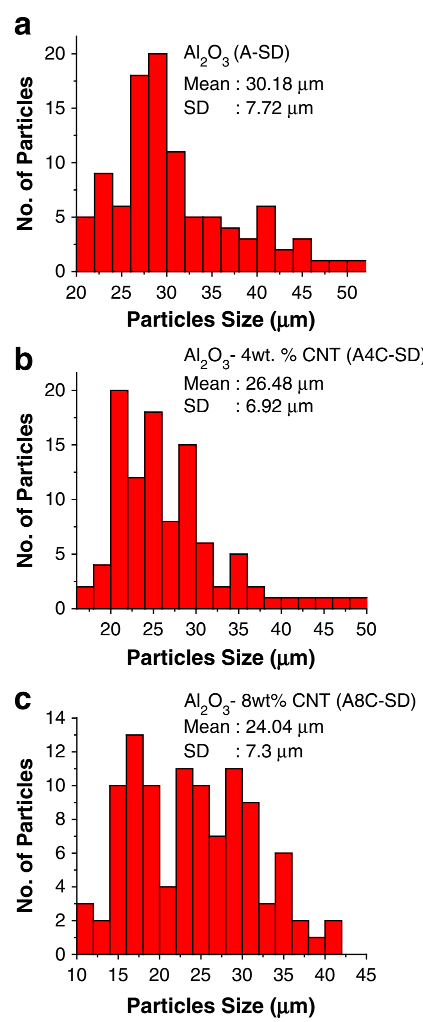

Fig. 1. Particle size distribution of (a) Al_2O_3 (A-SD) spherical agglomerates, (b) Al_2O_3–4 wt.% CNT (A4C-SD) spherical agglomerates and (c) Al_2O_3–8 wt.% CNT (A8C-SD) spherical agglomerates. A total of ~100 particles were considered from 5 to 6 different SEM images.