

The effects of gas and metal characteristics on sprayed metal coatings

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Abstract

Supersonic particle deposition (also known as cold spray) is a surface coating process whereby metal particles are accelerated to supersonic speeds while entrained in nozzle gas flow and are subsequently deposited by impact onto a surface. Particle velocity is critical for optimal deposition efficiency and coating quality, and several parameters, including gas conditions, particle characteristics and nozzle geometry affect particle velocity. This study investigates the relationship between particle velocity and coating quality and investigates how nozzle design influences particle velocity. Performance is described through modelling and verified by direct velocity measurements.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

The US Army utilizes metal coatings in many of its weapons systems for the strengthening or protection of vulnerable substrates. The quality of these coatings is characterized by the density of the metal coating and its ability to adhere to the substrate. Extremely dense and adherent metal coatings can be applied to surfaces by impacting metal particles onto the surface at supersonic velocities. This process, called Supersonic Particle Deposition (SPD), is carried out at the US Army Research Laboratory (ARL) in Aberdeen, MD.

Cold spray as a coating technology was initially developed in the mid-1980s at the Institute for Theoretical and Applied Mechanics of the Siberian Division of the Russian Academy of Science in Novosibirsk [1, 2]. The Russian scientists successfully deposited a wide range of pure metals, metallic alloys, polymers and composites onto a variety of substrate materials, and they demonstrated that very high coating deposition rates are attainable using the cold spray process. Currently, a variety of cold spray research is being conducted at institutions in the US, Russia, Germany and Japan [3].

The ARL system accelerates micron-sized particles to high velocities by entraining the particles in the flow of a supersonic nozzle. This system is shown in figure 1. High velocity

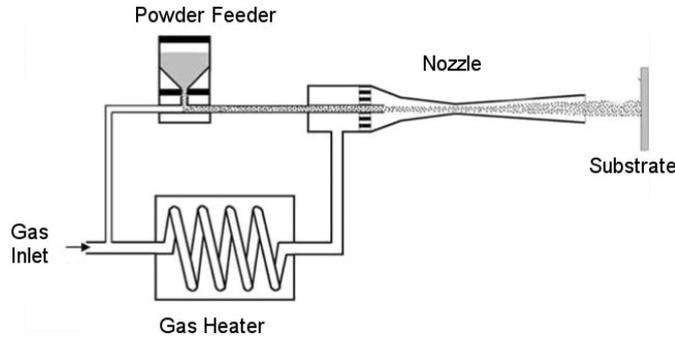


Figure 1. SPD operating principle.

is necessary for optimal particle deposition and density, and several parameters, including gas conditions, particle characteristics and nozzle geometry, affect particle velocity. This work examines the effects of these parameters on coating characteristics.

2. Procedure

Coating by SPD takes place in two stages—the deposition of particles on the bare substrate and the deposition of new particles over previously deposited particles. Both processes are strongly dependent on particle velocity and substrate and particle material properties. The effects of these parameters on the particle–substrate interface (bond strength) and particle-on-particle buildup (deposition efficiency (DE)) of SPD-deposited coatings can be effectively modelled by means of empirical impact study results and conventional nozzle flow relationships.

2.1. Particle–substrate Interface

The bond strength between a metal coating and its substrate is principally determined by the degree of intimate contact and interlocking sites between the two materials. These phenomena are controlled by the particle velocity and the hardness of the substrate, which together determine the cratering that results from the impact. An empirical projectile penetration law by Eichelberger and Gehring [4] relates the crater volume, m^3 , produced by micrometeoroid impact on spacecraft. This is given by equation (1):

$$\text{Volume} = \frac{(4 \times 10^{-5})E}{B}, \quad (1)$$

where E is the particle kinetic energy, and B is the substrate Brinell hardness number. It was shown [5] that this equation yielded accurate results for velocities below 10 km s^{-1} , the range of SPD particles.

In order to make use of equation (1) substitute $1/2(4/3\pi r^3 \rho_p)V_p^2$ for E , where ρ_p is the particle density, r is the particle radius and V_p is the particle velocity. The crater volume is assumed to be the particle face area (πr^2) times the penetration depth, L . Thus equation (1) becomes:

$$\text{Volume} = (\pi r^2)L = \frac{(4 \times 10^{-5})(1/2)(\rho_p 4/3\pi r^3)V_p^2}{B}. \quad (2)$$

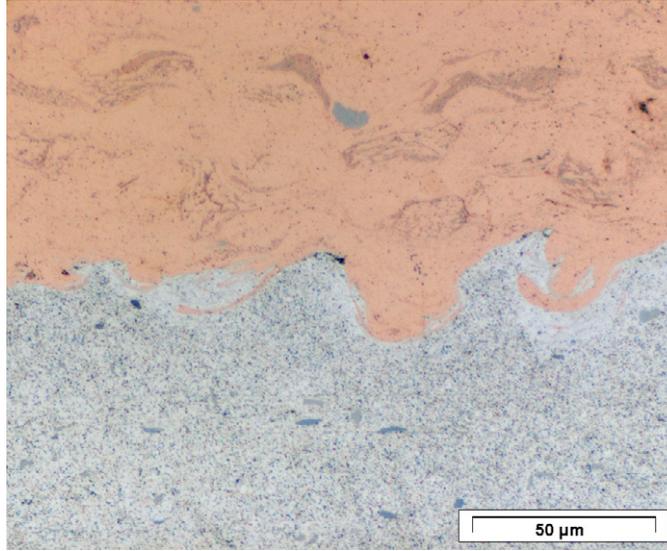


Figure 2. Copper–aluminium interface.

The penetration depth, L , in m is then given by the following:

$$L = (4 \times 10^{-5}) \left(\frac{2\rho_p r}{3} \right) \left(\frac{V_p^2}{B} \right). \quad (3)$$

If it is assumed that the onset of good interfacial mixing occurs when the particle is completely embedded at $L = 2r$, the onset velocity is found to be

$$V_p = \left[(7.5 \times 10^4) \left(\frac{B}{\rho_p} \right) \right]^{0.5}. \quad (4)$$

Equation (4) gives a simple, empirical method to estimate the attainment of interface mixing via particle penetration. This equation, along with the ability to calculate particle velocity (described in 2.2), is used to determine the compatibility of various particles and substrates. For example, equation (4) gives an onset velocity of 500 m s^{-1} for copper particles impacting 6061-T6511 aluminium. Under these conditions the interface shown by figure 2 results. Mixing between the copper and aluminium is clearly obtained with a measured bond strength exceeding 10 000 psi.

2.2. Deposition efficiency

The modelling of DE, or particles building up over previously deposited particles, can be broken down into three tasks.

1. The gas flow and temperature in the nozzle are calculated by means of isentropic (frictionless) gas dynamic principles.
2. Drag and heat transfer coefficients from solid rocket analyses are used to iteratively calculate particle velocity and temperature through the nozzle.
3. An empirical relationship between particle velocity and particle material characteristics is used to calculate the DE or the percentage of incoming particles that adhere and form the deposition.

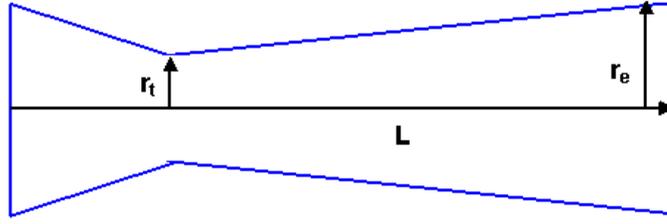


Figure 3. Nozzle geometry.

2.2.1. *Gas flow.* The gas flow model uses isentropic relationships and linear nozzle geometry. The assumptions for the calculation are as follows.

- The gas obeys the perfect gas law.
- There is no friction impeding the gas flow.
- The gas flow is adiabatic, i.e. no heat loss occurs to the surroundings.
- Steady-state conditions exist.
- Expansion of the gas occurs in a uniform manner without shock or discontinuities.
- Flow through the nozzle is one-dimensional, hence the flow velocity, pressure and density are uniform across any cross section normal to the nozzle axis.
- Particles do not influence gas conditions.

Under these conditions, the relationship [6] between nozzle area, A , and Mach number is given by equation (5), where γ is the ratio of gas specific heats (C_p/C_v).

$$\frac{A_1}{A_2} = \frac{M_2}{M_1} \left\{ \frac{1 + [(\gamma - 1)/2] M_1^2}{1 + [(\gamma - 1)/2] M_2^2} \right\}^{(\gamma+1)/2(\gamma-1)} \quad (5)$$

The simple, conical, nozzle geometry shown in figure 3 is assumed. A small initial subsonic Mach number and initial (stagnation) values of pressure and temperature are assigned at the converging section of the nozzle. The Mach number is then iteratively increased while gas characteristics are calculated for each point through the isentropic relationships of equations (6) and (7). Linear progression along the nozzle axis is calculated from the area change given by equation (5) and the assumed nozzle geometry.

$$\frac{T_0}{T} = 1 + \left(\frac{\gamma - 1}{2} \right) M^2. \quad (6)$$

$$\frac{p_0}{p} = \left[1 + \left(\frac{\gamma - 1}{2} \right) M^2 \right]^{\gamma/(\gamma-1)}. \quad (7)$$

Supersonic flow is obtained when the nozzle is choked, where the ratio of the exit pressure, p_E , to chamber pressure, p_0 , satisfies equation (8). This condition will be satisfied in all subsequent calculations.

$$\frac{p_E}{p_0} < \left[1 - \frac{\{(\gamma - 1)/2\}}{1 + \{(\gamma - 1)/2\}} \right]^{\gamma/(\gamma-1)}. \quad (8)$$

2.2.2. *Particle motion.* Once the gas conditions and velocity are characterized within the nozzle, particle velocity is iteratively calculated down the length of the nozzle through the use of a solid rocket nozzle particle drag relationship. This relationship predicts the accelerating force on the particle.

$$m \frac{dV_p}{dt} = C_D (\pi/8) \rho_g d^2 (V_g - V_p)^2, \quad (9)$$

where V_p and V_g are particle and gas velocities, m is particle mass, ρ_g is gas density and d is particle diameter.

Carlson and Hoglund [7] correct the simple Stokes drag law relationship for inertial, compressibility and rarefaction effects through the empirical relationship of equation (10).

$$C_D = \frac{24}{Re} \left[\frac{(1 + 0.15 Re_e^{0.687})(1 + e^{-0.427/M_p^{4.63} + 3.0/Re_e^{0.88}})}{1 + (M_p/Re)(3.82 + 1.28e^{-1.25Re/M_p})} \right]. \quad (10)$$

M_p is the Mach number of the gas–particle velocity difference and Re is the gas–particle Reynolds number.

Particle temperature is subsequently calculated through the application of the gas–particle heat transfer relationship for forced convection, given by equation (11).

$$c_p \frac{dT_p}{dt} = \left(\frac{N_u k}{d} \right) \left(\frac{A_p}{m} \right) (T_g - T_p), \quad (11)$$

where c_p is the particle heat capacity, T_p and T_g are the particle and gas temperatures, N_u is the Nusselt number, k is the gas conductivity and A_p is the particle surface area.

Ranz and Marshall [8] show that the Nusselt number for this situation is given by

$$N_u = 2.0 + Re^{0.5} Pr^{0.33} \quad (12)$$

where Pr is the Prandtl number.

2.2.3. *Apply empirical relationship.* The ability to predict DE allows one to choose gas and particle parameters that will yield good DE and reduce operating time and wasted powder. An empirical relationship between particle parameters and the critical velocity needed for a particle to stick to a previously deposited layer and the gasdynamic velocity model shown previously is used to predict DE. The empirical relationship for the particle critical velocity is given by Assadi *et al* [9] as

$$\text{Critical velocity (m s}^{-1}\text{)} = 667 - 14\rho_p + 0.08T_m + 0.1\sigma_\mu - 0.4T_e, \quad (13)$$

where ρ_p = particle density, T_m = particle melting point, σ_μ = particle UTS and T_e = particle exit temperature.

The critical velocity as determined by equation (13) and the particle velocities as calculated in section 2 above then allow an identification of the particle size that can achieve this velocity. The powders employed in SPD are not of uniform diameter but are characterized by a distribution of particle diameters. The particle size distribution is defined as normal. DE is thus calculated as the percentage of particles having a smaller diameter (and thus having a higher velocity than) than the particle diameter achieving the critical velocity. Equation (14) defines the mass percentage of particles having a smaller diameter than the particle diameter, d , which is the DE. It is a normal relationship where MMD is the mass mean diameter of the feed powder and σ is the geometric standard deviation of the distribution.

$$DE = \left(\frac{100}{2} \right) \left[1 + \operatorname{erf} \left(\frac{d - \text{MMD}}{\sigma \sqrt{2}} \right) \right]. \quad (14)$$

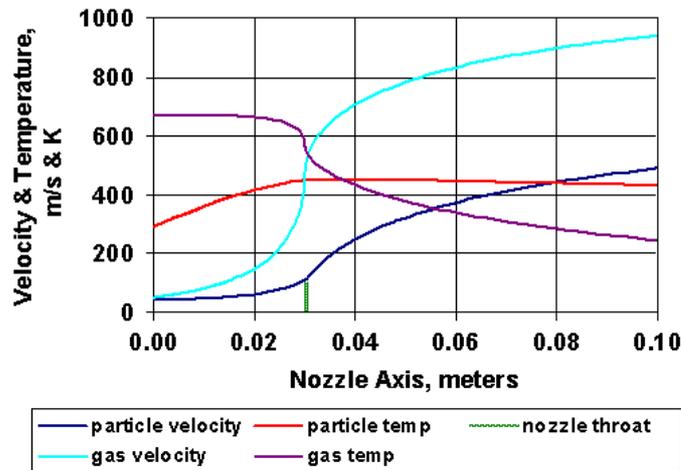


Figure 4. Gas-particle conditions during nozzle traverse.

3. Calculations and discussion

The gas stagnation (chamber) pressure and temperature are 400 psi and 673 K, unless otherwise noted. The initial particle temperature is 293 K. Nozzle length affects particle velocity through the duration of acceleration and is a variable in some calculations. The typical length for SPD equipment is 10–30 cm. Nozzle diameter does not directly enter the calculations, except in the form of area ratios. The typical throat diameter in SPD equipment is 2 mm.

All calculations are carried out for spherical copper particles. The mass ratio of particles to gas in typical SPD operation is less than 0.05; therefore, it is assumed that the presence of particles does not affect gas flow and that no particle-to-particle contact occurs. An individual calculation applies to a single particle of given diameter. Particle size effects are determined by multiple calculations for various particle diameters. Gross DE is then based on the particle size that achieves the critical velocity given by equation (13) and on the percentage smaller than that size given by the powder size distribution given by equation (14). The particle size distribution assumed to be normal with a standard deviation of 4, which describes the powder used.

The SPD system can utilize either nitrogen or helium gas. Helium gas yields higher gas and particle velocities due to its lower molecular weight. The type of gas used for each calculation will be noted. The independent variables are gas type, particle MMD and nozzle geometry. The dependent variables that are calculated are particle exit velocity, temperature and DE.

Figure 4 shows a gas-particle calculation for 20 μm copper particles. Nitrogen gas, initially at 400 psi and 673 K, is the accelerant. The gas converts temperature and pressure into velocity as it is expanded in the converging-diverging nozzle. The gas attains Mach 1 at the throat and is about Mach 3 at the nozzle exit, where the area ratio of exit to throat is 4. Particle velocity is related to the gas velocity through the drag relationship, equation (9). A gas exit velocity of 950 m s^{-1} and a particle exit velocity of 500 m s^{-1} are seen in this case. Particle temperature is related to the gas temperature through convective heat transfer, equation (11). The particles are seen to heat up when they are cooler than the gas and begin to cool down after the gas has expanded to temperatures lower than that of the particles. Particles smaller than 20 μm would more closely follow the gas velocity and temperature and would exit with a higher velocity and lower temperature.

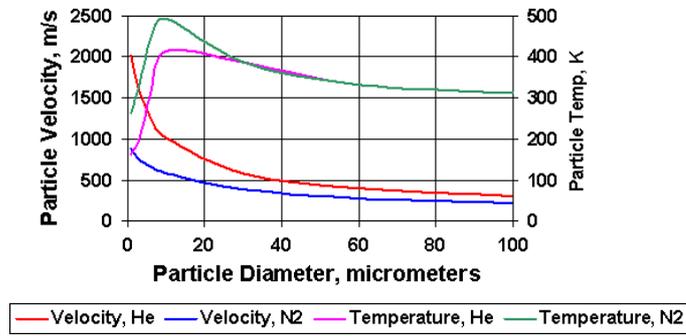


Figure 5. Particle conditions at the nozzle exit.

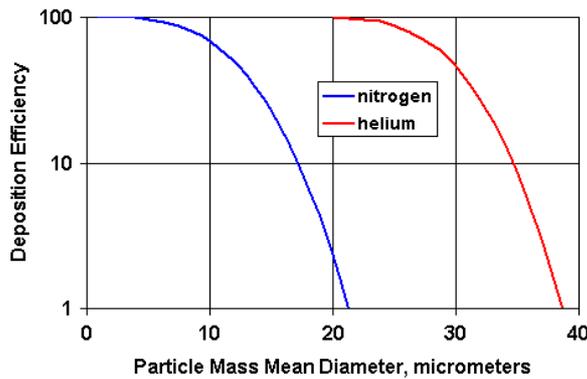


Figure 6. DE versus diameter.

Particle exit velocity and temperature are shown as functions of particle diameter in figure 5, for nitrogen and helium driving gases. A 9 cm long nozzle with an area ratio (exit area divided by throat area) of 4 is used for this calculation. Particle exit velocity decreases as particle diameter increases because the ratio of surface area to mass, and hence, the ratio of drag to mass (acceleration) decreases. Significantly higher particle velocity is achieved when using helium gas because much higher gas velocities are achieved for helium expansion in a nozzle. Particle velocity in helium decreases from 1000 to 500 m s^{-1} when the particle size is increased from 10 to 40 μm . Particle exit temperatures are somewhat lower for helium acceleration because helium expansion temperatures are lower than those for nitrogen. Particle temperature is relatively unchanged from that of injection temperature for larger particles because of the smaller surface area to mass ratio, (A_p/m) of equation (11).

Figure 6 results when the particle velocity and temperature values of figure 5 are applied to equations (13) and (14). Based on the particle temperature, density, melting point and UTS, a critical velocity can be calculated, for which all particles exceeding that velocity will deposit. For a given set of nozzle and gas parameters, calculations such as those producing figure 5 will identify the particle diameter that yields the critical exit velocity. A normal particle size distribution with a standard deviation of 4 then gives the percentage of particles that are smaller than the diameter yielding the critical velocity. Since these smaller particles have larger velocities, this percentage is the DE, or the percentage of particles that deposit. If, for example, the critical particle diameter is equal to the MMD of the powder distribution, then DE is 50%. The importance of particle diameter (hence particle velocity) is clear for

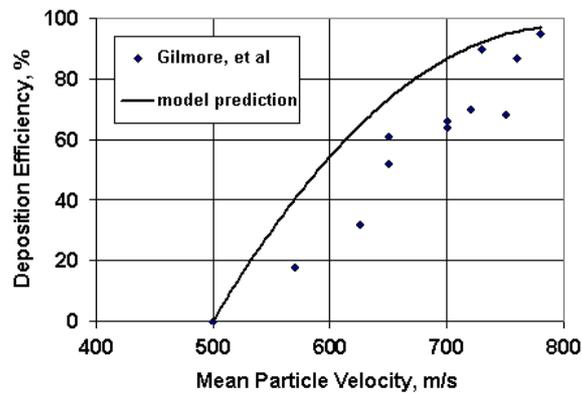


Figure 7. Experimental and theoretical copper deposition.

both nitrogen and helium accelerating gases. Figure 6 demonstrates the extreme importance of particle diameter, where DE can change by two orders of magnitude with a two-fold change in particle diameter.

4. Comparison with experiment

4.1. Deposition efficiency

Gilmore *et al* [10] measured the DE of copper particles impacting an aluminium substrate as a function of mean particle velocity. Copper particles of MMD of $19\ \mu\text{m}$ and helium gas were employed. Particle velocity was varied by changing stagnation pressure and temperature and was measured with a laser two-focus velocimeter. DE was calculated from the target weight gain versus powder usage. The experimental results are shown in figure 6.

Calculated DEs, using the same operational parameter values, are also shown in figure 7. The calculation utilized equations (5)–(12) for particle velocity and temperature versus diameter. Equations (13) and (14) were subsequently used to predict DE. The model correlates well at low and high particle velocities, and the model approaches 100% DE in an asymptotic fashion, as would be expected.

4.2. Nozzle length

Nozzle length obviously affects particle exit velocity, since this parameter controls the time during which the particles are acted upon by the gas. The exit gas velocity is not affected by the nozzle length as long as area ratio remains constant. On the other hand, longer nozzles yield higher particle velocities because the particles undergo acceleration for a longer period of time. Figure 8 shows how the velocity of $20\ \mu\text{m}$ particles increases with increasing nozzle length, for 12.25 and 4.0 area ratios (A/A^*). The figure shows both calculated and measured values. Although only three experimental points are available, they are included in the figure to show correlation at short nozzle lengths. Future work will include the experimental performance of longer nozzles. The advantage shifts from a 4.0 area ratio for shorter nozzles to 12.25 for longer nozzles. This occurs because longer residence times favour the lower gas density of the higher area ratio nozzle more than higher densities are favoured. This effect is clearly minor when compared with the magnitude of increased particle velocity brought about by longer nozzles.

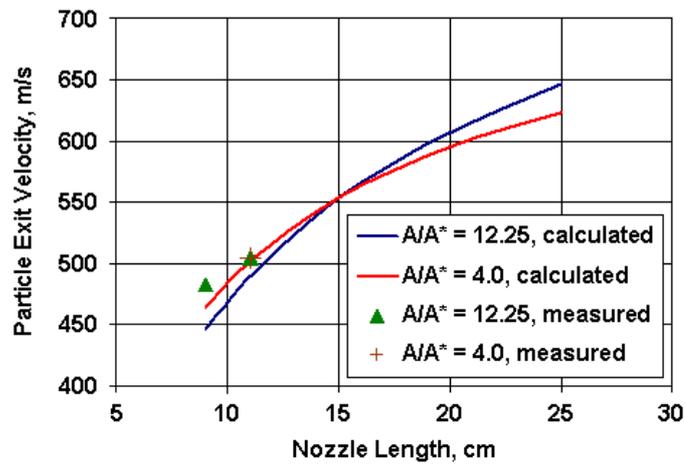


Figure 8. Longer nozzles yield higher particle velocities.

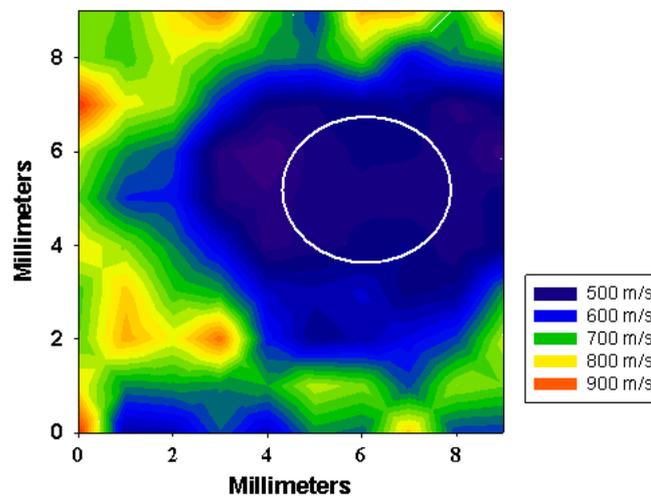


Figure 9. Measured particle velocity 25 mm downstream of the nozzle.

The experimental particle velocities shown in figure 8 were measured by means of a TECNAR DPV-2000, dual-slit, laser-illuminated optical sensor. The measurement for the 9 cm nozzle is shown in figure 9. This velocity distribution was measured 25 cm below the nozzle exit. The outline of the nozzle exit is superimposed. Since individual particle diameters vary, particle velocities also vary. The given velocity at each point is a time average of the individual particles traversing that point. The major particle flux (particles/second/area) is contained within the central core below the nozzle. The higher velocities seen outside the core area are representative of relatively few particles.

5. Conclusions

Particle deposition and consolidation by SPD has been modeled through the application of empirical particle-spacecraft collision relationships, the use of conventional rocket nozzle

flow equations and the application of an empirical materials-driven impact relationship. It was shown that the velocity onset of particle–substrate interface mixing can be predicted by simple particle and substrate material characteristics originally developed for the prediction of micrometeor impact on spacecraft. It was also shown that particle velocity and temperature can be predicted at the nozzle exit and that these conditions can then be used to predict the DE of the process. High particle velocity favours high DE. Modelling efforts showed that higher velocity is obtained from smaller diameter particles and longer nozzles. Experimental results verified particle velocity and nozzle length effects and showed good correlation with calculations. These observations have been qualitatively known in the SPD community but quantitative guidelines were not well established. The modelling effort presented here gives the SPD user the ability to anticipate coating results based upon the spray parameters and material characteristics, thus eliminating trial and error attempts at creating acceptable coatings.

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The sentence beginning 'For a given set of nozzle and gas parameters ' is ambiguous. Please clarify.