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Porosity Formation due to Splat Curling-up in Thermal Spray Coating Technology: A Numerical Approach

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Abstract

The curling up of the splat rim in a thermal spray coating process is simulated using a 2D numerical approach (Ansys). As a simplifying assumption, the splat is considered to be a flat disk of uniform thickness and temperature. The droplet is considered to be flattened completely and the solidification process starts afterwards. The solidification process is modeled using enthalpy method. A typical case corresponding to a thermal spray scenario was considered. By simulating different scenarios, it is found that the curl-up angle is sensitive to some parameters such as the thickness and radius of the splat, the splat and substrate temperature difference, and thermo physical properties of both splat and substrate materials such as their coefficient of thermal expansion (CTE), thermal conductivity, and the splat heat of fusion. Close inspection of the results reveals that the curl-up angle increases with increasing substrate temperature, the CTE, substrate thermal conductivity and adhesion of the splat to the substrate. Other factors, such as the splat heat of fusion and the splat thickness have a reverse effect on the curl-up angle.

Keywords: curling up, thermal spray coating, thermal stress, porosity, numerical approach

Introduction

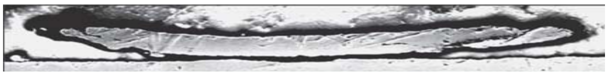
Thermal spray coating is a term used to describe a family of processes which employs a heat source to melt powders of metallic and nonmetallic materials and spray them with high velocity onto a substrate, forming a deposit. This technology is commonly used to apply protective coatings on components to shield them from wear and corrosion. Since the formed layer is not completely dense, coatings have certain percentage of porosity. Several possible sources of porosity in a coating have been identified. One of the main sources of porosity is the curling up at the edge of the splats which is frequently observed in the coatings. After a droplet impacts on a substrate it spreads radially and forms a disk-shape splat. As the splats solidifies its edges curls up forming pores close to periphery.

Cirolini et al [1] developed a model for the deposition of a thermal barrier plasma sprayed coating assuming that curling was caused by the temperature drop across the splat when the solidification front just reached the top. Fukanuma [2] proposed a physical and mathematical model for the production of porosity by considering deformation of a molten particle during thermal spray coating processes. He observed that most pores exist at the periphery of splats, starting at ~0.6 times the splat radius (*R*) from its center. Ghafouri-Azar et al. [3] presented a three-dimensional, stochastic model of thermal spray coating which could predict the porosity which was assumed to be solely due to the curl-up of the splats as a result of thermal stresses. Based on Fukanuma's experimental evidence, they assume the splats to detach from the substrate starting at a distance *0.6R* from the center where *R* is the splat radius. Xue et al [4] used a commercial finite element code to predict the angle of curl-up around the edges of metallic splats and showed that predictions agreed reasonably well with measurements for splats formed by the impact of both large (2–3 mm) and small (30–50μm) diameter droplets of molten metals.

We investigated this phenomenon using a commercial code (ANSYS) using a 2D axisymmetric coordinate system to define the geometry of the splat and substrate. As a simplifying assumption, the splat is considered to be a flat disk of uniform thickness and temperature. In this study, it is assumed that the droplet is flattened completely and the solidification process starts afterwards; therefore the flattening process of the droplet is not investigated. Solving the energy equation, the transient temperature distributions within the splat and the substrate are obtained. By having the thermal gradients within the splat, the structural problem is solved simultaneously that leads to the deformation of the solidified splat due to thermal stresses. The phase change process and solidification is modeled using enthalpy method. A typical case corresponding to a thermal spray scenario was considered. By simulating different scenarios, it is found that the curl-up angle is sensitive to some parameters such as the thickness and radius of the splat, the splat and substrate initial temperature, and thermo physical properties of both splat and substrate materials such as their CTE, thermal conductivity, and specific heat.

Curl-up Mechanism

Photograph 1 shows the cross section through the center of a nickel splat on stainless steel substrate with an initial surface temperature of 400°C [4]. The splat starts curling up at about 0.49*R*.



Photograph 1: Cross section through center of a nickel splat on stainless steel substrate with an initial surface temperature of 400°C [4].

The reason for the curl-up is the residual stresses due to the thermal mismatch of the splat and substrate. Microscopic stresses are found inside individual splats, and are generated by the gradient of the thermal expansion coefficient between the hot particle and the cooler substrate. The concentrations of residual stress components are located at different parts of the splat. High axial and shear stresses are located at the radial free edge while radial stress (in-plane stress) is concentrated at the top surface. The cracks could originate at the radial free edge due to the high concentration of axial and shear stresses. These cracks then may propagate either along or parallel to the interfaces, which leads to delamination and spalling of the coatings. On the other hand, the cracks may form at the top surface due to the high in-plane (radial) stress. These cracks are generally believed to originate within brittle layers, propagating towards the interface, and finally interact with the interfaces. Residual stresses are particularly severe in ceramic-metal composite coatings because of the generally large difference in the thermal expansion coefficients of ceramic and metal. After a droplet impacts on a substrate and spreads radially and forms a disk-shape splat, it cools down to room temperature rapidly. The cooling rate of the splat on the substrate is about 10^6 to 10^7 Ks^{-1}. The solidification time can be calculated using an approximate solution of the heat diffusion equation at the solid substrate/liquid droplet interface [5] as:

$$t_{sol} = \frac{h_s^2}{4p^2 a} \qquad (1)$$

where h is the splat thickness, a is thermal diffusivity and p is a constant[1]. It should be emphasized that Eq.1 is only a very rough zero-order solution of the heat transfer (Fourier) equation. Houben [5] has obtained an exact solution for solidification of a droplet on a substrate considering thermal contact resistance.

As the splat cools down to the room temperature, it shrinks. If a portion of the bottom is bonded to the substrate, it cannot shrink, but the upper surface of the splat is free to contract, so that the stresses are created in the splat. To relieve these stresses, the unbonded portion of the splat, along its periphery, curls up. Note that a splat that is not bonded to the substrate will not curl but will instead contract uniformly along both faces. Adhesion between the splats and the substrate is largely mechanical, when high pressure in the impacting droplet drives liquid into surface micro cavities where it freezes and forms interlocking connections. Good bonding would be expected to occur over the region of highest pressure in the droplet. Pressure distributions inside impacting droplet can be accurately calculated using a numerical model [6],[7]. One of the main applications of knowing the pressure distribution during droplet flattening is concerned with the possibility of predicting substrate-coating micro adhesion. To have a good bonding it is necessary that the dynamic pressure P_a exceeds the capillary pressure P_σ, where the P_σ is equal to:

$$P_s = 2s\cos t / R_c \qquad (2)$$

where σ is surface tension (N/m), R_c (m) is the cavity radius if we consider the substrate rough. However, even if it is considered to be smooth, some small roughness always exists. So we have:

$$\begin{cases} \dfrac{P_a}{P_s} \geq 1 \quad or \quad R \leq R_e \\ \dfrac{P_a}{P_s} < 1 \quad or \quad R > R_e \end{cases} \qquad (3)$$

where R_e is the point where the curl up starts [8].

The curl up angle can be calculated with the Xue's analytical formula [4] which has been produced from the linear thermal expansion theory.

$$q = tg^{-1}\left(\frac{xRa\Delta T}{h_s}\right) \qquad (4)$$

It's important to note that metallic splats are much more ductile than the ceramic splats and do not crack easily. Curl-up is therefore the only means of providing stress relief. Consequently curling-up is a much more important source of porosity in metallic coatings than in ceramic coatings.

Numerical Simulation

An axisymmetric coordinate system is used to define the geometry of the splat and substrate. Figure1 shows a schematic of the problem under consideration.

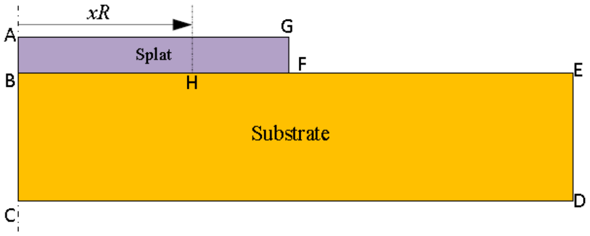


Figure 1: A schematic of the problem under consideration

As a simplifying assumption, the splat is considered to be a flat disk of uniform thickness and initial temperature. In addition, the thickness and initial temperature of the substrate are assumed to be uniform. The substrate thickness is 2.5mm and its radius is assumed to be 12mm. For the base case considered the splat had a thickness of 0.61mm and a radius of 5.61mm. When investigating the effects of splat thickness and radius on the curl-up angle, however, we considered a range of splat geometries.

The typical physical properties of the substrate and splat are shown in Table 1. Except enthalpy, the other thermo physical properties are not temperature dependent. The effects of these properties were also investigated in this study in a wide range of their variation. The reason for assuming the enthalpy to be temperature dependent is because the solidification process of the splat is also considered here. Figure 2 is the enthalpy vs. temperature diagram of the base material (Al380) that we used in this study. For simplicity, we considered the enthalpy in the three regions of this figure (solid, liquid and mushy zone) to be linearly changed with temperature.

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[1] According to Houben [5], p is the Neumann-Schwartz parameter that can be estimated as the fitting parameter from the solidification time versus layer thickness relationship.

Table 1: Material properties of the substrate and coating [9]

Material properties	Substrate (H13 stainless steel)	Coating (Al380)
Young’s module E(GPa)	210	71
Poisson ratio (υ)	0.3	0.33
CTE (1/°C)	12.4e-6	22.7e-6
Density ρ (kg/m^3)	7800	2760
Thermal conductivity (W/m.K)	24	109
Specific heat (J/kg)	460	963
Heat of fusion (J/kg.K)	-	389

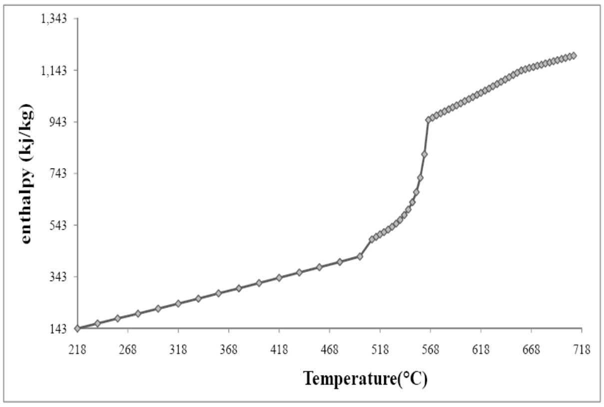


Figure 2: Enthalpy vs. temperature diagram for Al380 [10] in the three regions of solid, liquid and mushy zone.

The element type considered in the code (ANSYS) was “plane13” which is a coupled-field element for solving thermal-structural problems. This type of element solves the thermal and structural problems simultaneously. Figure 3 shows the finite element mesh of the model. The rectangular mesh for the specimen consists of square elements with 1mm sides.

The contact elements with thermal contact resistance are defined between the splat and the substrate. Splat boundaries were free to move except at the interface where perfect bonding between the splat and substrate were assumed over a distance equaling “*x*” times the splat radius. *xR* is the value from the symmetry axis to a point at the interface which the splat and substrate are bonded together (Fig. 1). The thermal contact resistance is assumed to be equal to 10^{-6}(m^2.K/W) at the bonded region (BH) and10^{-4}(m^2.K/W) at the unbonded part of the contact line near the periphery of the splat (HF).

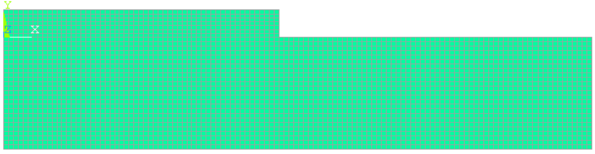


Figure 3: Computational mesh for finite element analysis. The left boundary is the axis of symmetry.

During spraying, heat will also be transferred to the substrate through two mechanisms. During the solidification of the molten particles, the latent heat of solidification associated with the phase change from liquid to solid state will be released and conducted to the substrate. After solidification, the solid splat continues to transfer heat due to high initial temperature (close to melting point) to the lower temperature substrate. Except the AC surface, the other surfaces are exposed to air, and heat transfer will be done through convection. The air temperature is considered to be equal to the substrate temperature. It was found, however, that the heat transfer due to convection has no significant effect on the curl-up angle. In this study we assumed that no melting occurs in the substrate. The latent heat effect (accompanying change in phase from liquid to solid), is approximated by specifying a rapid variation in enthalpy (material property ENTH), in a temperature range of ΔT (assumed to be 55^{o}C)[2]. The enthalpy variation is computed from the equation:

$$H = rc\int dT \qquad (5)$$

An adjusted specific heat of $L_f/\Delta T = C^*$ J/kg.K, is used in the freezing zone, resulting in a slope discontinuity, as shown in Figure 4.

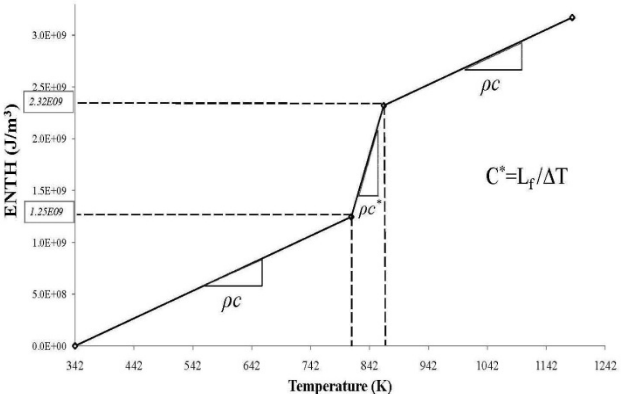
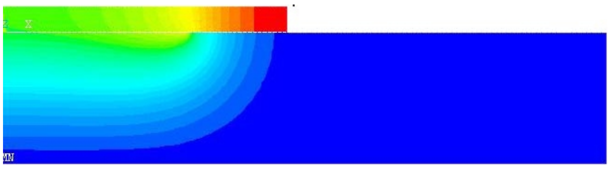


Figure 4: Enthalpy vs. Temperature diagram

The time at the end of time loadstep was 0.1s and the automatic time stepping was considered. The number of substeps was assumed to be 100. Solving the energy equation, the transient temperature distributions within the splat and the substrate are obtained. Simultaneously, by having the thermal gradients within the splat, the structural solution is performed that leads to the deformation of the solidifying splat due to thermal stresses. A typical case corresponding to a thermal spray scenario was considered. By simulating different scenarios, we studied the effect of different parameters such as temperature difference between substrate and splat, thermal expansion coefficient, thermal conductivity, heat of fusion, adhesion percentage (*x*), and splat thickness and radius.

Results and Discussion

Figure 5(a) shows the temperature distribution after the splat and the substrate had been cooling for 0.1 s. Figure 5(b) shows the corresponding thermal stress distribution and the deformation along the periphery of the splat at the same time elapsed from the initial condition.



a)

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[2] ΔT is the temperature difference between the liquidus and solidus of Al380.

b)

Figure 5: Typical simulation results of the temperature and structural deformation of the splat: a) temperature distribution; b) stress distribution

Figure 6 shows the y-displacement of the periphery of the splat at 15s with 30°C substrate temperature. At this time limit and even sooner (*t~8s*), the splat approaches the steady state and the splat temperature will reduce to a value close to that of the substrate and room temperature. In addition, according to this diagram, it is clear that the more significant displacement occurred in less than one second.

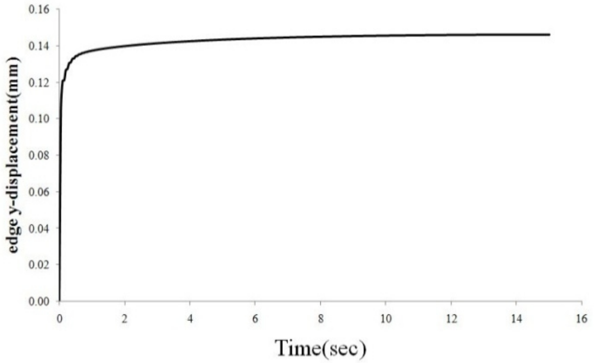

Figure 5: The y-displacement of the bottom splat edge with 5.67mm radius and 30°C substrate temperature at t =15s

Figure 7 shows the curl-up angle variations due to substrate temperature rise. As the substrate increases, the curl-up decreases. This is because increasing the substrate temperature results in a decrease of the temperature difference between the splat and substrate; this point is further displayed in Fig. 8. It is for this reason that the substrate should be preheated before the molten droplets spraying. Preheating of the substrate is used to increase the contact temperature[3] and to reduce the viscosity of the impinging molten droplets. Therefore, the residual stresses can be somewhat controlled by substrate preheating.

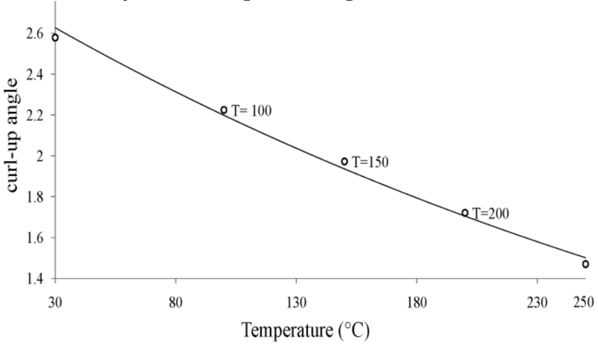

Figure 6: The curl-up angle vs. substrate temperature for T=30, 100, 150, 200 and 250°C.

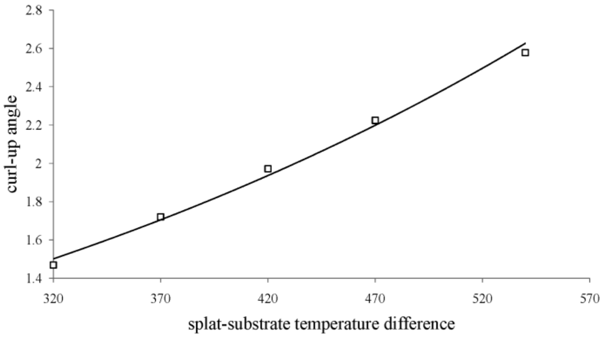

Figure 7: The curl-up angle vs. splat-substrate temperature difference at t = 0.1s

Figure 9 shows the curl-up angle versus splat thermal expansion coefficient (CTE). As seen from the figure, this coefficient has a significant effect on the curl-up. By increasing the CTE, the curl up will be increased. Stresses at the substrate/spalt interface are proportionaly changed with the differences in the thermal expansion coefficients of the coating and the substrate. These stresses can be determined approximately by the Dietzel equation [11] that uses the differences in the coefficients of thermal expansion of coating and substrate, the temperature gradient, and the thickness ratio to calculate the coating stress.

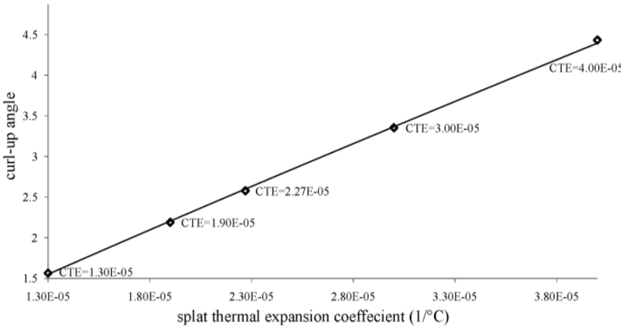

Figure 8: The curl-up angle vs. thermal expansion coefficient of splat for 30°C substrate temperature at t = 0.1s

Heat of fusion has a small effect on the curl up angle. To consider the heat of fusion effects in simulation, we need to know the variation of enthalpy due to temperature rise. This is also necessary because of splat solidification. Figure 10 shows the enthalpy vs. temperature diagrams for different L_f quantities. Figure 11 shows the relation between splat heat of fusion and curl up angle. An increase of heat of fusion results in a slight decrease of the curl up angle.

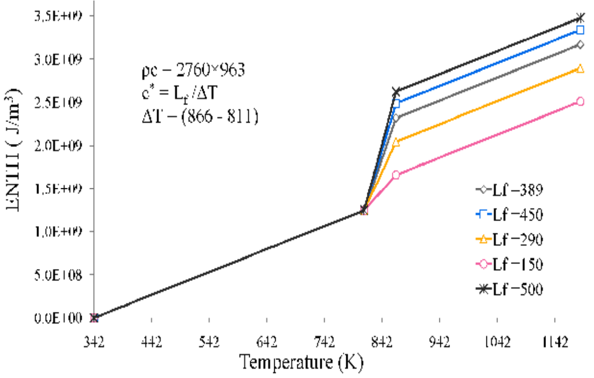

Figure 9: Enthalpy vs. temperature diagram for various heat of fusion quantities.

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[3] Physical adhesion is controlled by diffusive bonding, where the diffusivity increases with increasing contact temperature according to Fick's [11] law. This can be maximized by substrate preheating.

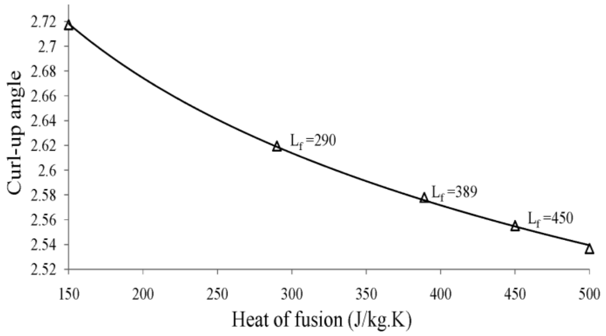

Figure 11: The curl-up angle vs. splat heat of fusion for 30°C substrate temperature at t = 0.1s

Figure 12 shows the effect of the substrate thermal conductivity on the curl up angle. It is clear that with the increase of the thermal conductivity, the curl up will be increased as well. Similar to thermal expansion coefficient, thermal conductivity of the splat has a more significant effect on the curl up. Unlike the substrate thermal conductivity, the thermal conductivity of the splat was found to have an insignificant effect on the curl up.

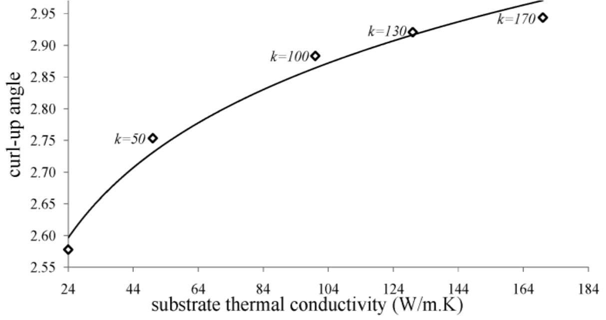

Figure 12: The curl up vs. substrate thermal conductivity diagram for 30°C substrate temperature at t = 0.1s

Figures 13, 14, and 15 illustrate the changes of the curl-up angle versus splat thickness (h_s), radius (*R*) and adhesion percentage of the splat to the substrate (*x*), for 30°C substrate temperature, respectively. From these figure, it can be seen that while the splat thickness and radius have a direct effect on the curl up angle, the adhesion percentage of the splat has a reverse effect. However, the combination of the splat radius and adhesion percentage of the splat has a direct effect on the curl up angle. Therefore, an increase of the product amount of *xR* increases the curl up angle as displayed in Fig. 16.

The effect of various parameters on curl-up angle is summarized in Table 2.

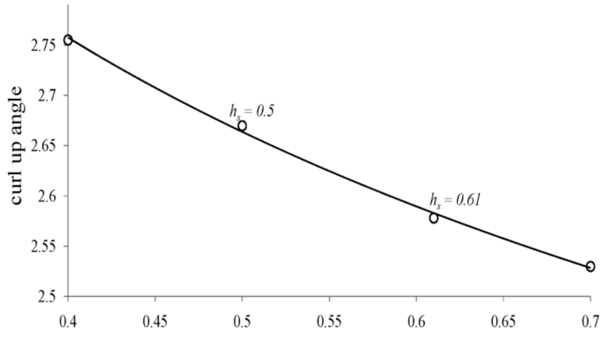

Figure 10: The curl-up angle vs. splat thickness for 30°C substrate temperature at t =0.1s

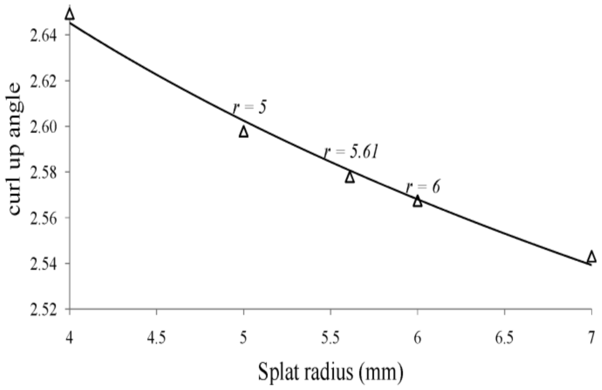

Figure 14: The curl-up angle vs. splat radius for 30°C temperature at t =0.1s

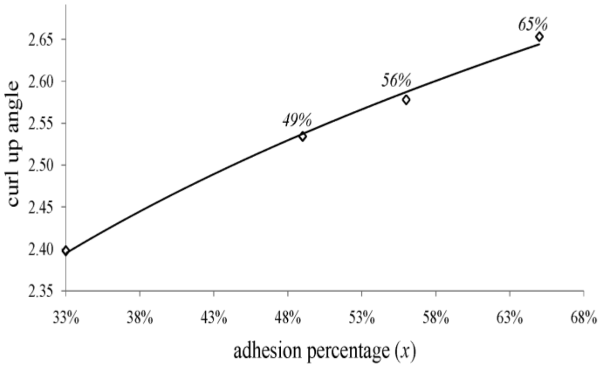

Figure 15: The curl-up angle vs. adhesion percentage of the splat to the substrate for 30°C substrate temperature at t =0.1s

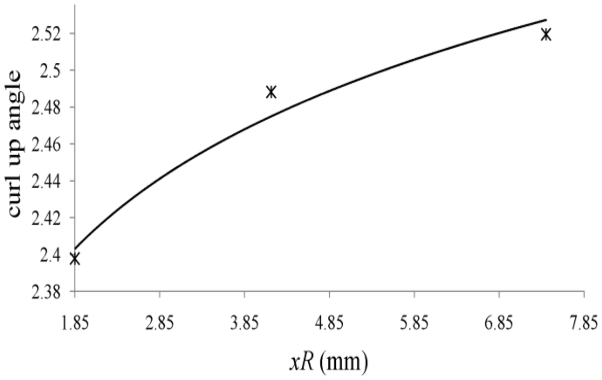

Figure16: The curl-up angle vs. the amount of the bonded part the splat to the substrate for 30°C substrate temperature at t=0.1s

Table2: A summary of the effects of various parameters on the curl-up angle

Parameters	Curl up angle
Substrate thermal conductivity (K_{sub})	↑[4]
Sub/splat Temperature difference (ΔT)	↑
Splat thermal expansion (CTE)	↑
Adhesion percentage (*x* %)	↑
Bonded part length (*xR*)	↑
Heat of fusion (L_f)	↓
Splat thickness and radius (*h_s* & *R*)	↓

Conclusions

In this paper, we studied the porosity formation due to the splat curling-up in a thermal spray process using a numerical approach with a finite element code. The

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[4] The sign ↑ and↓ denote the increase and decrease of the curl up angle, respectively.

effects of important parameters on the curl up angle were also investigated; they include: the substrate/coating temperature difference (ΔT), splat thermal expansion (CTE), heat of fusion of the splat (L_f), substrate thermal conductivity (K_{sub}), coating thickness (h_s), radius (R), and the adhesion percentage of the splat to the substrate (x). For the splat, the solidification and phase change of the splat is assumed to occur. The substrate melting is not considered in this study. The splat solidification process is modeled using enthalpy method. Consequently the enthalpy depends on the temperature during cooling process. While ΔT, CTE, K_{sub} and the adhesion percentage of the splat to the substrate, have a direct impact on the curl up angle, the remaining parameters such as splat heat of fusion (L_f), coating thickness and radius have a reverse effect. However, the combination of the splat radius and adhesion percentage of the splat has a direct effect on the curl up angle. Therefore, an increase of the bonded portion of the splat to substrate (xR) will increase the curl up angle. The results of simulations for splat curl-up characteristics agree well with those of the analytical correlations available in the literature.

List of symbols

E	Young's module
CTE	Thermal expansion coefficient
ΔT	Temperature difference
R	Coating radius
K_{sub}	Substrate thermal conductivity
L_f	Heat of fusion
h_s	Coating thickness
C	Specific heat
C^*	Specific heat of the phase change region
a	Thermal diffusivity
p	Neumann-Schwartz parameter
p_a	Dynamic pressure
p_σ	Capillary pressure
R_c	Cavity radius
x	Adhesion fraction of the splat to the substrate

Greek symbols

σ	Surface tension
θ	Curl up angle
α	Thermal expansion coefficient
τ	Wetting angle

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