Editorial

Formation of Plasma Sprayed Coatings

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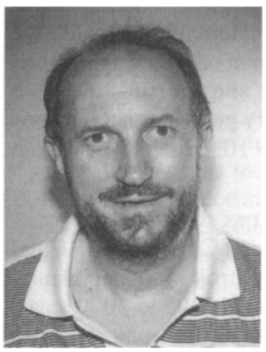

Introduction

Plasma spray deposition is a versatile technology that has been very successful as a reliable cost-effective solution for many industrial problems. It allows the spraying of a wide range of high-performance materials, from superalloys and refractory intermetallic compounds to ceramics, to produce protective coatings for various industries. The range of research and commercial applications is continuously increasing. However, all the involved phenomena are not yet clearly understood because for a long time the scientific research lagged behind the technical applications due to the complexity of the involved phenomena.

The velocity and molten state of the particles upon impact depend on their trajectories in the plasma jet. But, because the particles have size and injection velocity distributions, they exhibit widely different trajectories and thus different momentum and temperature histories. Also the thermal histories of the particle are complicated by heat propagation and evaporation phenomena (Ref 1). Such particle velocity and temperature distributions upon impact affect the coating thermomechanical properties through the size and distribution of porosity, oxide content, residual stresses, macro- and microcracks, and physical contact between the layered splats (Ref 2, 3). Moreover, the coating generated splat by splat with particles impacting on those already solidified exhibits a layered structure that is highly anisotropic (Ref 2). Therefore, a basic understanding of plasma sprayed coating formation requires knowledge of the thermal history of the droplets during their flattening and cooling process. Many recent studies have been devoted to the plasma jets and particles in flight (see Ref 4-6). However, the splat formation (Ref 7) as well as the quenching stresses within the splats (Ref 8) has received much less attention. The aim of this special issue of JTST emphasizes our knowledge in this field.

Historical Perspective

Russian workers have made a detailed description of alumina splats collected on smooth substrates, and their results are summarized in Ref 9 to 11. Similar work was performed by Houben for molybdenum splats (Ref 12). For example, the Russian workers, for a specific spraying condition, registered more than 30 different splat shapes from nearly unmolten particles stuck to the surface, to completely exploded overheated particles. If some of the splats exhibited the disk shape used in modeling, it was more an exception than a rule and many were "starlike" particles with strong disruption and fragmentation of material at the splat periphery, sometimes with discontinuity in the center or "sombrero"-type particles with an unmolten core at the splat center.

When sprayed on rough surfaces, the spreading of the droplets is limited by the irregularities of the surface resulting in smaller and thicker splats than on flat substrates, however their observation, even with SEM, is not very easy.

As already emphasized by McPherson (Ref 3), the contact between the piled splats is far from perfect and, very often, represents less than 20% of the total surface of the splat. According to Boswell (Ref 13), this infers that the heat transfer at the interface between the incoming molten particle and the previously solidified layers will be nonuniform with a high heat transfer coefficient in the good contact area and a low one elsewhere. This results in a nonuniform distribution of nucleation and growth centers within the melt with crystals nucleated preferentially near the melt-sink interface where they are not disturbed by fluid flow. In most cases, these nonuniformly distributed crystals will rapidly develop into a "chill" layer adjacent to the thermal interface, the layer then grows into the melt. This is the so-called columnar growth model, which has been the basis for most of the existing theoretical work on rapid solidification. Thus, the dynamics of splat formation determines the solidification, microstructure development, and phase formation, with the cooling rate being the most important parameter that determines the solidification parameters (Ref 14). Cooling rates, determined by indirect methods (e.g., splat thickness, dendrite arm spacing, and grain size correlations), for aluminum and nickel have shown values in excess of 10^7 K/s (Ref 15).

Particle Flattening Parameters

The recent development of techniques based on the detection of thermal radiation emitted by the hot particles when they flatten on the substrate surface allows experimental determination of the flattening time, flattening degree, and cooling time of the impinging particles (Ref 16). Such techniques have been improved to obtain the velocity, surface temperature, and diameter of the particle prior to its impact (Ref 17). The corresponding results are presented in the papers of C. Moreau, P. Gougeon, and M. Lamontagne ("Influence of the Substrate Preparation on the Flattening and Cooling of Plasma-Sprayed Particles") and of M. Vardelle, A. Vardelle, A.C. Leger, and P. Fauchais ("Influence of Particle Parameters at Impact on Splat Formation and Solidification in Plasma Spraying Processes"). The results of Moreau et al. clearly show the drastic influence of the substrate roughness on the flattening degree and time of the particles. For instance, the smoother the substrate, the larger the surface of the molybdenum splats and the longer flattening time. The data also reveal very small splat thicknesses (~0.5 μm) when impact occurred on a smooth substrate and a lower cooling rate at the periphery of splats with only the central part remaining attached to the substrate after cooling. The results of Vardelle et al. are related to zirconia particles impacting on flat smooth substrates. They show that at a specific measuring point (a cylinder ~160 μm in diameter and 160 μm in length) close (2 mm) to the substrate, the particles exhibit a wide range of diameter, velocity, and surface temperature distributions. This is due to their collisions with the injector wall and between themselves resulting in a large trajectory distribution. They also emphasize the dependence of the flattening and cooling processes on the particle velocity, size, and temperature at impact, and the influence of substrate roughness, temperature, and oxidation. A very interesting result is that obtained on smooth steel substrates at temperatures higher than 150 °C; the contact between the disk-shaped splat and the substrate induces cooling rates higher than 4.10^8 K/s. When particles are sprayed on steel substrates at 75 °C or on hot oxidized substrates, the resulting lamellae have distorted morphologies with a real interface restricted to small contact points and cooling rates in the range 3×10^7 to 10^8 K/s. The cooling rates calculated to match the experimental results depend very strongly upon the real contact area and the splat thickness. The comparison of the measured and calculated cooling rates allows determination of the thermal contact resistance R_{th} between the splat and the substrate. For disk-shaped splats obtained on hot substrates ($T > 150$ °C) $R_{th} < 10^{-7}\ m^2 \cdot K/W$, which corresponds to a very good contact between the splat and the substrate, while for extensively fingered splats collected on cold substrates $R_{th} > 10^{-6}\ m^2 \cdot K/W$, which corresponds to poor contact.

This last parameter, at least for disk-shaped splats, is strongly related to the particle velocity upon impact as shown by the paper of L. Bianchi, A. Grimaud, F. Blein, P. Lucchese, and P. Fauchais ("Comparison of Plasma Sprayed Alumina Coatings by RF and DC Plasma Spraying"). A method derived from the line-scan test (Ref 18), in which temperature can be controlled independently from the plasma jet heat flux and a very low powder flow rate (0.01 kg/h) is used, allowing the collection of 2000 to 4000 splats distributed all over the spray cone with almost no overlapping of the splats. Image analysis of the collected splats indicates their diameter and shape factor distributions and the splat thickness distribution can also be determined. For example, such thicknesses for the same size distribution of impacting particles vary from 1.1 μm for particles where the velocity is 250 m/s to 2.5 μm for particles at 40 m/s. Almost perfect lenticular splats are obtained all over the spray cone for hot (over 150 to 200 °C) nonoxidized substrates (heated by the plasma jet in less than 120 s), whereas extensively fingered splats are obtained on cold substrates. This occurs due to the flow, after flattening, of the molten material of splats that have poor contact with the substrate, resulting in a cooling rate much slower than that of lenticular splats. The particles are most extensively fingered when the impact velocity decreases and the mean diameter of the obtained splats is, of course, larger with the hot substrate than with the cold one where part of the impacting material has flowed away. Similar results were obtained during the plasma spraying of flat smooth alumina substrates. It is important to point out that the substrate temperature effect also plays a role for rough substrates, as shown by the paper of Bianchi et al., where there is better contact with the substrate for hot rough substrates than for cold ones.

Such results are in good agreement with adhesion measurements of coatings where, for the same range of particle velocities, an increase by a factor of almost three is observed when coatings are sprayed at 250 °C (with substrate preheating) and decrease, for the same substrate temperature, with the particle velocity (see the paper of Bianchi et al.).

Another way to study the splat distribution is statistical analysis between process parameters and the morphology of the splats. This is presented in the paper of G. Montavon, S. Sampath, C.C. Berndt, H. Herman, and C. Coddet ("Effects of Vacuum Plasma Spray Processing Parameters on Splat Morphology"). Spraying a nickel-base powder (Astroloy) under vacuum onto polished copper substrates established those parameters that have the greatest influence on the splat shape factors. In close agreement with the previous works, these parameters are linked to the plasma velocity and thus the particle velocities; that is, the arc current intensity, the argon mass flow rate, and the chamber pressure.

Residual Stresses

For metallic or ceramic materials the contact between splats can also be evaluated from the quenching stresses (Ref 8) as shown in the paper of S. Kuroda, T. Fukushima, and S. Kitahara ("Quenching Stress in Plasma Sprayed Coatings and Its Correlation with the Deposit Microstructure"). In this paper the authors define the quenching stress σ_q and explain the experimental setup (Ref 8) to measure them. They present an improved porosity measurement technique and two techniques to characterize the contact between the splats within the coatings by impregnating them with Cr_2O_3 or bismuth alloy. These methods allow the visualization of voids between splats even when their thickness is below 0.5 μm. The σ_q measurements performed with NiCr, Ni, Al_2O_3, ZrO_2-8 wt% Y_2O_3 with respect to substrate and coating temperature T_s during spraying under APS and VPS conditions, show that σ_q increases with temperature up to a maximum where creep and yielding occur. The porosity results indicate a large reduction of the pores below 0.1 μm when T_s increases. This reduction cannot be explained by a sintering process as shown by the annealing experiments at T_s and is confirmed by the disappearance of most of the impregnated voids. Such results are in good agreement with those of M. Vardelle et al. and L. Bianchi et al. concerning the behavior of splats. Thus, when T_s increases the contact between the splat and substrate increases, thereby reducing the voids and increasing the tensile quenching stresses.

Modeling Studies

The measurements of particle flattening and cooling allows comparison to the models of deformation and solidification of a droplet on a substrate, models to which many studies have been devoted (see the recent review of Bennett and Poulikakos [Ref 19]). All the models deal with flat substrates and start with an energy balance stating that the initial kinetic energy of the impacting droplet is dissipated as viscous energy and the surface tension energy. They are all expressed in terms of particle Reynold's number ($Re = \rho\ u\ d/\mu$, where ρ, μ, u, and d are, respectively, the liquid density and viscosity, and the particle velocity and diameter) and Weber's number ($We = \rho u^2 d/\sigma$, where σ is the liquid vapor surface tension). For thermal spraying, a popular model is that of Madejski (Ref 20), which relates the ratio $D/d = \xi$ (where D is the splat diameter, assumed to be a disk, and d is the spherical droplet diameter) to Re and We by:

$$\frac{3\xi^2}{We} + \frac{1}{Re}\left(\frac{\xi}{1.2941}\right)^5 = 1 \qquad \text{(Eq 1)}$$

However, as for alumina or zirconia plasma sprayed particles, the We values are extremely high (10^2 to 2.10^4); at least when the flattening starts and, since ξ is lower than 6, Eq 1 reduces to the expression:

$$\xi = 1.2941\ Re^{0.2} \qquad \text{(Eq 2)}$$

The lenticular splats obtained on smooth, hot ($T \geq 150$ °C), nonoxidized substrates are quite typical of good wetting character (or "wettability") of the molten flattening particle (at least at the end of the flattening when the viscous energy is almost dissipated). In this case the experimentally obtained disk shape is in good agreement with the model of Madejski. The fast cooling of the splat resulting from its excellent contact with the substrate preserves its disk shape. Thus, the coefficient of Madejski's equation (1.2941) is an accurate representation of the experimental results of M. Vardelle et al. When the contact between the splat and substrate is poor with extensively fingered splats, as shown by the results of Bianchi et al., the mean diameter of the splats is greatly reduced compared to that of the lenticular shaped splats. Therefore, the experimental results of M. Vardelle et al. are well represented by Madejski's equation but show a coefficient of 0.83 because some material is removed from the splat.

A more sophisticated model is presented in this issue by M. Bertagnolli, M. Marchese, and G. Jacucci ("Modeling of Particles Impacting on a Rigid Substrate under Plasma Conditions"). The model uses finite element simulation techniques to predict the geometrical shape of the splat on a smooth flat surface as a function of processing parameters, such as particle impact velocity and temperature, to follow the thermal field developing in the droplet up to solidification. Some slight discrepancies with the experimental results are present, for example the results of the simulations are reasonably fitted for small particles by a relation of Madejski's type (see Ref 2) but with a coefficient of 0.925. It is clear that a major problem concerns the introduction of wettability between the molten droplet and the substrate, which according to the results of Vardelle et al., plays a significant role at the end of the spreading (i.e., when We becomes very small). However, the model of Bertagnolli et al. allows prediction of:

- The final geometrical shape of the splat as a function of process parameters, such as initial temperature and velocity
- The thermal field developing in the droplet up to solidification; showing, for example, when solidification starts before flattening is terminated, and also permitting identification of the critical parameters such as thermal contact resistance and substrate temperature
- The curling of the splat after solidification and upon reaching thermal equilibrium with the underlying layer, a mechanism that has been proposed for the creation of porosity during deposition

Once the description of the particle on arrival at the substrate or previously deposited layers has been considered, it is possible to define a set of physically based rules for combining these events to obtain a coating. For example Knotek and Elsing (Ref 21) have constructed a model assuming that pores have been created between the splats without any other generation mechanism. Fukanuma et al. (Ref 22) tried to include trapping of the plasma gas.

J.H. Harding, P.A. Mulheran, S. Cirolini, M. Marchese, and G. Jacucci in ("Modeling the Deposition Process of Thermal Barrier Coatings") describe the growth of the coating by a stochastic process in which the surface roughness is represented as a fractal. They take into account the evolution of the coating surface temperature. The program builds the coating using experimental data on the behavior of particles in the plasma and calculations of the splashing and subsequent curling of the splats. It accounts for the following assumptions:

- Each particle impact is independent of the others.
- Solid particles do not adhere.
- Splats adhere strongly in an inner region, the outer region curls up to produce pores, and splats can be pinned by surface roughness or interlocking.

However, the basis of this model (as well as of the previous ones) is the splat shape and dimensions. For example, the change of the coefficient of Madejski's equation from 1.29 (the ideal value) to 0.82 (an experimentally determined value) can modify the porosity calculation by a factor of 2.

This model is a first step to a computer algorithm capable of generating an artificial microstructure with specific characteristics (e.g., porosity level, grain size distribution, etc.). These simulated microstructures could be used in further computer simulations of the micromechanical behavior of the material where information on the grain network in the coating is an essential requirement.

However, the results to date indicate that additional research is still necessary to improve the models; for example to take into account wettability (at the end of the spreading) and roughness. Such studies will allow the construction of more reliable models for coating generation—provided the temperature evolution during each spray pass is taken into account.

Memoria in Aeterna

These papers are dedicated to the memory of Prof. R. McPherson (Monash University, Melbourne, Australia), who was a pioneer in understanding the relationships between coating formation processes and thermomechanical properties. He was among the first to relate the coating properties to the contact between splats. Prof. McPherson accepted an invitation to write a paper for this special issue before he passed away.

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