JTTEE5 8:523-530
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Effect of Oxidation on Droplet Flattening and Splat-Substrate Interaction in Thermal Spraying

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(Submitted by 1 December 1997; in revised form 17 April 1999)

The processes of oxidation that occur during particle inflight motion and during splat solidification in an oxygen-rich atmosphere were considered for the thermal spray process. The effect of oxidation on droplet flattening, splat-substrate mechanical and thermal interaction, splat morphology, and development of coating porosity and adhesion was studied. The influence of wetting and oxygen dissolution on flattening and splat-substrate adhesion was also investigated. The results from theoretical treatment agree with experimental observations.

Keywords oxidation, particle inflight motion, splat solidification, splat-substrate interaction, thermal spraying

1. Introduction

Oxidation of coatings during thermal spraying influences their structure and properties (Ref 1-7). Due to the difference in the expansion coefficients of metallic and oxide phases, metal coatings that contain oxides may be subjected to irregular degradation during thermal cycling (Ref 2). Generally coatings with oxides seem to be more difficult to machine and exhibit less ductility in service (Ref 5). For wear resistant carbide-based coatings it is important to avoid a loss of carbides due to oxidation during spraying. Reference 6 shows that oxidation directly affects hardness and wear performance. The properties of corrosion resistant coatings also depend on the oxidation level (Ref 3). High temperature oxidation is a major concern in gas turbines, because above ~870 °C relatively rapid oxidation can occur unless there is a barrier to oxygen diffusion on the surface of the component (Ref 6). However, many currently used high strength alloys do not develop sufficiently protective barriers because their chemical composition has been optimized for high temperature strength and metallurgical stability rather than for oxidation resistance (Ref 6).

Oxidation influences the different processes involved in the development of the coating. Particularly, it has a marked influence upon the droplet flattening and the splat-substrate interactions that are important for coating formation (Ref 8-11). The presence of dissolved oxygen in a solidifying splat affects the splat-substrate wetting that influences the flattening process.

The coating structure obtained from the high velocity oxygen fuel (HVOF) spraying of the Cr_3C_2-NiCr powder onto a mild steel substrate shows that the main oxidation of chromium and the formation of Cr_2O_3 seem to occur during the inflight motion of the powder particles (Ref 9). According to the results presented in Ref 5, the main oxidation of the coatings obtained during the HVOF spraying of aluminum occurs at the substrate surface where the coatings are exposed to an oxygen-rich boundary layer that envelopes the substrate surface.

This article investigates the oxidation effect on the dynamics of flattening of powder particles and the development of the splat-substrate interactions during thermal spraying and presents analytical formulas that permit estimation of these processes. The analytical results take into account the roughness of the substrate, splat solidification, wetting, splashing, and place where oxidation occurs during the inflight motion of the powder particles and/or exposure of the solidifying splat to the surrounding oxygen-rich atmosphere at the substrate surface.

2. Inflight Oxidation

Due to the high temperatures of the surrounding gases during thermal spraying, the powder particles are usually melted at the spray distance, and the liquid phase that appears may react with oxygen. Conditions for the coating oxidation are rather favorable in the case of HVOF spraying because the combustion products contain excessive oxygen. These conditions are also favorable during plasma spraying due to very high gas temperatures.

Two mass transfer processes occur during interaction of the liquid particle with oxygen: development of oxides due to chemical reactions between the surface of the liquid phase and oxygen and diffusion of oxygen in the liquid. The rate of oxide formation can be estimated according to Ref 8.

2.1 Parameters of Oxidation

The mass of a developed oxidation layer, m_{ox}, can be presented in a form, $m_{ox} = q_{ms}S_p t_{ox}$, where q_{ms} is the mass flux of the oxide, S_p is the surface area of the particle subjected to oxidation, and t_{ox} is the characteristic time of oxidation. The ratio, Z, of m_{ox} to the particle mass, $m_p = 4\pi R_p^3 \rho/3$, is:

$$Z = 3q_{ms}t_{ox}(\rho R_p)^{-1} \quad \text{(Eq 1)}$$

The value of Z can be considered as the relative mass of oxidation, giving the level of oxidation. The thickness, δ_{ox}, of the oxidized layer is equal to the difference between the particle radius,

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R_p, and the radius of the inferior boundary of the oxidized region, R_{ox}: $\delta_{ox} = R_p - R_{ox}$ (Fig. 1). Because the value of $R_{ox} = R_p[1 - 3m_{ox}(4\pi R_p^3 \rho_{ox})^{-1}]^{1/3}$, where ρ_{ox} is the oxide density, the thickness of the oxidized layer can be presented in the form:

$$\delta_{ox} = R_p\,[1 - (1 - \rho Z/\rho_{ox})^{1/3}] \tag{Eq 2}$$

When $Z << 1$ ($\rho Z/\rho_{ox} << 1$), the second term in Eq 2 can be simplified, and it follows that the thickness, δ_{ox}, can be estimated by the formula $\delta_{ox} = \rho Z R_p\,(3\rho_{ox})^{-1}$.

Consider, for example, HVOF spraying of Cr_3C_2-NiCr powder when Cr_2O_3 oxide is formed during the particle flight (Ref 9). To provide estimations, assume that the oxide mass flux, q_{ms}, in this case has a value similar to that corresponding to the development of the FeO oxide when an iron droplet is oxidized (Ref 8), where $q_{ms} = 3.6$ kg/(m^{2}s). The value of the characteristic time of oxidation, t_{ox}, is equal to the characteristic time of the particle flight during thermal spraying, which is about 1 ms (Ref 8, 9, 12). Taking $\rho = 7500$ kg/m^3, $\rho_{ox} = 5210$ kg/m^3, and $R_p = 20$ µm, it can be obtained from Eq 1 and 2 that $Z = 0.072$ (7.2%) and $\delta_{ox} = 0.716$ µm (716 nm). When $R_p = 10$ µm, $Z = 0.144$ (14.4%) and $\delta_{ox} = 0.745$ µm (745 nm). It is seen that a decrease in the particle radius leads to an increase in the level of oxidation, Z, and the thickness of the oxidized layer, δ_{ox}. An increase in Z is more pronounced than that in δ_{ox}.

For further purposes it is convenient to introduce the volume fraction of oxidation, φ_{ox}, in the following manner. The thickness of the layer of oxidation, δ_{ox}, is equal to the difference between the radius of the particle, R_p, and the value of R_{ox} (Fig. 1): $\delta_{ox} = R_p - R_{ox}$. The volume fraction of the oxides, φ_{ox}, formed in the particle is equal to the ratio of the volume of the oxidized layer, V_{ox}, to the volume of the particle, V_p. Taking into account that $V_p = 4\pi R_p^3/3$ and $V_{ox} = 4\pi(R_p^3 - R_{ox}^3)/3$, the following expression for the value of δ_{ox} is:

$$\delta_{ox} = R_p\,[1 - (1 - \varphi_{ox})^{1/3}] \tag{Eq 3}$$

Taking into account that the volume of oxidation, V_{ox}, is equal to the volume of the spherical layer with the thickness δ_{ox}: $V_{ox} = 4\pi R_p^2\,\delta_{ox}$, the volume fraction of oxidation, φ_{ox}, can be presented in a form:

$$\varphi_{ox} = 3\delta_{ox} R_p^{-1} \tag{Eq 4}$$

Nomenclature

b	Splat thickness, M
B_p	Relative volume of oxygen diffusion during particle inflight motion
B_{sp}	Relative volume of oxygen diffusion in splat
D	Coefficient of diffusion, m^2/s
D_o	Coefficient of diffusion of oxygen in the liquid particle material, m^2/s
H	Relative mass of oxidation in splat
m	Mass, kg
M	R_1/R_2
P_m	Maximum pressure developed upon droplet impact onto substrate, N/m^2
q_{ms}	Mass flux of oxide, kg/m^{2}s
r_m	Radial position of maximum pressure, m
R	Radius, splat radius, m
Re	Reynolds number, $Re = 2R_pU\rho/\mu$
R_{pr}	Particle thermal resistance during its inflight motion, m^{2}K/W
R_{sp}	Splat thermal resistance, m^{2}K/W
R_1	Thermal resistance of oxidized layer during particle inflight motion, m^{2}K/W
R_2	Thermal resistance of nonoxidized particle part during inflight motion, m^{2}K/W
R_3	Thermal resistance of oxidized layer in splat, m^{2}K/W
R_4	Thermal resistance of nonoxidized part of splat, m^{2}K/W
S	Surface area, m^2
t	Time, s
t_{fl}	Time interval between starting of particle melting and its impingement onto the substrate, s
t_{im}	Particle impact time, s
t_s	Splat solidification time, s
T_{so}	Splat initial temperature, K
T_{tr}	Transition temperature, K
U	Velocity of particle impingement onto substrate, m/s
V	Volume, m^3
V_s	Solidification velocity, m/s
X	R_3/R_4
Z	Relative mass of oxidation in particle during its inflight motion
δ	Characteristic thickness in particle during its inflight motion, m
δ_{fl}	Thickness of layer of oxygen diffusion formed during particle inflight motion, m
Δ	Characteristic thickness in splat, m
Δ_{sp}	Thickness of layer of oxygen diffusion in splat, m
ΔT_p	Supercooling associated with pressure developed upon droplet impact, K
ζ	Dimensionless splat thickness, b/R_p
λ	Coefficient of thermal conductivity, W/(m · K)
μ	Dynamic viscosity of particle material, kg/(ms)
ξ	Dimensionless splat radius, R/R_p
ρ	Density, kg/m$_3$
σ	Surface tension coefficient, N/m
τ	Contact wetting angle, grad
φ	Volume fraction
φ_1	Solid volume fraction in oxidized particle

Subscripts

df	Diffusion
e	Effective
f	Final
ox	Oxidation
p	Particle
sp	Splat

It is seen that the relative volume of oxidation, φ_{ox} (as the relative mass of oxidation, Z), increases with a decrease in the particle radius. If the value of R_p for the Cr_3C_2-NiCr powder varies from 10 to 40 μm, the value of φ_{ox} changes from 22 to 5%. Therefore to decrease inflight oxidation it is necessary to have a narrow size distribution of the powder particles with a relatively large mean value.

2.2 *Diffusion of Oxygen*

Diffusion of oxygen occurs in the surface layer with the thickness, δ_{fl}, of a melted powder particle of the radius, R_p. Intensive turbulent motion of the surrounding gases can cause motion of the liquid phase in this layer. As a result, the coefficient of diffusion, D_o, of oxygen in the liquid phase of the particle increases by the value of D_{mv} associated with the liquid motion. Then the thickness of the diffusive layer, δ_{fl}, can be estimated using the effective coefficient of diffusion of oxygen, D_e, by the formula:

$$\delta_{fl} = (D_e t_{fl})^{1/2} \qquad D_e = D_o + D_{mv} \qquad \text{(Eq 5)}$$

where t_{fl} is the time interval between starting of particle melting and its impingement onto the substrate. If particle solidification occurs at the spray distance then the value of t_{fl} is equal to the difference between the finishing time of the solidification process and the starting time of the particle melting. With a decrease in R_p the value of t_{fl} approaches the time of the particle flight at the spray distance.

In the case of intensive motion of the liquid phase, the value of D_{mv} can exceed significantly the coefficient of diffusion, D_o (Ref 13). During HVOF spraying of the composite powder particles consisting, for example, of the carbides and a metallic binder, the velocity of motion of the liquid phase decreases because the presence of carbides increases the effective viscosity of the liquid-solid mixture, which arises after melting of the binder (Ref 14). This would lead to a decrease in the value of D_{mv} (and, hence, D_e) and to a decrease in the level of the oxygen diffusion in the particle in comparison with the homogeneous particle without carbides.

Taking the typical values of $D_o = 10^{-9}$ m²/s and $t_{fl} = 10^{-3}$ s (Ref 11-13) from Eq 5, $\delta_{fl} = 1$ μm when $D_{mv} = 0$. If, for example, $D_{mv} = 3 \times 10^{-9}$ m²/s, then from Eq 5 it follows that $\delta_{fl} = 2$ μm. It is seen that the thickness of the layer of the oxygen diffusion, δ_{fl}, exceeds markedly the thickness of the oxidation layer, δ_{ox}.

It is possible to introduce the relative volume or the volume fraction of the oxygen diffusion, φ_{df}. The thickness of the diffusive layer, δ_{df}, is equal to the difference between the radius of the particle, R_p, and the value of R_{df}: $\delta_{df} = R_p - R_{df}$ (Fig. 1). The volume fraction of the diffusive layer, φ_{df}, developed in the particle due to the diffusion of oxygen is equal to the ratio of the volume of the diffusive layer, V_{df}, to the volume of the particle, V_p. Thus, taking into account that $V_{df} = 4\pi(R_p^3 - R_{df}^3)/3$, the following formulas for δ_{df} and φ_{df} are $\delta_{df} = R_p\,[1 - (1 - \varphi_{df})^{1/3}]$ and $\varphi_{df} = 3\delta_{df}R_p^{-1}$.

These formulas are similar to those of Eq 3 and 4 for δ_{ox} and φ_{ox}, respectively. The volume fraction of oxygen diffusion, φ_{df}, decreases with an increase in the particle radius in a similar manner as the volume fraction of oxidation, φ_{ox}. When R_p varies from 10 to 60 μm, the value of φ_{df} changes from 30 to 5% if $\delta_{df} = 1$ μm and from 60 to 10% if $\delta_{df} = 2$ μm.

It can be seen that $\delta_{df} > \delta_{ox}$. The relative difference, B_p, between δ_{df} and δ_{ox} ($B_p = 1 - \delta_{ox}/\delta_{df}$) determines the relative volume of the powder particle where only diffusive (dissolved) oxygen is contained. In the case of HVOF spraying of Cr_3C_2-NiCr powder, $R_p = 20$ μm, the value of $A_p = 28.4\%$ when $\delta_{df} = 1$ μm, and $B_p = 64.2\%$ when $\delta_{df} = 2$ μm.

2.3 *Effect of Oxidation on Heat Transfer*

Consider an influence of oxidation on the heat transfer between the particle and the surrounding gases. This heat transfer depends on the thermal resistance, R_{pr}, of the powder particle being equal to the sum of the thermal resistances of the oxidized layer, R_1, and that of the rest of the particle, R_2 (Fig. 1a): $R_{pr} = R_1 + R_2$, $R_1 = \delta_{ox}\lambda_{ox}^{-1}$, and $R_2 = (R_p - \delta_{ox})\lambda_p^{-1}$, where λ_{ox} and λ_p are the coefficients of thermal conductivity of the oxidized layer and the particle, respectively. The ratio $M = R_1/R_2$ is:

$$M = \lambda_p\varphi_{ox}\,[3\lambda_{ox}(1 - \varphi_{ox}/3)]^{-1} \qquad \text{(Eq 6)}$$

The influence of the thermal resistance, R_1, of the oxidized layer increases with an increase in the particle thermal conductivity, λ_p, and the volume fraction of oxidation, φ_{ox}, and a decrease in the thermal conductivity of the developed oxides, λ_{ox}.

Consider, for example, the HVOF spraying of the Cr_3C_2-NiCr powder onto a mild steel substrate when Cr_2O_3 is formed during the particle motion at the spray distance (Ref 9, 11). Taking $R_p = 20$ μm, $\lambda_p = 70$ W/(m · K), and $\lambda_{ox} = 22$ W/(m · K) from Eq 6, $M = 0.31$. Thus in this case the thermal resistance, R_1, of the oxidized layer constitutes about one-third of that of the rest of the particle, R_2.

Turbulent mixing of the liquid part of the powder particle during its inflight motion destroys the surface layer of oxides and make the oxides distributed more uniformly through the bulk volume of the particle (Fig. 1b). Because the thermal diffusivity of the oxides is significantly less than that of the metallic (or carbide) phase, the presence of oxides in the particle volume decreases the particle thermal diffusivity and, hence, slows

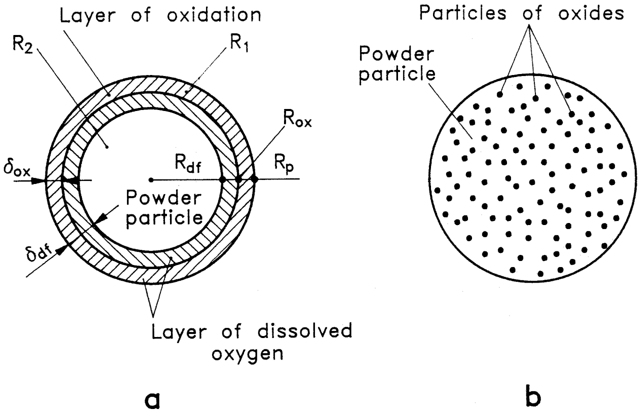


Fig. 1 Development of layers of oxides and dissolved oxygen in the powder particle during its (a) inflight motion and (b) mixing of the oxides in the bulk volume of the particle due to turbulence of the surrounding gases

down the heat exchange between the particle and the surrounding gases.

Usually the reactions of oxidation are accompanied by heat release. This occurs in the surface layer of the particle, and, due to the very small thickness of this layer, it seems reasonable to assume that most heat is transferred outside of the particle. Some part of this heat may be transferred inside the particle and contribute to the particle melting. But this effect is weakened because of a decrease in the particle thermal diffusivity caused by oxidation.

The oxides developed during particle flight play an important role in droplet flattening and the splat-substrate interaction. Oxidation also occurs at the upper liquid surface of the solidifying splat. This oxidation is considered in the following paragraph.

3. Splat Oxidation

During droplet flattening the upper surface of the forming splat is exposed to the surrounding oxygen-rich atmosphere and is oxidized during the splat solidification time, t_s, when this surface remains liquid (Fig. 2a). The process of oxidation is similar to that mentioned previously for the inflight oxidation of the powder particle.

Consider the formation of a regular disk splat with the radius, R, and thickness, b, as a result of flattening of the droplet with the radius, R_p, impinging onto the substrate surface. Using the arguments similar to those given previously it is possible to show that the ratio, H, of the mass of the oxidized layer in the splat to the splat mass is determined by the formula:

$$H = q_{ms} t_s \, (\rho b)^{-1} \quad \text{(Eq 7)}$$

The thickness of an oxidized layer, Δ_{ox}, can be presented as:

$$\Delta_{ox} = \rho b H / \rho_{ox} = q_{ms} t_s / \rho_{ox} \quad \text{(Eq 8)}$$

The relative volume of oxidation, A, is equal to the ratio of the oxidized volume, V_{os}, in the splat to the splat volume, V_{sp}. For the disk splat with the radius, R, and thickness, b, $V_{os} = 4\pi R^2 \delta_{ox}$ and $V_{sp} = 4\pi R^2 b$, it can be obtained that:

$$A = b^{-1} \Delta_{ox} \quad \text{(Eq 9)}$$

Following is an estimation of the oxidation parameters in the case of HVOF spraying of the Cr_3C_2-NiCr powder when Cr_2O_3 is formed. Taking $t_s = 10^{-3}$ s, $b = 3$ μm, $q_{ms} = 3.6$ kg/(m^{2}s), $\rho = 7500$ kg/m^3, and $\rho_{ox} = 5210$ kg/m^3, it can be obtained from Eq 7 to 9 that $H = 0.016$ (1.6%), $\Delta_{ox} = 0.07$ μm (70 nm), and $A = 0.023$. It can be seen that under the conditions considered, splat oxidation is less pronounced than oxidation that occurs in flight.

The characteristic thickness of the oxidized layer, Δ_{ox}, in the case of the regular disk splats is about two orders of magnitude less than the splat thickness. Turbulent mixing of the splat liquid phase causes more uniform oxide distribution in the bulk volume of this phase (Fig. 2b), which leads to a decrease in the thermal diffusivity of the liquid phase and slowing down of its solidification. As a result, the coating would exhibit a more coarse crystalline structure that weakens the coating mechanical properties.

The diffusion of oxygen can also take place. The thickness, Δ_{sp}, of the layer of diffusion can be estimated by the formula (Ref 13):

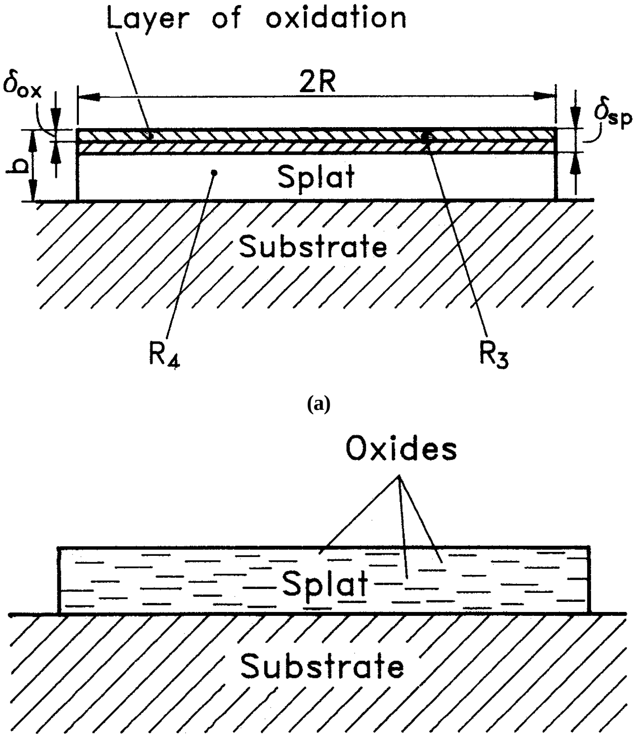
$$\Delta_{sp} = (D_e t_s)^{1/2} \quad \text{(Eq 10)}$$

Taking $t_s = 10^{-5}$ s and $D_e = 4 \times 10^{-9}$ m^2/s, from Eq 10, $\Delta_{sp} = 0.2$ μm. Thus, the thickness of the diffusion layer is essentially greater than that of the oxidation layer. The relative difference, B_{sp}, between Δ_{sp} and Δ_{ox} ($B_{sp} = 1 - \Delta_{ox}/\Delta_{sp}$) gives the relative volume of the splat containing only dissolved oxygen. For HVOF spraying of the Cr_3C_2-NiCr powder, $B_{sp} = 65\%$. Thus, the value of B_{sp} has the same order of magnitude as the value of B_p.

Oxidation contributes to the development of splashing, and the thickness of the splash splats formed could be of the same order of magnitude as the value of the oxidized layer, δ_{sp}. In the case of the marked splashing when the value of A could be of the order of unity, the coating would have a substantial quantity of oxides.

Formation of the coating structure and properties depends on the coating cooling and solidification which, in turn, depend on the thermal resistance of the splat, R_{sp}. In the case of regular disk splats the value of R_{sp} is the sum of the thermal resistance of the oxidized layer, R_3, and that of the rest of the splat, R_4 (Fig. 2a): $R_{sp} = R_3 + R_4$, $R_3 = \Delta_{sp} \lambda_{ox}^{-1}$, and $R_4 = (b - \Delta_{sp}) \lambda_p^{-1}$. The ratio $X = R_3/R_4$ has the form:

$$X = \lambda_p A [\lambda_{ox}(1 - A)]^{-1} \quad \text{(Eq 11)}$$



(a)

(b)

Fig. 2 Formation of layers of oxides and dissolved oxygen in a splat exposed to the (a) oxygen-rich boundary layer enveloping the splat and (b) mixing of the oxides in the bulk volume of the splat due to turbulence of the surrounding gases

In the case, for example, of HVOF spraying of the Cr_3C_2-NiCr powder onto a mild steel substrate when disk splats are formed, $b = 2$ µm and $\Delta_{sp} = 0.2$ µm, from Eq 10 and 11, $X = 0.035$. Therefore, the thermal resistance of the oxidized layer in this case does not play any significant role. The situation changes when a marked splashing occurs and thin splash splats are formed.

The splat initial temperature also plays an important role in the splat oxidation. An increase in this temperature accelerates the kinetics of oxidation and increases the time, t_s, of the splat solidification due to an increase in the heat content of the splat. Both these factors lead to an increase in splat oxidation.

4. Influence on Droplet Flattening

First consider an agglomerate composite particle consisting of small high melting point oxides and metal. Such a particle can be formed as a result of the inflight oxidation of an initial powder particle and mixing of the oxides with the melted binder due to turbulence of gases surrounding the particle. Assume that during thermal spraying, this particle of radius, R_p, impinges normally with a velocity, U, onto the surface of a substrate or previously deposited coating layer and forms a cylindrical splat of radius, R, and thickness, b, which vary with time, t, during flattening. Assume further that the solid oxide components are significantly smaller than the splat thickness and that the surface roughness, ε_o, and a liquid-solid mixture of the impinging droplet can be considered as a quasi-homogeneous medium with a solid volume fraction, φ_1. Such a splat can also be formed from a powder particle that had a regular surface layer of oxides destroyed during the droplet impingement onto the substrate surface.

When oxidation of the splat upper surface occurs, the oxides developed increase the oxide volume fraction, $\varphi_1 = \varphi_{ox} + \iota_1$, of the liquid-solid mixture. Because the value of ι_1 is a function of time due to the continuous formation of oxides in the liquid phase of the splat, the volume fraction, φ_1, is also a function of time: $\varphi_1 = \varphi_1(t)$. This is one of the main differences between the flattening of the oxidized particles and the composite powder particles consisting, for example, of carbides and a metallic binder (Ref 14).

An effective viscosity, μ_e, and an effective velocity of solidification, V_{se}, were introduced in the same manner as in Ref 14. Using the equations, methods, and ideas described in Ref 14-16 and taking into account that the Reynolds number, $Re_e = 2R_pU\rho\,\mu_e^{-1}$, in thermal spraying is much more than unity ($Re_e >> 1$), the equations for the dimensionless transient values of the splat thickness, ζ, and radius, ξ, can be obtained. The formulas for the final values of the splat thickness, ζ_f, and radius, ξ_f, when $Re_e >> 1$ are similar to those given in Ref 12.

The formulas discussed are similar to those for the flattening parameters of the composite powder particles (Ref 14), but they are more general and correspond to the case when the solid volume fraction, φ_1, can vary with time and the correction factor, $\psi < 1$. With an increase in the volume fraction of oxidation the final splat thickness increases and the final splat radius decreases (Fig. 3).

It can be seen that oxidation leads to an increase in the splat thickness and to a decrease in the splat radius due to an increase in the effective viscosity of the flattening droplet and a decrease in the velocity of solidification of the lower part of the splat.

The presence of dissolved oxygen can be established to cause a decrease in the contact wetting angle and, therefore, an improvement of wetting between the substrate and the flattening droplet (Ref 17). With an increase in the particle velocity at the spray distance, the time of the particle flight decreases, and the value of the time, t_{ox}, available for oxidation also decreases. Under such conditions the volume fraction of oxidation, φ_{ox}, could be negligible, the value of B_p is about unity, and the main result of interaction of the molten particle with the surrounding oxygen could be its diffusion in the liquid particle material.

If in this case a liquid splat oxidation is also very small and the value of B_{sp} is about unity, in the final splat it will be practically only dissolved oxygen that improves wetting between the splat and the substrate and contributes to an improvement of the substrate-splat adhesion. A similar situation can occur when the main contribution to oxidation is splat exposure to the surrounding oxygen-rich atmosphere. With an increase in the splat solidification velocity, which can take place, for example, when the thermal diffusivities of the splat and the substrate are high enough, the time of solidification, t_s, decreases and the volume fraction of oxidation in the splat, ι_1, can become negligible compared with that of the oxygen dissolution. Thus, the presence of dissolved oxygen can improve the quality of the coating.

5. Effect on Splat-Substrate Mechanical Interaction

High pressure, P_m, is developed during the droplet impingement onto a substrate surface. Using the method and equations given in Ref 18, the formulas for P_m and position, r_m, of the maximum pressure can be obtained, taking into account oxidation. Because oxidation causes a decrease in the effective value of the Re_e due to an increase in the viscosity, μ_e, the value of r_m

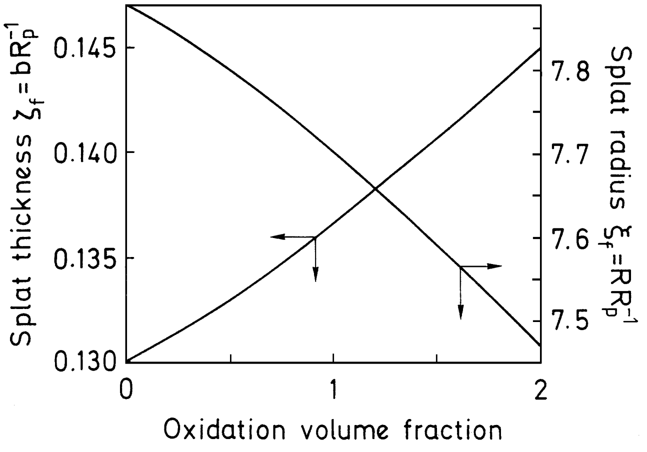


Fig. 3 Variation of the final values of the splat thickness and the splat radius with a volume fraction of oxidation

increases and the value of P_m decreases. Thus, the pressure developed during impact of an oxidized droplet is less than that which is formed when oxidation is absent. Behavior of P_m is illustrated in Fig. 4 for plasma sprayed molybdenum particles on a smooth substrate when the time, t, is equal to the characteristic impact time, $t_{im} = R_p U^{-1}$, and $R_p = 20$ µm, $U = 150$ m/s, and $\rho = 9900$ kg/m^3. Thus oxidation is detrimental to substrate-coating adhesion.

Inflight interaction of the powder particle with oxygen may result not only in oxidation of the particle material but also in diffusion (dissolution) of oxygen in the liquid phase of the moving particle. The presence of the dissolved oxygen in the impinging droplet can decrease the surface tension coefficient, σ, and the contact wetting angle, τ, and this contributes to a decrease in splashing and in the capillary pressure. These factors work in favor of an improvement of the splat-substrate mechanical interlocking. An important question that remains to be answered is whether their influence can overcome an effect of a decrease in the pressure developed upon the droplet impact due to oxidation that contributes to a decrease in the mechanical interlocking between the splat and the substrate (Ref 19).

From the results of Ref 20 it follows that porosity increases with an increase in the surface tension coefficient, σ. Diffusion of oxygen causes a decrease in σ and, hence, a decrease in porosity. But because the value of P_m exceeds markedly, the capillary pressure, $2\sigma R_o^{-1}$, this factor can hardly ever compete with an increase in the coating porosity due to a decrease in the pressure developed upon impact when provoked by oxidation.

6. Effect on Splat-Substrate Thermal Interaction

Oxidation decreases the pressure developed upon the droplet impact and the solidification velocity of the splat. Therefore, when the initial splat temperature, T_{so}, is less than a transition temperature, T_{tr}, which is specific for each substrate material (Ref 21), the pressure developed could be not sufficient for the formation of the supercooling, ΔT_p, associated with this pressure in the whole central part of the flattening droplet (Ref 22). As a result a regular disk splat could be developed only in the reduced area of the central part or, if the level of oxidation is high, splashing could occur everywhere.

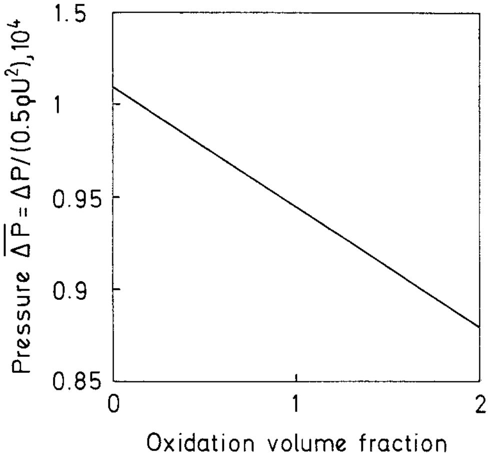


Fig. 4 Variation of pressure developed upon the droplet impact with a volume fraction of oxidation

With $T_{so} > T_{tr}$, the thermal supercooling developed could be not enough for starting solidification in the lower part of the whole splat. As a consequence splashing could take place at the periphery of the flattening droplet and even in its central part.

Thus, oxidation makes the development of splashing more favorable. This is detrimental to substrate-coating adhesion and increases the coating porosity. It seems that the negative effect of oxidation on the splat morphology and the coating properties may be weakened by an increase in the initial temperature of the substrate, at least for the relatively low levels of oxidation.

It should be mentioned that the presence of dissolved oxygen causes a decrease in the contact wetting angle and the coefficient of surface tension that contributes to a decrease in splashing.

7. Comparison with Experimental Data

The results obtained in Ref 5 indicate that coating oxidation decreases with an increase in the spray distance when the influence of the heated products of combustion on the solidifying splat decreases and splat solidification occurs more rapidly. The results of Ref 5 also show that an increase in the splat initial temperature (which gives rise to the substrate temperature) leads to an increase in the coating oxidation.

Plasma spraying of yttria-stabilized zirconia powder onto the steel and zirconia substrates demonstrated that on the oxidized substrate surface, splashing always occurred and splash splats were formed (Ref 23). This occurred in spite of the fact that the substrate initial temperature exceeded the critical temperature when the regular disk splats were usually formed (Ref 22).

This phenomenon, as indicated previously, is associated with a decrease in the pressure developed upon the droplet impact onto the substrate surface. It is also explained by a decrease in the velocity of the splat solidification caused by a decrease in the thermal diffusivity of the splat and an increase in the contact thermal resistance at the splat-substrate interface due to oxidation.

Experimental data established in Ref 24 for the parameters of flattening and solidification of the splats formed after impingement of the tin droplets onto a stainless steel substrate show that a contact wetting angle decreases with an increase in the substrate initial temperature that contributes to an increase in the splat radius. This agrees with the results presented in this article.

Analytical expressions for the maximum splat size derived in Ref 25 also show that it increases with decreasing contact angle of wetting. Finally, the results of modeling of the droplet flattening presented in Ref 25 and 26 indicate that the influence of wetting between the substrate and the flattening droplet on the droplet spreading on the substrate surface decreases with an increase in the velocity of the droplet impingement. The experimental data also show that the presence of dissolved oxygen in the liquid splat causes a decrease in the contact wetting angle (Ref 17).

Experimental data concerning HVOF spraying of stainless steel 316 on a mild steel substrate show that the level of oxidation increases with an increase in the spraying distance. At 0.3 m there are 12.49% of oxides in the coating, and at 0.45 m there are 25.66% of oxides (Ref 27). This supports a view that the main oxidation in this case occurs during the inflight motion of the powder particles. A similar situation occurs during plasma spraying of the stainless steel 431 on a mild steel substrate. It is clearly seen from the scanning electron micrograph of the coating (Fig. 5) where the oxides are distributed chaotically because it usually occurs during the inflight oxidation of the powder.

The coating structure obtained as a result of the HVOF spraying of the Cr_3C_2-NiCr powder onto a mild steel substrate shows that the main oxidation of chromium takes place during the inflight motion of the powder particles (Ref 9) (Fig. 6). This can be attributed to an increase in the particle residence time (and the value of t_{fl}) at the spray distance due to inflight dissolution of Cr_3C_2 (Ref 9).

The experimental results show that during HVOF spraying of the Cr_3C_2-NiCr powder the relative mass of chromium oxide in the coating is about 4.95% (Ref 28). Taking into account that the main oxidation occurs during the inflight motion of the powder particles, it is possible to estimate theoretically the level of oxidation as follows: The relative mass of oxidation, G, is equal to the ratio of the mass of the oxidized layer in the particle, m_{ox}, to the mass of the particle, m_p. Taking into account that $m_{ox} = \rho_{ox} V_{fl}$ and $m_p = \rho_p V_p$, $G = 3\delta_{fl}\rho_{ox}(\rho_p R_p)^{-1}$, where ρ_p and ρ_{ox} are the densities of the particle and the oxide, respectively. From Ref 9 the value of t_{fl} is equal to 0.5 ms. Taking into account that the presence of carbides decreases the effective coefficient of diffusion of oxygen, $D_e = 10^{-9} m^2/s$. Then taking $R_p = 25$ μm, $\rho_p = 7800$ kg/m^3, $\rho_{ox} = 5200$ kg/m^3, and using Ref 5, it can be obtained that the theoretical value of G is equal to 0.57 and is not far from the experimental value of $G = 0.495$.

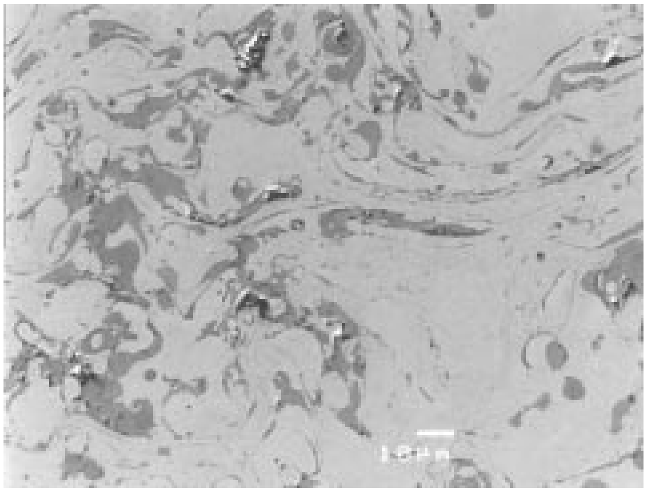


Fig. 5 Scanning electron micrograph of stainless steel 431 coating on a mild steel substrate obtained by plasma spraying

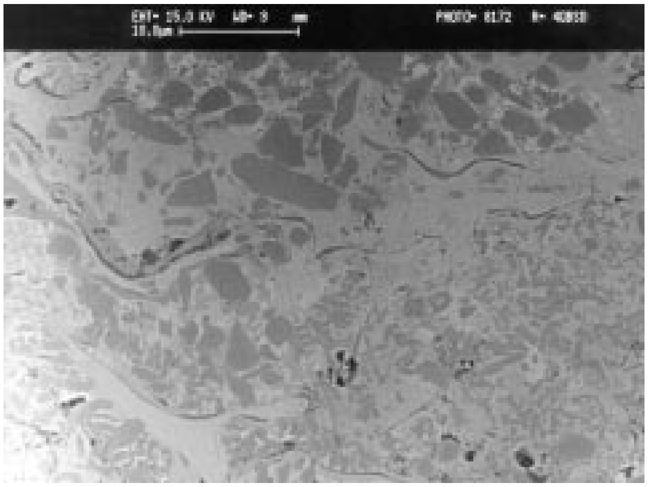


Fig. 6 Scanning electron micrograph of high velocity oxygen fuel sprayed Cr_3C_2-NiCr coating on a mild steel substrate

Thus, the theoretical results agree well with the observed tendencies of the development of oxidation and its influence on the formation of the coating. The results obtained are also in agreement with the experimental data showing the effect of oxygen dissolved in the splat on wetting and with the experimental, analytical, and modeling results relating to the influence of wetting on the flattening parameters.

8. Conclusions

The following conclusions can be drawn:

- A decrease in the powder particle radius leads to an increase in the level of the particle inflight oxidation and the thickness of an oxidized layer. To decrease the particle inflight oxidation it is necessary to have a narrow size distribution of the powder particles with a relatively large mean value. Besides oxidation, diffusion of oxygen in the liquid phase of the particle occurs. The relative volume of oxygen diffusion and the thickness of the diffusive layer exceed the values corresponding to the oxidation process and also decrease with an increase in the particle radius. For the composite powder particles (e.g., consisting of carbides and a metallic binder) the level of oxygen diffusion is smaller than for a homogeneous particle without carbides. Behavior of parameters of oxidation and diffusion of oxygen in the solidifying splat exposed to the oxygen-rich atmosphere is similar to that in the particle during its inflight motion.
- The thermal resistance of the oxidized layer in the particle and in the splat increases with an increase in the particle thermal conductivity and the volume fraction of oxidation and a decrease in the thermal conductivity of the developed oxides. In the case of inflight oxidation, this thermal resistance has the same order of magnitude as the total thermal resistance of the particle and plays an important role in heat transfer processes. For the case of splat oxidation, the thermal resistance of the oxidized layer does not play any significant role when the regular disk splats are formed. This resistance becomes important when significant splashing occurs and thin splash splats are developed.
- Flattening of the oxidized droplets impinging onto the substrate surface is similar to that of the composite powder particles with an exception that, due to the splat oxidation, the volume fraction of oxides varies with time. Oxidation leads to an increase in the splat thickness and a decrease in the splat radius.
- Oxidation decreases the pressure developed upon the droplet impact that is detrimental to the contact between the substrate and splat. Oxidation diminishes the contact heat transfer coefficient at the splat-substrate interface and the

velocity of solidification of the splat. This leads to a decrease in the coating-substrate adhesion and an increase in the coating porosity.

- A decrease in the contact wetting angle corresponding to an improvement of wetting between the splat and the substrate leads to a decrease in the splat thickness and an increase in the splat radius that contributes to reinforcement of the splat-substrate adhesive bonding. Influence of wetting on the flattening process decreases with an increase in the velocity of the droplet impingement onto the substrate surface and a decrease in the substrate initial temperature.
- The analytical results agree with the observed processes of flattening of droplets and the formation of splats in thermal spraying. This enables better understanding of these processes and predicting the parameters involved.

Acknowledgments

The authors are grateful to Generalitat de Catalunya (project SGR 97-15) and CICYT (project MAT 96-0426) for financial support.

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