MODELING OF IN-FLIGHT OXIDATION AND EVAPORATION OF PLASMA-SPRAYED IRON PARTICLES

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Abstract
Metal particles injected in a plasma jet issuing through atmospheric air may be subjected to chemical reaction with entrained oxygen and also partial vaporization. These phenomena are undesirable from the viewpoints of quality of coating, efficiency of powder utilization, and increased environmental load due to fume formation. This paper presents the results of a mathematical model that simulated these phenomena for the case of plasma spraying of iron powder.

1. Introduction
Metal particles entrained in a plasma jet are subjected to chemical reaction with oxygen in the surrounding air either in flight or after impinging on the substrate. Also, the presence of an oxidizing atmosphere enhances the diffusion-limited rates of vaporization of the metal droplets in the plasma jet by decreasing the concentration of metal vapor within the gaseous boundary layer around the particle [1].

Oxidation of the particles can significantly affect the microstructure and, therefore, the properties and performance of the plasma-sprayed coatings. Evaporation results in a decrease of deposition efficiency, possible alteration of the microstructure of the coating when the vapor re-condenses on the substrate, and the formation of fume and submicronic dusts that are environmentally undesirable. Evidently, better understanding of metal oxidation and evaporation can be of help in developing cost-effective ways to control these phenomena in the plasma spraying of metals in the presence of air.

This study examines the various stages of particle oxidation in flight by means of a mathematical model. The effect of gas-phase oxidation on the rate of evaporation from individual particles is examined. The sprayed metal was iron that is more susceptible to oxidation than the metal and alloy powders that are used in thermal spraying. However, in view of the peculiarities of the iron-oxygen phase diagram, certain complications are involved in the oxidation of this metal which do not apply to other metal-oxygen reactions.

2. Experimental Observations
The principal source for validation of the mathematical model was a series of experiments carried out at the University of Limoges [2]. Iron particles were injected in an argon-hydrogen plasma jet flowing through atmospheric air. Instead of impinging on a substrate, as in normal plasma spraying, the jet was quenched by means of a counter-flowing inert gas stream and the contained liquid iron particles were solidified in flight. The collected particles were embedded in acrylic disks that were sectioned and polished. Examination of sectioned particles by Scanning Electron Microscopy, revealed an outer thin shell of iron oxide around the solidified iron spheres; small spherical occlusions of iron oxide were also
observed within the iron core [2]. Neiser et al [3] made the same observation for individual splats of iron produced in a wire-fed HVOF thermal spraying device. Analysis of the solidified spheres by X-Ray Diffraction and Mössbauer spectra [2] and of the iron splats by Auger Electron Spectroscopy [3] showed that both the occlusions and the oxide shell had a composition close to FeO which is the phase expected to form during high temperature oxidation of iron.

The phase diagram of iron and oxygen shows that at 1700 °C, the highest temperature in the diagram, liquid Fe dissolves up to 0.32%f oxygen by weight, at higher oxygen concentrations, coexist two immiscible liquids, iron and wüstite [4]. It is therefore reasonable to assume that during cooling of the particles collected in flight [2], and also the splats formed on the substrate surface [3], FeO can precipitate within iron and stays as a metastable phase at room temperature thanks to the high cooling rates (> 10⁶ °C/s) undergone by the collected particles and splats.

For plasma spraying conditions similar to those used in this modeling study and a 45-90 μm iron powder, the mass content of oxide of the solidified particles collected in flight was about 12 %, i.e. approximately 3% oxygen by weight; the thickness of the outer oxide shell was less than 100 nm thick. After treatment in the plasma jet, the powder had a particle size distribution of 5-65 μm. For a powder with an original size distribution ranging between 14 and 55 μm, the mass lost by vaporization was estimated at about 25 %.

3. Oxidation and Evaporation Under Thermal Plasma Spraying Conditions

For a set of plasma operating conditions, the evaporation and amount of oxygen pick-up will depend on the trajectories followed by individual particles. The particle trajectory determines the gas-particle relative velocity, temperature, and oxygen concentration encountered by a particle as it travels from torch to substrate and, therefore, its residence time and degree of melting.

Depending on particle trajectory, oxidation may proceed according to one of the following possibilities:
- gas-liquid phase oxidation, for particles that penetrate in the core of the plasma jet and are molten in a zone where oxygen has not penetrated as yet;
- gas-solid phase oxidation, while the particles are being heated to their melting point, followed by gas-liquid phase oxidation of the molten droplets. This two-stage oxidation occurs for particles that do not penetrate in the hottest region of the plasma jet after injection;
- gas-solid phase oxidation for injected particles that do not have sufficient momentum to penetrate into the plasma core and travel along the fringes of the jet flow.

In that last scenario where particles do not melt, the metal oxide will grow as an oxide shell round the particle. In any case, the rate of oxidation depends on the following consecutive phenomena: (i) oxygen transfer within the particle boundary layer, (ii) chemical reaction at the particle surface, (iii) transfer of oxygen from the reacting surface to the interior. Rough estimates of the oxygen mass transfer coefficient for particles in the conditions of the present study shows that the limiting step is the diffusion inside the particle. However, for fully molten particles, the shear stress at the interface between the gas flow and the molten particles can be large enough, under plasma spraying conditions, to induce internal flow within the liquid droplet [3,5]. In effect, the ratio of the kinematic viscosity of gas to liquid iron ranges between 600 and 2500 in the conditions of the present study. The motion of the fluid inside the droplets moves the outer oxidized layer inward to the molten core and explains the occlusions of oxide observed in the solidified droplets.
When the metal particles evaporate in an oxidizing atmosphere, the counter-diffusing oxygen and metal vapor can react and form a metal oxide mist in the gas close to the metal-gas interface. As a result, the partial pressure of oxygen in the boundary layer influences the rate of vaporization (Figure 1). The latter can also be affected by the process of condensation of the vapor near the surface of the vaporizing droplet, when decreasing temperatures in the gas phase result in supersaturation of the vapor and spontaneous nucleation of the condensing phase. The collection of the submicron particles resulting from vapor condensation by means of an electrical low pressure impactor [6] showed that the concentration of submicronic particles ranged from $2.5 \times 10^8$ at 20 mm to $5 \times 10^9$ at 110 mm and exhibited a rapid increase at 40 mm. This corresponds to the mixing of the plasma jet with the surrounding air that results in a rapid decrease in flow temperature and also practically to the end of particle vaporization, except for the finest ones. Therefore, the condensation process does not affect appreciably particle vaporization in thermal plasma conditions.

Finally, the rate of vaporization can be enhanced by forced convection within the particle boundary layer and by the sweeping of the vapor away from the particle due to the relative velocity between particle and plasma gas.

4. Calculation Procedure
4.1 Operating Conditions

A plasma torch with a 7-mm nozzle exit diameter was assumed in the numerical simulations. The plasma jet issued in air at atmospheric pressure. The inlet gas was a mixture of argon (45 slm) and hydrogen (15 slm) and the plasma torch was operated at 600 A; the corresponding power effectively dissipated in the gas was 21.5 kW. Iron powder with particle sizes ranging from 10 to 100 µm was injected through a 1.8-mm diameter injector located at 4 mm downstream of the nozzle exit and 8.5 mm away from the jet centerline. It should be noted that the above operating conditions, combining high arc current (600 A) and hydrogen content (25%), may result in "over-vaporization" of the metal powder, as compared to that observed under the industrial conditions generally used to spray iron-based powders.

4.2 Mathematical Model

The numerical simulation is carried out in two stages. The first one consists of the calculation of the plasma jet fields and the particle trajectories, velocities and temperatures within the jet envelope. In the second stage, the projected gas and particle parameters are used
as input data in the computation of the mole fraction of vaporized and oxidized iron along the particle trajectory, as shown in the flow chart of Figure 2.

The model of the plasma jet issuing in air is based on the following assumptions: Steady-state two-dimensional and axisymmetric flow; local thermodynamic equilibrium; optically thin plasma; and turbulent flow, except within the potential core and close to the walls. Turbulence is modeled by the standard k-ε model.

For the chemical reactions in the plasma gas and the entrained air, the dissociation and molecular reactions are modeled using the reduced set of equations proposed by Park and al for a nitrogen-hydrogen plasma jet flowing into atmospheric air [7]. The ionized species are not incorporated in this work.

\[ J_{O_2} = 0 \]
\[ J_{Fe} = 2(l/d) \]
\[ J_{Fe} + J_{O_2} = 2(l/d) \]
\[ J_{Fe} + J_{O_2} = 0 \]

Figure 2

The multicomponent Navier-Stokes equations are solved using the FIDAP software package [8] that allows the modeling of chemical reactions in turbulent flows.

The acceleration and heating of particles are calculated with a Lagrangian scheme under the following assumptions: Spherical particles; no interaction between particles; turbulent dispersion; pressure forces due to density gradients and drag forces acting on particles; and lumped capacitance method for particle heating. The effect of the powder carrier gas is not taken into account in the calculations since both experiments and mathematical simulations [9] have shown that it does not have an appreciable effect on the plasma flow except in cases when the powder is injected inside the nozzle.

The increase of the solid oxide layer with time is represented by a parabolic law [10]:
\[ \delta^2 = 2k \times t \]
where \( \delta \) is the oxide thickness, \( t \) the time of oxidation and \( k \), a temperature-dependent rate constant. The latter is determined from the following Arrhenius-type equation:
\[ D_{O,P0} = 1.18 \times 10^6 \exp (-29,700 \text{ cal/mol } /RT) \text{, in m}^2/\text{s} \text{ where } R \text{ is the universal gas constant [3].} \]

When the particles are fully molten, the potential circulation flow inside the particle and also the gas-liquid phase oxidation are computed using the FIDAP CFD code. The procedure and assumptions are described in [5].

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5. Results and discussion

Figure 3 shows the mole fraction of molecular oxygen (upper part of the drawing) and atomic oxygen (lower part) in the plasma jet. The O2 partial pressure is high in the fringes of the plasma jet and further downstream in the jet plume while the O pressure is significant at the tip of the potential core where the molecular oxygen entrained from the surroundings is dissociated in high-temperature regions.

The most influential parameters on particle behavior in a plasma jet are the particle size and injection velocity [11,12] that condition the particle trajectory. The present simulation deals with both variables.

Figure 4 shows the trajectory of a 40 μm iron particle injected at 5, 10 and 15 m/s in the plasma jet. Figure 5, the evolution of the mole fraction of oxidized and evaporated iron droplet with time according to particle trajectory. The oxidation of particles starts when they penetrate the fringes of the plasma jet. However, as shown in [5], the extent of gas-solid phase oxidation is very limited and oxide shells less than 100 nm are predicted. In effect, iron particles that have a low melting point (1535°C) and a low heat of fusion (2.7 \( 10^3 \) J/kg), are rapidly melted when they penetrate in hotter zones of the jet.

When particles are fully molten, a circulation flow generally develops inside the droplets and the liquid oxide is no longer sustained on the surface. The liquid iron flows along the vortex streamlines inside the droplets and the oxide formed on the surface is swept away such a flow as observed in Figure 6; the latter shows the concentration field of oxide in a 60 μm droplet, at 0.1 ms after particle melting. Therefore, for most of the particles, the thickness of the oxide shell observed by SEM [2] of sectioned particles is probably determined by the intensity of the internal vortex and not by the solid-gas phase oxidation process.

For 40 μm particles injected at various injection velocities, the total vaporized volume fraction ranges between 15 and 20 % while the total oxidized fraction varies between 9 and 4%. A 15-m/s injection velocity favors the penetration of the particles into the hottest zones of the jet where evaporation rapidly occurs and limits the oxidation process. If we consider a 22-45 μm powder and assume that all the particles are injected with the same velocity, i.e. 10 m/s, the calculated total mass lost by vaporization is about 23% and the oxide content of the
powder about 9%. These results are in fair agreement with the experimental observations (section 2).

![Figure 5: Mole fraction of evaporated and oxidized iron versus time for 40-μm particles injected into the plasma jet with various injection velocities.](image1)

Figure 6: Concentration field of oxygen inside a 60 μm iron droplet, 1.1 ms after the melting of particle.

Figure 7 compares the behavior of a 40-μm and 80-μm particle, both injected at 10 m/s. The surface of both particles is rapidly oxidized, then particles melt and, when droplet temperature reaches 2950 K, evaporation starts. The iron vapor reacts with the oxygen close to droplet surface to form oxide vapor. The latter is swept away by the gas flow around the particle. and, in the zones of high temperature, decomposed into iron vapor and oxygen that are also entrained by the flow. The heavier 80 μm particle penetrates less deeply in the plasma jet. Therefore, evaporation is limited and stops after a short time (a few tens of μs), because of an increase in the partial pressure of oxygen close to droplet surface, even though the droplet is still at high temperature. Under these circumstances, the oxide layer covers the surface of the droplet and is entrained inside the droplet by the internal convection. For the 40-μm particle, the evaporation rate is high and prevents further surface oxidation. However, mixing of oxide layer with the recirculating flow may also occur.

The computation of vaporization and oxidation of particle with sizes ranging from 10 to 100 μm show a clear dependence of these phenomena on particle diameter. The finer the particles are, the higher the evaporated fraction is and, the lower the oxidized fraction. The predictions of the model show that particles of diameters higher than 90μm do not undergo any evaporation.

The experiments on powder vaporization described in [6] shows that, as expected, evaporation is higher for the finer-size particles. However, the observation of the iron particles collected in-flight does not show an obvious connection between particle oxidation and size while the predictions reveal that the oxide content of particle increases with size due to a lower evaporation rate and longer residence time. This discrepancy may partly result from the under-estimation of the mixing of the ambient air with the plasma jet as shown by the comparison of the predicted and experimental fields of N₂ [13] and also from the simplified system of chemical reactions used of the chemical reaction models.
Figure 7: mole fraction of evaporated and oxidized iron along particle trajectory. 
(a) : initial particle size: 40 μm ; injection velocity : 10 m/s  (b) 80 μm ; 10m/s

References

Nomenclature
\( c \) Concentration \( Re \) Reynolds number \( \delta \) Oxide thickness
\( d_p \) Diameter of particle \( Sc \) Schmidt number \( \rho \) density
\( D_{AB} \) Diffusion coefficient \( Sh \) Sherwood number
\( k_d \) Mass transfer coefficient \( u \) Velocity \( gas \) Plasma gas phase
\( k_r \) Coefficient of reaction rate \( t \) Time \( s \) Surface of particle
\( M \) Molecular weight \( T \) Temperature \( p \) particle
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<tr>
<td>( n )</td>
<td>Mole number</td>
<td>( J )</td>
<td>Molar flux of species max maximum</td>
</tr>
<tr>
<td>( p )</td>
<td>pressure</td>
<td></td>
<td>Greek symbols b Bulk flow</td>
</tr>
<tr>
<td>( R )</td>
<td>Universal gas constant ( \alpha )</td>
<td></td>
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