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On-Line Measurement of Plasma-Sprayed Ni-Particles during Impact on a Ti-Surface: Influence of Surface Oxidation

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The objective of this study was to analyze the impact of plasma-sprayed Ni5%Al particles on polished and grit-blasted Ti6Al4V samples under oxidized and nonoxidized conditions. For this purpose, measurements of thermal radiation and velocity of individual plasma-sprayed particles were carried out. From the thermal radiation at impact, splat diameter during flattening and temperature evolution during cooling were evaluated. Characteristic parameters related to the quality of contact between the splat and the substrate were retrieved. The flattening speed was introduced to characterize wetting, while the cooling rate was used to characterize solidification. The idea was to get a signature of particle impact for a given surface roughness and oxidation state by identifying parameters which strongly affect the splat behavior. Sieved Ni5%Al powder in a narrow range (+65 −75 μm) was sprayed on four sets of titanium alloy surfaces, consisting of polished and grit-blasted samples, one set had a nonoxidized surface and the other one was oxidized in an oven at 600 °C for two hours. Resulting splats after impact were characterized by scanning electron microscopy, the splats on oxidized surface showed pores in their core and detached fingers at the periphery. The cooling rate and flattening degree significantly increased on the oxidized smooth surface compared to the nonoxidized one. This trend was not found in grit-blasted surfaces, which implies that impact phenomena are different on grit-blasted surfaces than on smooth surfaces thus further work is needed.

Keywords coating-substrate interaction, plasma spray forming, roughness effects, splats cooling

1. Introduction

Thermal spraying is a process whereby a feedstock material is heated up and accelerated before impact on a substrate to form layered coatings with different properties. A prerequisite to fully beneficiate of these coatings is good adhesion strength between the coating and the substrate. Therefore grit blasting of the substrate is usually performed prior to coating deposition in order to provide a good mechanical anchoring, which is assumed to be the dominant mechanism involved in adhesion. However, no clear agreement between the adhesion strength and the surface features has been found in literature. This can be due to the variation of the surface status (oxides, preheating temperature, difficulties to control the grit blasting process…) and the statistical spread of particle properties at impact (temperature, velocity) which directly affect the residual stresses and porosity of the coating. Therefore a thorough study of the surface status and its interaction with impacting particles is needed, which is the aim of this study.

Phenomena involved at impact of thermal-sprayed particles on a substrate—or deposited layers—have a strong influence on the coating build-up and microstructure. It has been shown in previous studies that the way sprayed particles flatten and solidify at impact is a key factor controlling the coating mechanical properties (Ref 1, 2). Consequently, a better understanding of the phenomena during the first microseconds after impact is important to improve the coating adhesion.

A broad review of different major works concerning splat formation (impact and flattening) and the effect of various parameters, both particle related (velocity, temperature, molten state, oxidation state) and substrate related (tilting angle, oxide layer, adsorbates, condensates and wetting properties) was presented by Fauchais et al. (Ref 3). Three main theories explaining the splashing-flattening transition temperature can be found:

(i) Pasandideh et al. (low-solidification-rate controlled) claim that preheating the substrate creates oxides that delay solidification and prevent the splashing at the splat rim due to the solidification front (Ref 4).
(ii) Fukumoto et al. (good-wetting controlled) claim that preheating promotes wetting and avoid the splashing (Ref 2).
(iii) Moreau et al. (high-solidification-rate controlled) claim that the fast cooling rate freezes the splat and avoid the splashing (Ref 5).

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One possible explanation of the discrepancy between the first and the other theories might be that in the modeling, the two main physical phenomena involved at impact, i.e., wetting and solidification were separated from each other. In fact these two phenomena occur simultaneously and are interdependent.

A lot of studies have been devoted to particle flattening, from the first analytical model of particle flattening developed by Madejski (Ref 6) considering only the dissipation of the kinetic energy into frictional energy due to viscous forces to the more advanced models (Ref 7) considering the surface energy, contact angle, and solidification effects, the final splat diameter could be predicted in some cases but not always due to many simplifications made in the models derivation. The splashing transition (from an exploded splat shape to a disk shape) was closely related to the Sommerfield number, which includes several particle parameters (diameter, velocity, density, viscosity, and surface tension). Solidification is controlled by the contact resistance at the splat-substrate interface, the wetting angle, and the surface tension. It is also influenced by surface roughness, temperature, and contamination (including oxidation, adsorbates, and condensates). In more recent works, Fukumoto et al. (Ref 8) tried to identify the reason of splat shape transition on a laser treated and/or heated in air stainless steel substrate, they concluded that removal of adsorbates and contaminates is the reason for the transition and not the surface roughness nor the oxides induced by surface treatment. Cedelle et al. (Ref 9) claimed that the presence of nanopeaks on oxidized surface increased the wettability of the liquid on the substrate and reduced the thermal contact resistance at the interface. McDonald et al. (Ref 10, 11) compared flattening on both room temperature and preheated Inconel and glass substrates, they found that the contact on the rougher oxidized Inconel surface was improved while on glass it was not, they concluded that the oxidation effect through improved contact was more important than evaporation of condensates and adsorbates. Li et al. (Ref 12) investigated the substrate nature and contamination as well as the particle kinetic energy on the behavior of sprayed copper particles, they concluded that removal of the adsorbates/condensates by laser ablation promotes the formation of disc splats. However, increased particle velocity or surface conductivity increased the splat fingering.

In this study, characterization of the wetting and cooling at impact using thermal radiation signals prior and during particle impact was performed to retrieve the particle flattening speed and cooling rate. These two parameters are then compared for different surface conditions (smooth, grit blasted, and oxidized). It is expected for instance that oxidation affects the wetting angle, the contact area, and the thermal resistance at the interface.

2. Experimental Setup and Procedure

2.1 Experimental Setup

Plasma spraying was carried out using the F4 gun attached to a A3000S system (automated and robotized) from Sulzer Metco. A titanium-based alloy (Ti6Al4V) plates (100 mm × 20 × 1.6 mm) were prepared with two different average roughness values, namely mirror polished (Ra < 0.1 μm) and grit blasted with alumina grit to Ra ~ 3μm in a robotized suction fed machine. Two surface conditions samples were prepared, oxidized in air at 600 °C for 2 h and nonoxidized condition. The samples were not sprayed immediately after treatment for convenience reasons but were saved in sealed plastic bags to reduce any time effect to a minimum. During the splat capture all the samples were at room temperature.

A commercially available powder material, Ni-5wt.%-Al, Metco 450 NS was sieved within a narrow interval range (−75 and +65 μm). Plasma spraying operating conditions were set according to Table 1.

A special set up (Fig. 1) for isolating single particle and collecting its thermal radiation using a modified DPV2000

Table 1 Operating conditions used for plasma spraying (F4 spray gun)

Operating conditions	
Powder material	Ni5%Al
Current/Voltage	600 A/65-75 V
Primary gas [Ar] flow rate	40 SLPM
Secondary gas [H_2] flow rate	13 SLPM
Carrier gas [Ar] flow rate	4 ± 0,2 SLPM
Powder feed rate	10 ± 2 g/min
Spray distance	150 mm

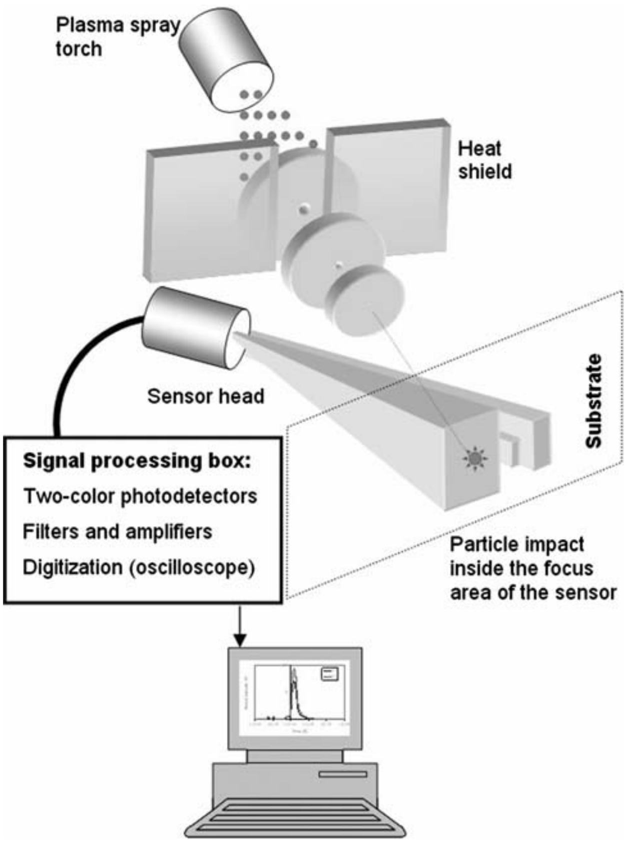

Fig. 1 Experimental setup for the splat capture

sensor system similar to previous works performed at NRC-Canada (Ref 5, 13) was constructed. Between the plasma spray torch and the substrate, three successive shielding plates with 3, 1, and 0.6 mm diameter holes were horizontally aligned allowing just a single particle to reach the substrate at a time, in combination with a rapid torch sweep. After each impact (acquired signal), the substrate was moved 3 mm horizontally by a motor driven support for a further microscopy splat identification. Ten impact signals were collected for each surface condition and used for studying reproducibility.

2.2 Signal Analysis

The particle that manage to cross the three shielding plates would penetrate the field of view (generated by a three-slits mask between the fiber tip and the magnification set of lenses) of an optical sensor generating a radiation that is split and filtered at two wavelengths (800 and 1000 nm) then focused each on two fast photodetectors, where the optical signal is converted into electrical one. This latter signal is digitized using a 14-bit acquisition board (digital oscilloscope) with a 100 MHz sampling rate, the trigger level was set at 1 V. When the particle crosses the field of view of the two small slits (Fig. 1), it generates two identical peaks (P1, P2) (Fig. 2) from which both temperature and velocity of the particle prior to impact can be retrieved. Entering the field of view of the third slit, a shoulder followed by a rapidly raising peak (P3) (Fig. 2) is generated due to flattening followed by a slower decrease mainly due to the particle cooling since the signal is a measure of both area and temperature. It is worth noting that the temperature measurement with the two-pyrometer technique assume a grey body behavior of the particle (Ref 14). The temperature was calibrated with a tungsten lamp with an accuracy of about 4% (~100 °C for our case). The in-flight velocity is calculated from the known mask geometry corrected by the angle of distortion, the lens magnification (0.2) and the time of flight of the particle. The flattening time is between the beginning of rising of peak (P3) until its maximum, while the flattening degree is defined as the ratio of particle diameter before and after impact, it is determined indirectly from the root mean square of the ratio of signals before and after impact by assuming that during flattening, the particle emitted radiation is mainly proportional to its area (Ref 13). The flattening speed or average radial speed was computed from the ratio of the splat equivalent radius (retrieved from the previously calculated flattening degree and the known initial particle radius) and the flattening time.

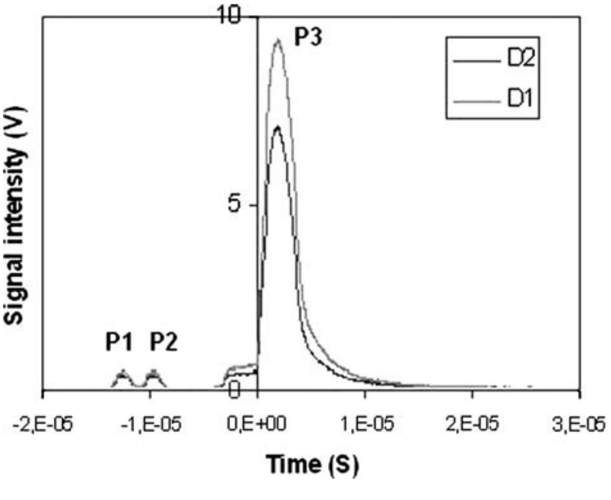

Fig. 2 Typical radiation signals generated in the detectors D1, D2 at two different wavelengths

3. Results and Discussions

3.1 Analysis of Particle Characteristics

In Fig. 3 the acquired thermal radiation signals and corresponding cooling curves for different surface conditions are given. In addition, the particle in-flight properties (temperature and velocity are displayed) as well as the flattening degree, flattening speed and the cooling rate within a 5 µs time period after impact and its linear regression coefficient (R^2). All these data were directly computed in a constructed program and used for the characterization of each splat.

The 5 µs cooling interval marked by two stars in the thermal radiation signals in (Fig. 3) was chosen in the liquid region of the splat to obtain the maximum linear correlation (regression coefficient $R^2 > 0.65$) in the temperature evolution curve, a longer interval would give a nonconstant cooling rate. This has reduced the number of useful signals to at least five by each surface condition with a good reproducibility. The flattening speed was introduced to characterize the surface wetting capability.

The in-flight temperatures and velocities are almost constant, about 2400 °C and 100 m/s respectively, implying that the particles reaching the substrate had similar trajectories and sizes. Physical properties of the molten Ni5%Al particles at this spraying temperature were approximated to pure nickel and retrieved considering a linear temperature dependence of density and surface tension and an exponential function for the viscosity (Ref 15). These properties were used to evaluate some key parameters such as the Reynolds number (*Re*), Weber number (*We*) and the Sommerfeld number (K), Table 2 summarizes these results.

Average values of cooling rate and flattening speed with their corresponding standard deviations (error bars) are given in Fig. 4. The effect of oxidation on smooth surface significantly increased the cooling rate from 35 to 50 K/µs implying that the splat/substrate contact was enhanced, which is in agreement with the investigation of Cedelle et al. (Ref 9), which attributed this increase to the improved wetting and contact through the nanostructured grown oxides. Another explanation can be that the oxidized surface contains less adsorbates than the nonoxidized thus leading to a better contact. However, in this study the flattening speed increased from 43 to 63 m/s on the oxidized surface, this might be due to the bad wetting of the oxidized surface leading to an easier and faster

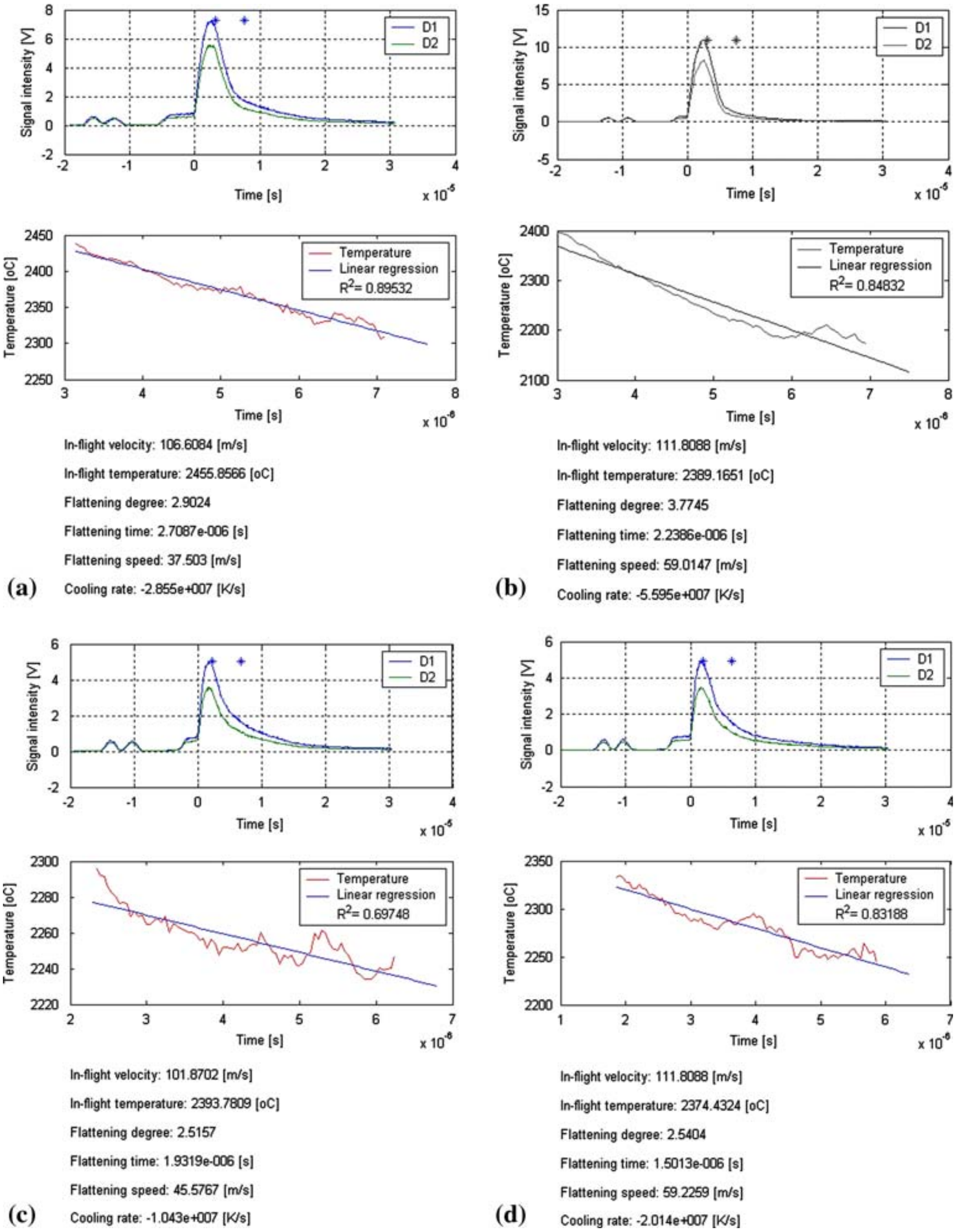

Fig. 3 Thermal radiation signal and corresponding cooling curve on: (a) a smooth nonoxidized surface, (b) a smooth and oxidized surface, (c) a grit-blasted and nonoxidized surface, (d) a grit-blasted and oxidized surface

Table 2 Physical properties of pure Nickel at 2400 °C (spherical particle ($d = 70$ μm) at 100 m/s)

Density ρ, kg/m^3	Viscosity μ, mPa s	Surface tension σ, mN m^{-1}	Reynolds number *Re* ρVd/μ	Weber number *We* ρV^{2}d/σ	Sommerfeld number *K* We$^{1/2}$Re$^{1/4}$
6700	1.8	1507.4	26055	3111	709

flowing of the liquid during flattening. The presence of pores and detached fingers in the splat (Fig. 5b) encouraged the idea of bad wetting on the oxidized surface. However, on the grit-blasted surface, the effect of oxides on cooling rate and flattening speed was not significant.

Concerning the effect of grit blasting, it seems to lower drastically the cooling rate regardless whether the surface is oxidized or not (from 35 to 15 K/μs on the clean surface and from 50 to 12 K/μs on the oxidized surface). However, it doesn't affect the flattening speed significantly. This is probably due to the fact that on rough surfaces both the flattening degree and flattening time decreases simultaneously, thus not affecting their ratio, i.e., the flattening speed as shown by Moreau et al. (Ref 5).

3.2 SEM Analysis

Figure 5 shows SEM micrographs of splats on nonoxidized and oxidized polished surfaces. On the oxidized surface, the satellite fingers are separated from the central disk and the presence of pores within the splat core itself (Fig. 5b) were noticed as compared with the nonoxidized surface (Fig. 5a), suggesting that the retraction of the inner core is due to bad wetting, which agrees with the previous statement about the increase of the flattening speed. The leading edge or rim of the splat seems to be more recoiled on the nonoxidized surface (Fig. 5c) than the oxidized surface, which might be due to the presence of the nanostructured thermally grown oxides (Fig. 5d) or to the amount of adsorbates underneath. This implies that several mechanisms at contact on oxidized surfaces exists, the oxide nanopeaks texture enhance the contact area thus the cooling rate while the oxide chemistry reduce the wetting thus increasing the flattening speed.

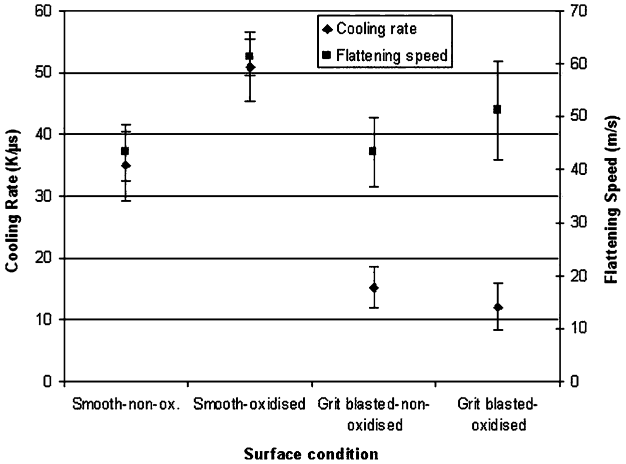

Fig. 4 Evolution of the cooling rate and flattening speed for different surface conditions

4. Conclusions

A fundamental understanding of the physical phenomena occurring at impact of thermally sprayed particles is crucial for the control of the final coating properties. Therefore, measurement of the particle's thermal radiation and the introduction of characterization parameters for these phenomena was the aim of this study.

The effect of the surface oxidation was outlined through the cooling rate and flattening speed of the particle at impact. Indeed, these two parameters significantly increased on oxidized smooth surface suggesting that the cooling is faster and the wetting is worse. However, this trend was not found on grit-blasted surfaces. Also, the cooling rate decreases on the grit-blasted surface compared to the smooth one while the flattening speed was not affected. SEM analysis revealed a poor wetting on the oxidized surface, i.e., pores and detached fingers, which confirmed that the flattening speed is a good indicator of wetting.

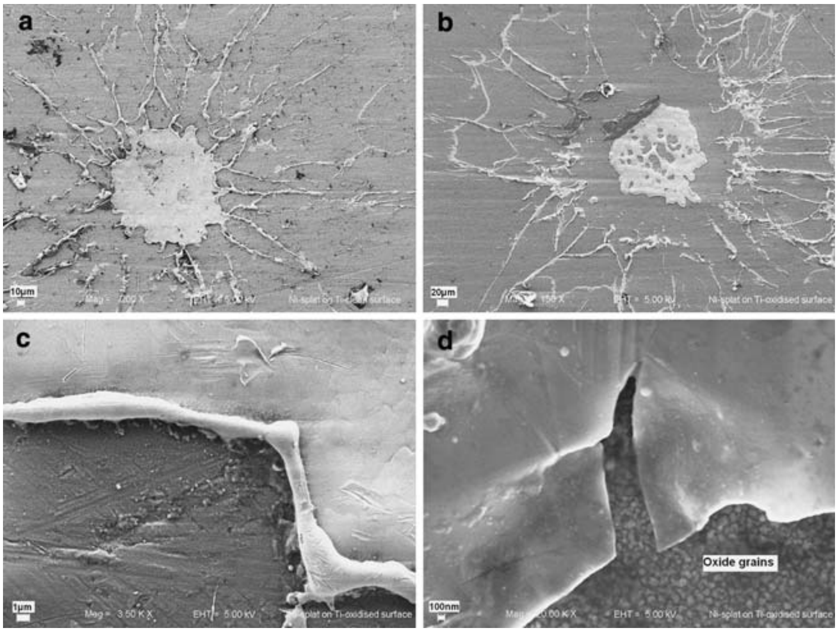

Fig. 5 SEM micrograph of a splat on: (a) a smooth and nonoxidized surface, (b) a smooth and oxidized surface. (c) Magnification of the coiled splat rim in Fig. 5a. (d) Magnification of the splat rim in Fig. 5b on the top of the thermally grown oxides

The use of the flattening speed and cooling rate as indicators for the characterization of wetting and cooling respectively seems to be useful guidelines for understanding particle impact. In fact, intimate contact between the rough substrate and the impacting particles leading to an enhanced mechanical grip, can be improved by increased wetting or penetration capability of the liquid particle into the surface roughness and increased cooling rate for a faster solidification hindering the splashing.

Most of the splat studies are carried out on smooth surfaces, which is far from the real industrial conditions. The results of this paper imply that studies have to be performed on rough surfaces. On-going work of particle impact on grit-blasted and preheated surfaces will be compared with non-preheated surfaces in order to verify if the characterization parameters used in this study could reveal any change in the splat behavior especially at the transition temperature.

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