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Influences of Spray Conditions on the Morphologies of Copper Splat in Cold Spray Process

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Abstract

The deposition mechanism of cold spray process has not been fully understood at present. It has been widely accepted that particle velocity prior to impact is one of the most important parameter for cold spray process, and bonding occurs when the impact velocities of particles exceed a critical value. For cold spray, the splat is the basic element of coatings and determines the coating properties, such as porosity, bonding strength. Therefore, the study of splats is helpful to understand the deposition mechanism of cold spray process. In this work, copper powder was utilized to prepare splats on three substrates, aluminum alloy, copper and stainless steel, under different spray conditions. Particle velocities were measured by DPV-2000 system experimentally. The morphologies of copper splats and cross sections were characterized by scanning electron microscope (SEM). In order to control the cross sections of splatted particle passing the center of particle as much as possible, the cross sections were polished by a new method with ion beam. The influences of particle velocity on cold-sprayed splat morphologies and cross-sections were discussed.

Introduction

Cold spray is an emerging spray coating technology that was first developed in the mid 1980's at the Institute of Theoretical and Applied Mechanics in the former Soviet Union (Ref 1). Cold sprayed coatings can be achieved only when the velocity of in-flight particles exceeds a certain critical velocity (Ref 2-3). Therefore, the velocity prior to impinging on the substrate is the most important parameter in cold spray (Ref 4).Compared to traditional thermal spray processing, the deposition of particles takes place through intensive plastic deformation upon impact in solid state at a temperature well below the melting point of the spray materials. Therefore, cold spraying is particularly suitable to prepare coatings that are sensitive to oxidation or applications in the fields in which oxidation and thermal influences during the coating process have to be avoided (Ref 5).

In the present study, a proprietary copper powder was utilized to prepare the splats and measure the particle velocities. In order to control the particle velocity, the splats were prepared under different gas temperature and pressure. The in-flight particle velocity was measured by DPV-2000 system. The morphologies and the cross sections of the copper splats were characterized by SEM. The effects of gas temperature and pressure on particle velocity were investigted, and effects of particle velocity on the morphologies and cross-sections of copper splats were also discussed.

Experimental Procedures

Feedstock Powder and Cold Spray Process

A proprietary copper powder (25~33μm) was used as the feedstock in the current study. The typical morphology of the copper powder is shown in Fig. 1. The copper powder presents a spherical shape. The powder size distributions were characterized by a laser diffraction particle size analyzer (Seishin Trading Co., Ltd. Kobe, Japan). The measured volumetric distributions of particle diameter are shown in Fig. 2. The volumetric average diameter is about 30 μm, with an extremely narrow distribution owing to the pre-classification.

In this study, a commercial cold spray system, model number PCS-1000 designed by PLASMA GIKEN CO. LTD., was used to prepare the copper splats. A converging–diverging (De-Laval) nozzle was configured in the cold spray system. The nozzle is cooled by chilled water in order to alleviate nozzle clogging and improve the reliability of this system. As a gas pressure controlled system, in the cold spray system the gas flow rate is adjusted by the change of gas pressure. The details of the cold spray conditions are shown in Table 1. In order to investigate the effects of working gas temperature on the splat morphologies, the splats of the copper particles were performed on a substrate of A5052 with nitrogen gas at the different gas temperatures of 200, 400, 600 and 800℃ keeping the gas pressure at 3 MPa. In order to investigate the effects of working gas pressure on the splat morphologies, the splats of copper particles were performed on a substrate of

A5052 with nitrogen gas at the different gas pressure at 3, 4 and 5MPa keeping the gas temperature of 400℃. In order to investigate the effects of the different gas types and substrates on the splat morphologies, both nitrogen and helium were also used as driving gas at the inlet pressure of 3MPa and gas temperature of 400℃ on three substrates, A5052, Cu and stainless steel. The Vickers hardness of substrate was measured with a FM-700 micro-hardness tester (Future-Tech. Crop) under the load of 25 g and the load-time of 15 seconds. The micro-hardness of the three substrates is shown in Table 2.

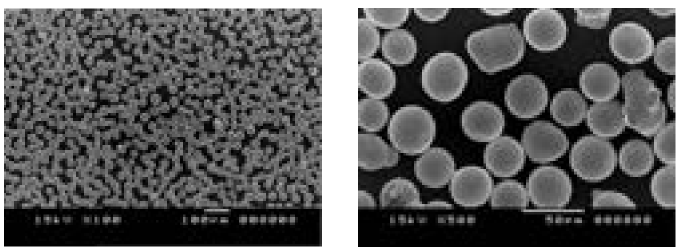


Figure 1: Morphology of the feedstock powder.

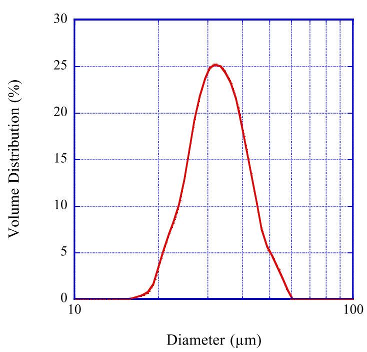


Figure 2: Diameter distributions of the copper powder.

Table 1: The spray conditions

Gas Type	N_2	He
Working gas pressure (MPa)	3, 4, 5	3
Working gas temperature (^oC)	200, 400, 600, 800	400
Spray distance (mm)	20	
Substrate	A5052, Cu, stainless steel	

Table 2: The hardness of the three substrates

Substrate	A5052	Cu	Stainless Steel
HV	84.5	101.1	236.8

The Measurement of In-Flight Particle Velocity

The in-flight particle velocity was measured at the center of the flow, using a DPV-2000 system (Tecnar Automation Ltd., St-Bruno, Québec, Canada) under the conditions of preparing splats as shown in Table 1. The substrate was removed during the particle velocity measurement process. In cold spray process, the radiation intensity emitted from the in-flight particles is too weak to be detected by the optical sensor because of the low temperature of the particles. Therefore, a high-power diode laser system, CPS-2000, is equipped in the DPV-2000 system to beam the in-flight particles. By detecting the monochromatic light scattered by the particles, the velocities of particle can be measured by DPV-2000 system. In this study, the velocity measurements were made at a position in the center of the gas flow 20 mm away from the spraying gun exit.

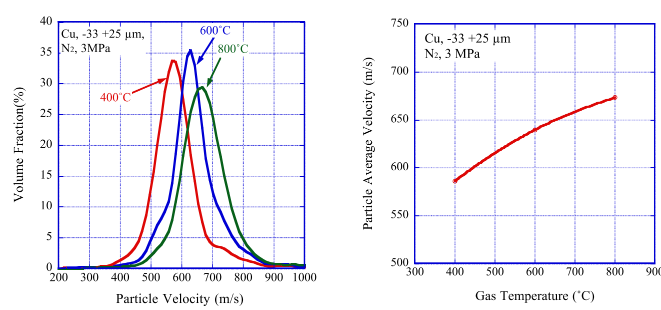
Splat Characterization

In this study, the cross sections of splatted copper particles were prepared vertically to their surfaces by a relatively new polishing method of Cross-section Polish (CP) using a broad ion beam. The method minimizes the artifacts such as exaggerated densification and/or reduced porosity which can be induced by the plastic deformation of sprayed metallic powder particles during sample preparation (Ref 6). The broad ion beam milling was conducted with a commercially available apparatus named cross section polisher (SM-09020CP, JEOL, Japan). The acceleration voltage and milling speed were 4 kV and 50 μm/h, respectively, under the chamber pressure of 2 × 10^{-3} Pa. The morphologies and prepared cross sections of the splatted copper particles were examined by a emission scanning electron microscope (JSM-5200LV, JEOL, Japan).

Results and Discussions

The Effects of Gas Temperature

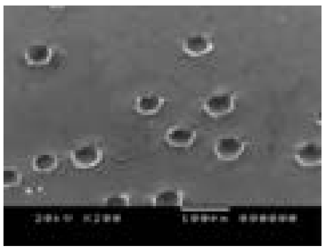
Figure 3 shows the particle velocity measured by DPV-2000 system under different working gas temperatures. It can be seen that the particle velocity ranged from 400 to 900 m/s, and the average particle velocity increased with the increase of gas temperature.



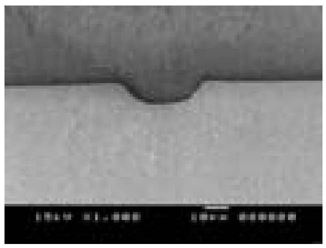
(a) *(b)*

Figure 3: Particle velocity number distributions (a) and average velocity (b) measured by DPV-2000 at different gas temperature.

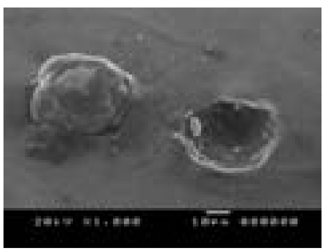
Figure 4 shows the morphologies and cross-sections of the copper splats on the substrate of A5052 under different working gas temperature keeping the gas pressure of 3 MPa. It can be seen that the particle rebounded from the A5052 substrate and only some craters remained in the substrate when the gas temperature is less than the temperature of 200℃. It seems that deposition cannot happen on the A5052 substrate at the conditions of N_2, 3MPa, 200^oC owing to low particle velocity. With the increase of the working gas temperature, not only the deposition of copper particles on the substrate occurred but also the particle was embeded into the substrate more deeply owing to the increase of particle velocity. Jetting can be observed when the gas temperature exceeds 600^oC as shown in Fig.4 (f) and (h).



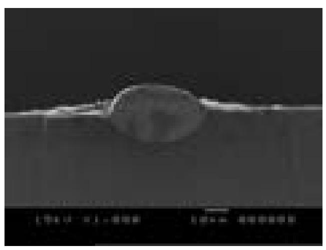
(a) Surface at 200^oC



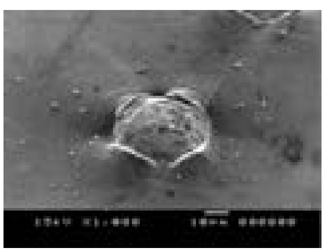
(b) Cross-section at 200^oC



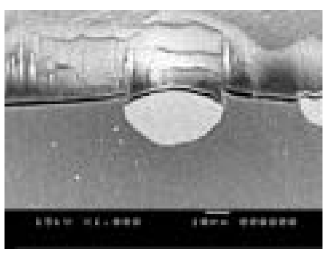
(c) Surface at 400^oC



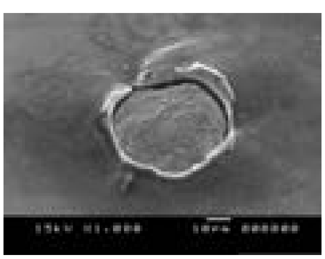
(d) Cross-section at 400^oC



(e) Surface at 600^oC



(f) Cross-section at 600^oC



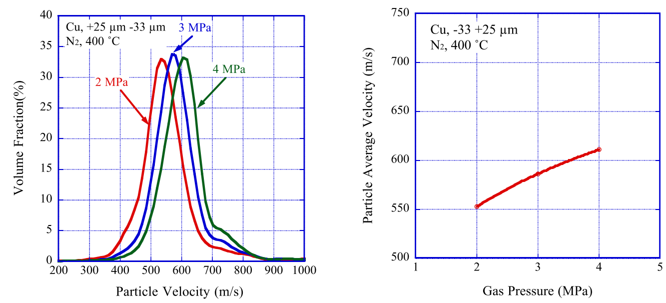
(g) Surface at 800^oC

(h) Cross-section at 800^oC

Figure 4: Morphologies (a) (c) (e) (g) and cross-sections (b) (d) (f) (h) of copper splats sprayed on A5052 substrate at the working gas pressure of 3 MPa and different gas temperatures.

The Effects of Gas Pressure

Figure 5 shows the particle velocity measured by DPV-2000 system under different working gas pressure. Simlar to the effects of gas temperature, it can be seen that the particle velocity ranged from 400 to 900 m/s, and the average particle velocity also increased with the increase of gas pressure.



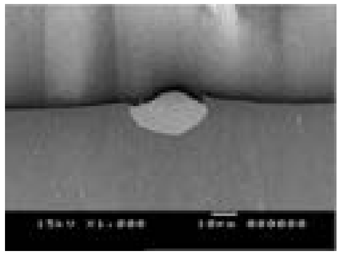
(a) *(b)*

Figure 5: Particle velocity number distributions (a) and average velocity (b) measured by DPV-2000 at different gas pressure.

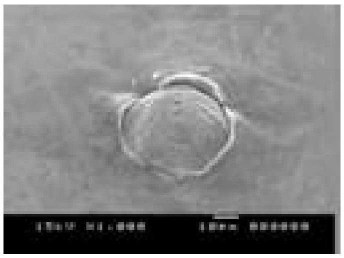
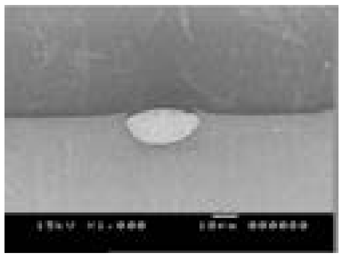
Figure 6 shows the morphologies and cross-sections of the copper splats on the substrate of A5052 under different working gas pressure keeping the gas temperature of 400^oC. Together with the Fig. 4 (c) and (d), it can be seen that the particles are embedded into the substrates more deeply with the increase of working gas pressure from 3 MPa to 5 MPa. This is caused by the increase of particle velocity with the increase of gas pressure. A small jetting can be observed for the copper splat at the gas pressure of 4 MPa as shown in Fig.6 (b), and the jetting became more remarkable while the working gas pressure increased to 5 MPa.

The Effects of the Substrate Material

Figure 7 shows the morphologies and cross-sections of copper splats on the substrate of Cu and stainless steel at working gas pressure of 3 MPa and the gas temperature of 400^oC with nitrogen gas. Compared with the copper splat on A5052 substrate as shown in Fig. 4 (c) and (d), it seems that the hardness of substrate has a great influence on the morphologies of the copper splat. As the hardness of the copper particles is higher than A5052 substrate, the deformation of the substrate is larger than that of the particle for the A5052 substrate. As a result, the copper particle was embeded into the A5052 substrate more deeply compared with the two other substrates. For the Cu substrate, both the particle and the substrate were deformed to some degree, and the particle was embeded into the substrate a little as shown in Fig. 7 (a) and (b). For the hard substrate of stainless steel, the substrate almost did not deform at all, and the kinetic energy of the in-flight particle mainly contributed to the particle deformation. Consequently, a flattened splat was obtained on the stainless steel substrate.

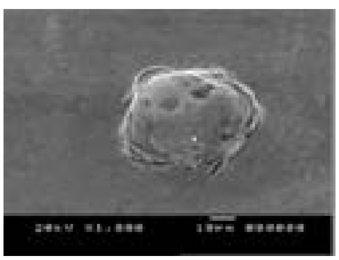
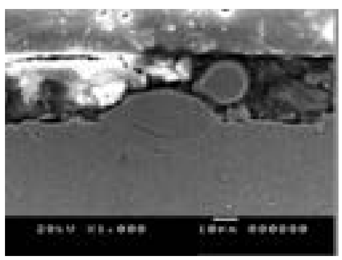



(a) Surface at 4MPa *(b) Cross-section at 4MPa*

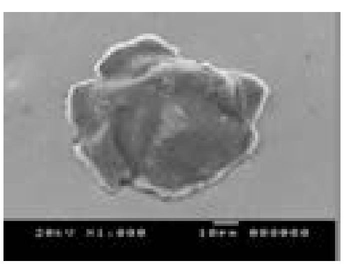
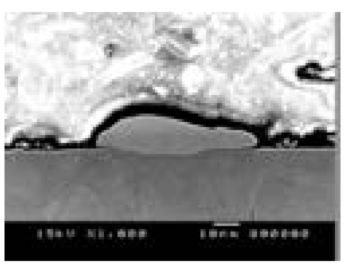



(c) Surface at 5MPa *(d) Cross-section at 5MPa*

Figure 6: Morphologies (a) (c) and cross-sections (b) (d) of copper splats sprayed on A5052 substrate at the working gas temperature of 400^{o}C MPa and different gas pressure.

(a) Surface, Cu substrate *(b) Cross-section, Cu substrate*

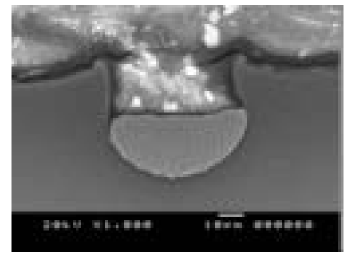



(c) Surface, SS substrate *(d) Cross-section, SS substrate*

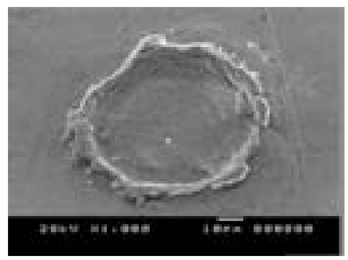
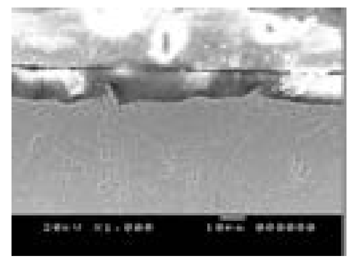
Figure 7: Morphologies (a) (c) and cross-sections (b) (d) of copper splats sprayed on Cu and stainless steel substrate at the working gas temperature of 400^{o}C MPa and pressure of 3 MPa with nitrogen gas.

The Effects of the Gas Type

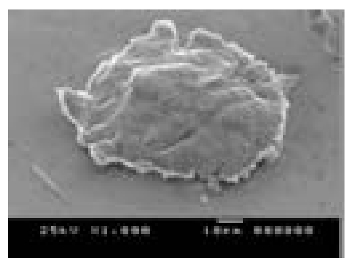
Figure 8 shows the morphologies and cross-sections of copper splats on the substrate of A5052, Cu and stainless steel at the working gas pressure of 3 MPa and temperature of 400^{o}C with helium gas. Compared with the copper splats as shown in Fig. 4 (c) - (d) and Fig. 7, it can be seen that the splat on all of the three substrates are much deeper if helium gas is employed as the working gas as opposed to nitrigen gas. The particle velocity with helium is much higher than that with nitrogen gas (Ref 7). As a result, a much deeper embeded splat was obtained. Even though the substrate of stainless steel is significantly hard, the copper particle was embeded into the substrate and also caused some deformation of the substrate with the higher particle velocity as shown in Fig. 8 (e) and (f).

(a) Surface, A5052 substrate *(b) Cross-section, A5052 substrate*

(c) Surface, Cu substrate *(d) Cross-section, Cu substrate*




(e) Surface, SS substrate *(f) Cross-section, SS substrate*

Figure 8: Morphologies (a) (c) (e) and cross-sections (b) (d) (f) of copper splats sprayed on A5052, Cu and stainless steel substrate at the working gas temperature of 400^{o}C MPa and pressure of 3 MPa with helium gas.

Discussions

As the basic element of coatings, the splat's characteristics determine the coatings properities, such as density, strength and bonding strength. Bonding strength of coatings prepared by cold spray determines its applications in the industrial field. Therefore, it is important to clarify the bonding mechanism of cold spray coatings for this emerging process. The previous studies on the bonding mechanism of cold spray suggested that the adhesive strength is mainly affected by the mechanical interlock (Ref 8-9) and impact molten for a physical-chemical adhesion (Ref 10-11) based on the shear instability (Ref 12).

All the studies showed that particle velocity is the key factor to determine the coating properties.

The changes of the spray conditions in the current study attribute to the change of particle velocity. The increase of gas temperature and pressure caused the increase of particle velocity, and the utilization of helium gas effectively raised the particle velocity too, compared to nitrogen gas. With the increase of particle velocity, the copper particles deeply embedded into the substrate, and more intensive plastic deformation occurred in both particles and substrates. Owing to the plastic deformation of substrate, jetting can be generated and becomes much larger with the increase of particle velocity. Unlike the splat, which is only one particle impacting on the substrate, in the actual cold spray process, the subsequent particle will impact on the jetting and mechanical interlock will occur between the coating and substrate. The severe mechanical interlock resulting from the intensive plastic deformation leads to a high bonding strength as shown in Fig. 9 (Ref. 7).

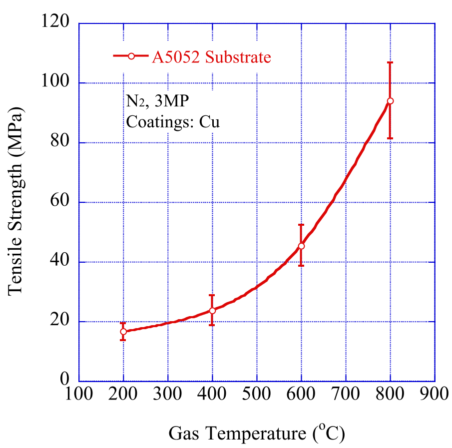


Figure 9: The bonding strength of copper coatings on A5052 substrate (Ref 7).

Conclusions

In this study, the influences of the cold spray conditions on the morphologies of copper splat were discussed. The particle velocity of copper powder was measured by DPV-2000 system. The results show that the particle velocity increased with the increase of working gas temperature and pressure. As a result, the morphologies of copper splats were greatly influenced by the working gas temperature, pressure, gas type and the hardness of the substrate. All of the changes of the morphologies of copper splat attribute to the difference of the particle velocity on the same substrate. Observing the surface and cross-section of the copper splats, it can be found that the kinetic energy of in-flight particle caused the deformations not only of the particle but also the substrate. The hardness of the substrate has also a great influence on the morphologies of copper splats based on their plastic deformations. For soft substrates, the deformation mainly occurs in the substrate instead of the particle, resulting in the formation of a deeply embedded splat. In contrast, the deformation mainly generates in the particle for a hard substrate. In general, the copper particle was embedded into the substrates more deeply with the increase of particle velocity regardless of which substrate was used. Jetting was formed by the substrate deformation with the increase of embedded depth. It seems that the jetting improves the bonding strength between the coatings and substrates owing to the improvement of the mechanical interlock effect.

References

1. P. Richer, B. Jodoin, K. Taylor, E. Sansoucy, M. Johnson and L. Ajdelsztajn, Effect of Particle Geometry and Substrate Preparation in Cold Spray, *Thermal Spray 2005: Explore Its Surfacing Potential,* (Ed.) E. Lugscheider, May 2-4, 2005 (Basel, Switzerland), DVS-Verlag, Düsseldorf, Germany, p. 193-198
2. C.-J. Li, G.-J. Yang, C.-X. Li, H.S. Bang and W.-Y. Li, Examination of the Estimating Approaches for the Critical Velocity in Cold Spraying, *Thermal Spray 2007: Global Coating Solutions,* Eds. B.R.Marple, M.M. Hyland, Y.C. Lau, R.S. Lima and G. Montavon, Pub. by ASM International, Materials Park, OH, USA, p 128 – 134
3. C-J. Li, W-Y Li and Y-Y Wang, Effect of Spray Angle Deposition Characteristics in Cold Spray, *Thermal Spray 2003: Advancing the Science and Applying the Technology*. B. R. Marple, C. Moreau, Eds., ASM International, Materials Park, OH, 2003, p 91-95
4. F. Raletz, M. Vardelle, G. Ezo'o, Critical Particle Velocity under Cold Spray Conditions, *Surface and Coatings Technology*, Volume 201, Issue 5,p 1942-1947 (2006)
5. J. Voyer, T. Stoltenhoff and H. Kreye, Development of Cold Gas Sprayed Coatings, *Thermal Spray 2003: Advancing the Science and Applying the Technology*. B. R. Marple, C. Moreau, Eds., ASM International, Materials Park, OH, 2003, p 71-78
6. K. Nakamura, H. Amita, S. Takahashi and S. Matsumoto, Application of Cross Section Polisher to Sample Preparation for Surface Analysis, *Journal of Surface Analysis*, Vol. 15, No. 1, p 50-58 (2008)
7. R. Huang, H. Fukanuma; Study of the Influence of Particle Velocity on Adhesive Strength of Cold Spray Deposits; *Journal of Thermal Spray Technology*, Vol. 21, Iss. 3-4
8. M. Grujicica, J.R. Saylor, D.E. Beasley, W.S. DeRosset, D. Helfritch, Computational Analysis of the Interfacial Bonding between Feed-Powder Particles and the Substrate in the Cold-Gas Dynamic-Spray Process, *Applied Surface Science* 219 (2003) 211–227
9. S. Kumar, Gyuyeol Bae, Changhee Lee, Deposition Characteristics of Copper Particles on Roughened

Substrates Through Kinetic Spraying, *Applied Surface Science* 255 (2009) 3472–3479
10. C-J. Li and W-Y Li, Impact Fusion Phenomenon during Cold Spraying of Zinc, *Thermal Spray 2004: Advances in Technology and Application,* May 10-12, 2004 (Osaka, Japan), ASM International, 2004, p 356-361
11. S. Guetta, M. H. Berger, F. Borit, V. Guipont, M. Jeandin, M. Boustie, Y. Ichikawa, K. Sakaguchi and K. Ogawa, Influence of Particle Velocity on Adhesion of Cold-Sprayed Splats, *Journal of Thermal Spray Technology,* Volume 18, Number 3, 331-342
12. M. Grujicic, C. L. Zhao, W. S. Derosset, D. Helfritch, Adiabatic Shear Instability Based Mechanism for Particles/Substrate Bonding in the Cold-Gas Dynamic-Spray Process, *Mater. Des.,* 2004, 25, p 681-688