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Discussion Topics and Threads on Thermal Spray

Compiled and edited by Dr. R.S. Lima, National Research Council of Canada (NRC). These questions and answers were extracted from the discussion group of the Thermal Spray Society of ASM International. The content has been edited for form and content. Note that the comments have not been reviewed. To sign up to the discussion group visit www.asminternational.org. Go to Affiliate Societies, Thermal Spray Society, and under Technical Resources sign up for e-mail discussion list—or simply send e-mail to join-tss@maillists.com.

Question 1

Spraying at low substrate/coating temperatures. What is the current technology, concerning thermal spray application, for maintaining a coating surface temperature at or below 60 °C?

Answer 1.1: You have to use cold-spray.

Answer 1.2: Cold spray is a good suggestion; however, a low substrate temperature does not come automatically with cold spraying. Depending on the spray parameters (and substrate material), the maximum temperatures in the gas jet can be in the range of up to 650 °C or even higher.

Answer 1.3: Cold spray does not mean always low substrate temperatures. In cold spraying the gas temperature increases near the substrate. This is predicted from the one-dimensional gas flow model. Our observations during cold spraying have shown that the substrate temperature can rise due to impingement of the hot gas. For example, we sprayed copper using helium gas heated to 673 K, we observed that the substrate (aluminum: 25 mm × 100 mm × 3 mm) was hot, such that we could not touch it with bare hands even a few minutes after spraying. Having said this, we found that for most of our trials we could spray copper using gas heated to 523 K, and in this case the substrate did not get very hot; that is, it remained below 373 K. The substrate temperature will depend on spray parameters and this in turn will depend on material sprayed.

Answer 1.4: On expansion cooling in cold spraying: With positive Joule-Thompson (JT) coefficient ($\mu = \partial T/\partial P$), real gas cools on expansion, with the negative one it warms up. Real gases have positive JT values above their specific inversion temperature. This is 621 K for nitrogen and only 40 K for helium. Thus, an expanding N_2 jet cools on expansion if it is colder than 347 °C (658 °F) at the nozzle, but it warms up on expansion if it was first preheated to more than that inversion temperature. It is obvious that preheating N_2 to above 350 °C satisfies three needs at the same time: (a) increasing sonic speed (absolute gas speed when choked in nozzle at $M = 1$), (b) keeping feed powders warmer/more plastic, and (c) preventing the expanding jet cooling. As to He jets, they always warm up on expansion unless, of course, someone precools compressed He to below −233 °C first. That would be a nonstandard approach to cold-spraying technology.

On keeping sprayed surface at or below 60 °C: A range of production-proven cryogenic gas cooling methods exist (e.g., liquid CO_2, liquid N_2 and liquid Ar), and they can meet this 60 °C requirement even with HVOF spraying. Cooling equipment sizing for heat balance depends on process/substrate parameters. The most common practice is to keep the surface above 65 °C in order to avoid ambient (or combustion flame-sourced) moisture condensation on coating surface and, additionally, ensure neutral or moderately compressive residual stresses after cooling to room temperature. Nevertheless, if a specific application requires lower temperatures, one of the mentioned cryogenic-cooling methods may be fully successful if coating is done in a dry atmosphere enclosure or chamber. Considering the boiling points of the three cryogens mentioned, liquid N_2 offers the fastest, most effective cooling, while liquid CO_2 is the slowest, but also most error-forgiving, coolant in the situations in which the thermal spray operator does not have access to the correct temperature sensors (infrared) or measurement procedures.

Answer 1.5: Is this applicable to compressible gas flow as well? Our experience while using helium gas has been that it cools upon expansion in the divergent part of the nozzle. We have observed deposition of ice on the outside of cold spray nozzle while spraying for long duration (10 min or more). The gas temperature rises when it impinges on the substrate because the velocity of gas decreases almost isentropically near the substrate leading to rapid increase in pressure and temperature (bow shock).

Answer 1.6: Inversion temperature data are scattered in many old thermodynamics books, but you could start with Google searching and checking http://www.en.wikipedia.org/wiki/Joule-Thomson_effect. Since Joule-Thompson effect is a manifestation of molecular interactions in real gases, the degree of powder loading of expanding stream surely affects it. The point is isentropic gas expansion models are insufficient for the theoretical or practical evaluation of cold-spraying technology.

Question 2

Relationship between bond and shear strength. I am interested to know if experimental data exist regarding the relationship or general trend between the relative values of adhesion and shear strength of plasma sprayed ceramic coatings.

Answer 2.1: You can check the following reference: C. Colin, M. Boussuge, D. Valentin, and G. Desplanches, Mechanical Testing of Plasma-Sprayed Coatings of Ceramics, *J. Mater. Sci.*, 1988, **23**, p 2121-2128. The tensile strength and shear strength values of chromium oxide and magnesium zirconate coatings (deposited on metallic substrates) were measured. For the chromium oxide, the tensile strength and shear strength values were 26 MPa and 20 MPa, respectively. For the magnesium zirconate, the tensile strength and shear strength values were 13 MPa and 10 MPa, respectively.

Question 3

Thermal spray coatings on marine structures. Has anyone heard of thermal spray aluminum coatings being used in lieu of conventional coatings and cathodic protection anodes on marine pilings (i.e., steel pipe pilings on marine structures—docks, piers, and wharves)?

Answer 3.1: I know that thermal spray Al coatings are ideal coatings for splash zone protection. However, can thermal spray coatings be applied to provide the same level of protection in the submerged zones as that of conventional anode systems? How about the cost of thermal spray versus conventional coatings and anodes? Can it be competitive?

Answer 3.2: It was my understanding that the splash zone was the area of greatest corrosion risk due to the presence of salts and much oxygen; therefore if it can protect the splash zone, maybe it can protect anything.

Answer 3.3: These are some sources of information:

- "Development, Testing & Field Application of Metallised Cathodic Protection Coatings on Reinforced Concrete Substructures," CALTRANS Report, State of California, Department of Transportation, Division of Construction, Office of Transportation Laboratory, DS-TL-1242, May 1989, Contract or Grant No. F81TL09
- "Specifications, Protective Coatings of Iron and Steel," Association of Metal Sprayers, 658 Chester Road, Erdington, Birmingham B23 5TE, B.S. 5493: 1977, Code for Protective Coating of Iron and Steel Structures against Corrosion

Answer 3.4: In the Netherlands, there is an experience with thermal spray Al coatings on dockside sheet piling and submerged lock gates. Although thermal spray coatings have an excellent track record for corrosion control in marine environments, their application is either labor intensive or heavy on capital investments for robotics in the case of automated application. That is the reason why there appears to be a "fine tuning" in corrosion control in marine environments. Thermal spray Al coatings in the splash and tidal zone up to 1.5-2 m below the low water tide level, and sacrificial anode protection below that mark (simply because sacrificial anodes are very effective in the totally submerged environment and much less expensive to install).

Answer 3.5: We recently published a paper titled "18-year Exposure Test of Thermal Sprayed Zn, Al and Zn-Al Coatings in Marine Environment," *Corrosion*, 2006, **62**(7), 2006, p 635-648. You will find some useful information about several exposure tests of pipe piles conducted in the past. Our test reported in the paper is not really piles, but 2 m long steel pipes exposed from the tidal, splash to sea-air zone. Our results as well as the previous reports by others suggest that thermal sprayed aluminum acts as a barrier rather than a sacrificial anode if the steel is completely covered. We measured the thickness of thermal spray Al coatings over 20 years, and it hardly changed. When a pile is only partially sprayed, however, it is consumed rather quickly. There is an example of such tests conducted in Japan, where steel pipe piles were only covered from the tidal to splash zone. The thermal spray Al coatings were consumed after a few years most likely due to the galvanic coupling with the bare steel pipe in the sea.

Answer 3.6: I found a paper about this issue on this site: http://www.nims.go.jp/yousha/00049.pdf#search = %2218-year%20exposure%20test%2.

Question 4

Spraying tantalum with HVOF. Compared to molybdenum, what problems should I anticipate spraying tantalum with HVOF?

Answer 4.1: A significant level of oxidation.

Question 5

Avoiding nonmolten particles in thermal spray coatings. In general, what are the reasons for the presence of nonmolten particles in thermal spray coatings? How can it be avoided?

Answer 5.1: Nonmolten particles are particles that do not receive sufficient energy, or lose their energy prior to impacting the substrate. Any energy source, be it plasma, HVOF, flame, and so forth, can only impart so much heat to a particle in flight. One can slow the feed rate, increase the heat, or extend the time in the flame. Most times, we have found that lowering the feed rate will increase the overall enthalpy effect on the particles.

Answer 5.2: There are particles in the microstructure that may appear to be nonmolten, which are in fact particles that have resolidified in flight. They can be identified by etching the mount and observing the grain orientation. Semimolten/resolidified particles can also be identified in this way.

Answer 5.3: Another consideration; feedstock particle size distribution. Let's assume that the spray parameters have been established and proven for a particular coating and feedstock. A new lot of powder is delivered that generates "nonmolten particles" when using the same parameters and settings. Here, the root cause of the problem is more likely due to variations in particle size distribution from lot to lot. Unfortunately, this variation is greater than most of our powder suppliers would like to admit. Monitoring the screen analysis of each lot can assist in controlling coating quality. Sometimes simply screening off the "rocks" can get rid of the nonmolten particles.

Answer 5.4: Well, let's get down to most basic aspect of the question at hand. My interpretation of the question is: what can I do today to reduce the number of nonmolten particles that I see in the microstructure with the powder and spray system that I am currently using? Assumptions: subsonic air plasma spray, some standard particle size distribution that is said to work, good torch components, and that the nonmolten particles are really nonmolten particles, and not entrapped junk. What knobs should be turned? The most powerful ones are probably hydrogen fraction in the total gas flow and nozzle diameter (larger diameter = lower velocity, longer resident time, hotter particles). The next thing is that carbides and dense metallic powders are easy to push right through the plasma, especially the largest particles. You probably cannot back off on the particle injection velocity too much, so lower carrier gas flow and increase powder port diameter.

Answer 5.5: Good explanation—also, if using plasma to spray, one should be sure that the powder injection tip is not worn, which would allow particles to stray to the side and not remain inside the temperature shroud of the heat source.

Answer 5.6: How about looking at his particle temperature and velocity with a sensor, then adjust the parameters to match the profile with the data saved during qualifications?

Answer 5.7: Minimization of nonmolten particles and other undesirable coating defects is one of the key ways to better satisfy the needs of our existing and potential new customers, improve coating performance, develop new advanced applications, and consequently to expand the thermal spray industry. Instability of plasma process seems to be one of the major root causes for the presence of nonmolten particles and other undesirable coatings defects, even if powder feedstock is perfect. Conventional plasma units such as F4, MB family of torches, SG-100, and so forth possess inherent short- and long-term instabilities that presently cause a major portion of quality control related issues, especially for Hi-Tech applications. This disadvantage of the conventional plasma torches has been well studied and has been described in several papers. Short-term instability relates mainly to plasma parameters fluctuation with frequency of several thousand Hz. The fluctuations may vary by up to 30% from the average plasma parameters. These fluctuations are a prime source of statistical variance in the in-flight particle velocity and temperature. For example, particle temperature variations as extensive as 600 °C and particle velocity variations as large as 200 m/s were observed when ceramic particles were sprayed by F4-MB plasma torches. Thus, a particle traveling on a peak of plasma energy may be overheated while another particle traveling at the minimum plasma energy may have temperature below the melting point, thus forming "nonmolten particles" and other related defects in a coating. Drifting of voltage is one of the major sources of long-term instability. Drifting is explained by erosion and wear of electrodes, as well as arc tendency to minimize its length. The major issues regarding the influence of plasma stability/parameters on coating formation, defects, and so forth were partially summarized in a book *Thermal Spraying for Power Generation Components*, recently published by John Wiley & Sons. In that same book, it was also shown that an integration of a cascade plasma torch and system into thermal spraying is the most promising method of minimizing or even avoiding plasma instabilities and related coating inconsistencies, while simultaneously providing the end-users with a very wide operating window and some additional important advantages in comparison with plasma torches and systems presently utilized for thermal spraying. The cascade plasma definitely merits more attention from the thermal spray community.

Question 6

Residual stress in HVOF-sprayed coatings. I would appreciate from the readers/participants in providing available article on residual stresses in HVOF thermally sprayed coatings: HOW can residual stress develop? How can residual stress be measured? How does it form? How it can be relieved/eliminated? What are the effects of residual stress on the base material and the coat?

Answer 6.1: These are possible causes for the formation of residual stress:

- Splat to splat quenching (shrinkage) stress is one contributor
- Overall coating versus substrate coefficient of thermal expansion (CTE) differences are another
- Mechanical "peening" (plastic deformation) of the material during deposition by impacting particles is another

These are possible ways to measure residual stress levels:

- Qualitatively using Almen Strips (need to take into account the effects of grit blasting and the thermal effects of the process itself)
- Quantitatively by X-ray diffraction (changes in the d-spacing, peak shifts, etc.) and also by mechanical techniques involving strain gages and either hold drilling or layer removal. X-ray diffraction requires a lot of careful calibration and suitable peaks, and life gets very difficult in multiphase materials

These are possible mechanisms to relief residual stress:

- Annealing/heat treating
- Shot peening to compensate for an excessive tensile residual stress

These are possible effects of residual stress:

- Excessive residual stress can cause coatings to debond
- Excessive tensile stress can reduce fatigue life. Generally, compressive residual stress is good; tensile is not, at least for fatigue performance

Question 7

Cleaner/solvent for thermal spray preparation. I am looking for a suitable cleaner/degreaser (solvent) for use on stainless steel (410, 17-4 PH, 316) workpieces for thermal spray preparation (in the nuclear industry). The cleaner must be halogen (chloride, fluoride) free. Also, is it acceptable practice to degrease after grit blasting as well as before undercutting?

Answer 7.1: You may want to consider Solvent 140 and various blends of Solvent 140. Two nonchlorinated organic solvents have been implemented to replace chlorinated solvents used for cleaning of typical machine shop components with paper wipes. Oak Ridge Y-12 National Security Complex developed blend of solvent 140 and dipropylene glycol methyl ether are used in these "squirt bottle" applications. Although a patent (Patent 5,207,838) was been issued on the solvent blend, it is now free to use.

Question 8

Spraying TBCs. I am trying to set up a spray process for TBC on MCrAlY, Ni-based substrates. Could somebody suggest the following items? (a) Spray strategies for TBC with APS F4 torch to achieve high powder flow rates and deposition efficiency, 10-20% TBC porosity while aiming to keep the cost lowest. (b) What powders are good compromises between the deposit quality and cost (powder cost, deposition efficiency, etc.)? (c) Powder injection procedures: number of injectors, position of injectors, influence on the deposition efficiencies, how to increase the powder flow rates and still have good deposition efficiency? (d) Spray parameters: current, power, plasma gases nature/flow rates, cathode-nozzle attributes (diameter, type, etc.), spray distance. (e) Part cooling parameters: is air cooling enough? (f) For high powder flow rates, what pressure/flow rates, number, types and position of cooling nozzles: two nozzles at the gun, two at the back of the part and one above? (g) Is preheating of the part necessary before TBC spraying? At what temperature? (h) What are other important issues when spraying TBC? (i) How to make up for the worn cathode-anode: by increasing the current, lowering the plasma %Ar flow rate while maintaining %H_2, or what are other solutions? (j) For the service life, does it make sense to "close" the porous TBC with a final layer more compact sprayed with small particle size of TBC powder? (k) Have somebody experience with SiC grit blasting? (l) Is there a negative effect of the grit particles implanted at interface between Ni substrates and MCrAlY deposits? (m) Has someone experience with zirconia grit blasting? (n) Is that right that using grit zirconia reduces the grit implants at deposit interface when compared with alumina grit particles?

Answer 8.1: I am going to address a few of your questions. Start with parameters that are recommended by your torch manufacturer. If your powder manufacturer will provide parameters, compare them and run them. Compare them metallographically. Use a parameter for the bond strength that provides the strongest bond strength and the roughest surface. Are you going to diffuse your NiCrAlY? If so, SiC will react with superalloy base metals and form a eutectic, so do not use SiC. Also, at high component operating temperatures SiC may also form a eutectic and cause component failure. Grit blasting with alumina is fine, but try to use new grit, and try to use the coarsest grit you can. Blast at lower pressures and blast at a 45° angle to the surface so that the grit will recoil from the surface and away from the blast gun. Blasting at 90° will cause recoiling grit to bounce back toward the gun, causing grit degradation and grit entrapment. Air cooling and grit blasting should be with oil-free and moisture-free air only. For cooling, use an array of cooling jets that blows overspray away from the thermal spray jet and workpiece. Cooling air that impinges on the thermal spray jet may increase its velocity, but the trade-off is that it may induce porosity as it causes melted powder to solidify before it deposits. So use impingement if you want to increase porosity in the top coat TBC. I prefer to have the cooling air parallel to the axis of the thermal spray jet during bond coat, and impinging for the top coat. I also prefer to have other cooling jets positioned to cool the part about 6 in. from the deposit, and so that they carry dust toward the exhaust system. If the component is hollow, aim a cooling jet into the hollow. Preheating is usually a good thing if done in moderation. It reduces the amount of thermal stress that forms at the coating/base-metal interface and dries the part. For nozzle-electrode wear, develop parameters for new nozzles, and then develop acceptable parameters for worn nozzles, and work within the parameter envelope you develop. You should be able to figure out a current per mass flow rate. As your mass flow of gases increases, increase your current to that the ratio stays the same. "Closing" the surface pores with finer powder is good for cosmetic appearance. It impresses accountants and other non-techs. However, in my experience, TBC surfaces degrade due to thermal mechanical fatigue almost as soon as a turbine is started, and the coating surface ablates. If you do not have to impress a bean counter with pretty microstructure, why bother? Keep us informed on using zirconia as a grit blast agent. It should prove very interesting. Lastly, if you have experienced technicians, always seek their advice, and consider it. Sometimes they may not be able to be precise in presenting their ideas, but they usually have merit and can usually save a development project a lot of time and effort with their tribal knowledge. If your techs are "primadonnas," seek their advice; it keeps them happy, and sometimes their advice is extremely valuable.

Question 9

Cold spray equipment. Is there an effective cold spray unit being sold today?

Answer 9.1: I would like to clarify. There are two types of cold spray equipment: low pressure and high pressure. The low-pressure equipment uses air at 80 psi, whereas the high-pressure equipment goes to 600 psi. The low-pressure system sprays at 2 lb/h with 20% deposition efficiency (DE). The high-pressure system sprays at 5-8 lb/h with 80-90% DE.

Answer 9.2: I understand low-pressure systems require surface activation for deposition, and this is achieved by incorporating a second-phase material (e.g., alumina) in the metal powder being sprayed. I also found (during demonstration) that low-pressure systems were unable to spray the powder that did not have second phase mixed in it. I have used/seen high-pressure (up to 30 bar) equipment being used for materials such as copper, tin, titanium, aluminum, among others. It is necessary to have a proper nozzle design and parameter setup to achieve high DE.

Question 10

Measuring O_2 contamination in LPPS chambers. I am looking for information on measuring contamination of the LPPS chamber during operation due to leaks and so forth. Is it possible to install partial pressure oxygen sensors in the chamber to monitor the oxygen level?

Answer 10.1: You could measure a leak rate at all joints with the help of helium gas leak detection system. I am doubtful about the oxygen sensors to sense such low level of oxygen or impurity.

Answer 10.2: I have used lambda sensors to measure level in Ar and combustion gases. Lambda sensor (used in cars exhaust pipes) can measure oxygen levels as low as 10^{-30} bar. Of course you may need heater for the lambda sensor, because solid electrolytes starts to well operate above 450 °C.

Answer 10.3: About 12 years ago in a LPPS chamber I was using portable multichannel mass spectrometer from Leybold Heraeus GmbH, which did a perfect work. One of surprises for me was that it was water vapor (rather than oxygen) that affected oxygen content in MCrAlY coatings (moisture on the walls and in "dead pockets" of the chamber, not leakage of cooling water).

Answer 10.4: To detect leaks in vacuum system, the easiest way to find leaks is to use 0.01 bar over pressure in the chamber and check all joints with soap water. Bubbles will appear immediately, even with very small leaks. You can find the place and the leak rate.

Question 11

Replacing garnet as a grit blaster. Can any of you give me advice in these issues regarding abrasive for surface preparation for in situ thermal spray work? We got a project in which we have to perform thermal spray application for a vessel external, located inside a running chemical plant. The specification from the client specifies the abrasive to be used for the blasting is "garnet," which is considered costly as you all know. Now we need to know whether there is any other alternative abrasive for the surface preparation to be carried out in situ condition. Normally we use copper slag for blasting. Is it possible to use copper slag for this project? If no, then what is the best alternative abrasive we can replace for garnet? As this job is to be performed inside a running plant, the safety is also to be considered. This is the reason why we are also unable to use steel grit.

Answer 11.1: The following technique has been used for preparing large surface areas, such as power station/utility boiler tube, for thermal spray applications to save on preparation costs. Recommend using Cu slag to clean the surface as a first step. The Cu slag is also slower in breaking down in size compared to garnet. Because the Cu slag is the first step, it can be recycled. Using the Cu slag will thus be more cost effective than using garnet only for the full surface preparation. Use garnet as a final step to obtain the desired clean profile as per specification.