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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 e-mail 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. It is important to point out that the e-mail discussion group was relaunched on Aug 29, 2007. To sign up to the e-mail discussion group, previous and new subscribers will have to follow the instructions listed below:

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Question 1

On-site versus in-shop spraying. Does anyone know if large steel plate and I-beams (low-profile steel structures) for infrastructure, shipbuilding, or other applications are commonly sprayed with zinc/aluminum in a "shop environment" versus "on-site" (at a bridge, etc.) for corrosion control? For example, is steel plate commonly sprayed with zinc or aluminum in-house before being used for large steel fabrications (obviously touch-up would be required after welding, etc.)? "On-site" corrosion control spraying is widely reported, but wanted to know more about in-shop spraying.

Answer 1.1: I certainly saw this type of work done in Europe, spraying subassemblies prior to construction, with touch-up of welded joints, etc. done on-site during assembly.

Question 2

Zn and Al coatings on ships. One of our potential clients is a big shipyard. We are wondering whether any of you are applying coatings on ships or floatables; has anyone researched about the use of thermal spray coatings for corrosion protection (Zn and Al) on ships especially on ship boards and for decks or any other infrastructure within the ship? Are there any military standards that we can refer to other than MIL-STD-1687(SH)?

Answer 2.1: Extensive work has been done employing thermal spray coatings for corrosion protection of marine and ship structures and components. The appropriate U.S. standards governing this type of work are:

- MIL-STD-2138A (SH) "Metal-Sprayed Coatings for Corrosion Protection aboard Naval Ships"
- AWS C2.23M and NACE No.12, SSPC-CS 23.00 (commercial/industrial revisions of the above MIL-STD) "Specification for the Application of Thermal Spray Coatings (Metalizing) of Aluminum, Zinc, and Their Alloys and Composites for the Corrosion Protection of Steel"

Answer 2.2: Arc-sprayed coatings were applied on ship decks for the U.S. Navy. They used an automated system, where they lay out a temporary rail system on the ship deck and then use robotic sand blasting and spray equipment that run on the rails that they have laid out.

Question 3

References on nanostructured thermal spray coatings. I would appreciate hearing of any sources of nanostructured thermal spray powders. I would also be interested in references to published nano thermal spray coatings.

Answer 3.1: There are different references available on the literature about the deposition of metallic, cermet, and ceramic coatings produced from nanostructured powders for antiwear, aerospace, and biomedical applications. These are just some of them concerning ceramic oxides:

- J. Ahn, B. Hwang, E.P. Song, S. Lee, and N.J. Kim, Correlation of Microstructure and Wear Resistance of Al₂O₃-TiO₂ Coatings Plasma Sprayed with Nanopowders, *Metall. Mater. Trans.*, 2006, **37A**, p 1851-1861
- M. Gell, E.H. Jordan, Y.H. Sohn, D. Goberman, L. Shaw, and T.D. Xiao, Development and Implementation of Plasma-Sprayed Nanostructured Ceramic Coatings, *Surf. Coat. Technol.*, 2001, 146-147, 2001, p 48-54
- G.E. Kim and J. Walker, Successful Application of Nanostructured Titanium Dioxide Coating for High-Pressure Acid-Leach Application, *J. Therm. Spray Technol.*, 2007, **16**(1), p 34-39
- B. Liang and C. Ding, Thermal Shock Resistances of Nanostructured and Conventional Zirconia Coatings Deposit by Atmospheric Plasma Spraying, *Surf. Coat. Technol.*, 2005, **197**, p 185-192
- R.S. Lima and B.R. Marple, Thermal Spray Coatings Engineered from Nanostructured Ceramic Agglomerated Powders for Structural, Thermal Barrier and Biomedical Applications: A Review, *J. Therm. Spray Technol.*, 2007, **16**(1), p 40-63
- R.S. Lima, C. Moreau, and B.R. Marple, HVOF-Sprayed Coatings Engineered from Mixtures of Nanostructured and Submicron Al₂O₃-TiO₂ Powders: An Enhanced Wear Performance, J. Therm. Spray Technol., 2007, 16(5-6), p 866-872
- T. Varis, J. Knuuttila, E. Turunen, J. Leivo, J. Silvonen, and M. Oksa,

Improved Protection Properties by Using Nanostructured Ceramic Powders for HVOF Coatings, *J. Therm. Spray Technol.*, 2007, **16**(4), p 524-532

 W.Q. Wang, C.K. Sha, D.Q. Sun, and X.Y. Gun, Microstructural Feature, Thermal Shock Resistance and Isothermal Oxidation Resistance of Nanostructured Zirconia Coating, *Mater. Sci. Eng. A*, 2005, 424, p 1-5

There are several other interesting references in this area available in the literature.

Question 4

Microhardness of Al_2O_3 coatings. Is anybody familiar with performed hardness test HV300 on aluminum oxide (Metco 105NS) coating? We can not get a regular pyramid imprint during the indentations. Is there any special surface preparation?

Question 4.1: I guess you are looking for the HV300 hardness number for aluminum oxide (Metco 105NS) and not the method of performing the test. The microhardness obviously depends on the microstructure, but for dense coatings the published value is around 700.

Question 5

Substrate heating during arc spraying of Al. I have a number of fabrication contracts starting shortly where extensive Al arc-sprayed coatings will be employed; the wire alloy type is 99.5% Al-0.5% Mg and the required coating thickness 200-250 µm. Some concern has been expressed by site supervision about the heat that may be transmitted through typically 8 mm thick steel plate during application. I know that the splats of molten material cool reasonably quickly upon hitting the substrate, but I am unable to demonstrate just how quickly that heat is dissipated. Is there a formula or rule of thumb for determining heat retention/ dissipation in the workpiece?

Answer 5.1: This is not something you need to concern yourself about. You will typically apply this coating in multiple passes of $25-50 \ \mu m$ (to control residual stresses and produce a quality coating), which will mean maintaining a relative traverse rate or movement between spray gun and substrate, and given the low melting point of this

material and its very high thermal conductivity, it is very doubtful the substrate will ever get beyond 50 °C.

Question 6

Metallographic preparation: cold versus hot mounting. I have a question about metallographic examination for plasma coating, especially Cu-Ni-In. There are two types for mounting: cold mounting and hot mounting (in a press). I am researching the effects of the mounting. Can hot mounting (in a press) affect the porosity levels at the microstructure for Co-Ni-In coatings? Is there anyone who tests it? I need your recommendations about hot mounting and cold mounting. Additionally I wonder about mounting TBCs. Does anyone use hot mounting (in a press) for TBCs?

Answer 6.1: Application of heat and/or pressure will almost inevitably change the porosity of a hot-mounted TS coating. Use hot mounts for "bulk" or monolithic material samples (hunks of steel or brass). Use a cold mount to TS samples. The easiest way to evaluate the effect in a specific case would be to take identical samples, or better still, pieces of the same sample, mount them the two ways, polish them, and then measure the porosity. Doing more samples would improve the statistical validity of the data.

Answer 6.2: Vacuum impregnation should be even better for most TS coatings.

Answer 6.3: I know vacuum impregnation. But it takes a long time to prepare it. We have to prepare metallographic reports immediately. Hot mounting takes 30 min.

Answer 6.4: The goal of metallography is to present the true, undisturbed microstructure of the coating, since it is the microstructure that governs the properties, and hence the performance of the coating. Taking the easy option (hot mounting) just to save time is not good science/engineering in my opinion. Decisions then made based on the incorrect observation of microstructure may lead to premature coating/component failure.

Answer 6.5: My opinion is different from posted messages. I have strong reasons to believe that using hot mounting for Cu-Ni-In coating might be more beneficial than epoxy mounting in

terms of minimizing damage to the original coating structure. This is true for dense coatings, which Cu-Ni-In should be. The epoxy mounting is beneficial when epoxy penetrates into the surface layer of the coating, strengthening it, and minimizing the so-called "edge effect." If the coating is dense or pores are very small (like HVAF or HVOF Cu-Ni-In coatings), epoxy does not penetrate in the coating, losing its major advantage over hot mounting. On the other hand, the majority of mounting epoxies are softer than hot mounting thermoplastics. Unlike the latter, during grinding/polishing of the mounts, epoxy wears away faster than the coating material, creating the step between the coating and epoxy. The actual mechanical load from grinding on this step edge is huge (if not for plastic deformation of metal, stress should go to infinity). This results in pullouts and other damages, deep to 150-200 µm of top layer thickness. Spray 1 mm thick Cu-Ni-In or other dense metallic coating, and you see this difference clearly: top layer "porous," the rest for the coating dense. Apply electrolytic copper on the coating before cutting/mounting, or spray the arc layer of metal and the top layer "porosity" of your coating is gone. But if you hot mount it, the damaged top layer would be practically zero. I have done it dozens if not hundred times, for different metallic coatings, comparing structures of epoxy mounted and hotmounted samples from the same cuts. The results were very consistent, showing less damage in top layer when hot mounting the samples. Again, the above is true if the coating is relatively dense. If it is porous, and epoxy is able to penetrate in it, then the epoxy mounting is the best choice to go with.

Now about saving time on sample porosity measurement:

For many years, I have been using a simple device to measure coating gas permeability. Have 1 in. porous metal disc. Spray the coating on it of chosen thickness. Set it in the cell. Apply pressure of gas (I use nitrogen or air) beneath it and measure the gas flow through it with precise flowmeter. The gas permeation coefficient would be the linear function of gas flow through total area, pressure drop, and coating thickness. It is directly correlated to the coating through porosity, but much more sensitive than measuring metallographic

porosity (order of magnitude). It would register tiny changes in spray parameters, hardware performance, etc.—the ones you would never register with metallography. And, unless the coating is fused, there is always measurable gas flow through it. As soon as you establish correlation between acceptable metallographic porosity and corresponding gas flow range through given coating thickness, you just need to measure the total gas flow through the coating at fixed gas pressure drop to complete your coating porosity control. And it would take 3-5 min.

Answer 6.6: A permeability apparatus would definitely be useful, especially in predicting coating penetration in corrosive environments. The thermal spray community should encourage a broad use of such quantifying testers and, in general, focus its efforts on developing more reliable and replicable coating test procedures and standards. The acceptance of TS coatings in manufacturing depends on that. An example of another test area that needs revamping is so-called "coating adhesion." The same coating sprayed the same way may reveal completely different "adhesion" characteristics depending on the part being sprayed: substrate material, shape, size, configuration, and the

time-length of spraying operation. The piece missing here is thermal history of the part and coating along with resultant microstresses and macrostresses, controlled or recorded only by the industry leaders. Consequently, people rely on those 1 in. diam pull-plugs representing fairly different coating conditions. This takes me back to the permeability apparatus: a WC-Co coating sprayed on preheated aluminum would probably show somewhat different characteristics than the same coating sprayed on a porous, i.e., low-CTE, blank. Worth checking/calibrating. While developing arc-sprayed cermet coatings some 20 years ago, I was quite successful with helium porosimetry, a standard method for testing catalytic surfaces.

Question 7

References off-angle thermal spraying.

Our company is performing R&D on coatings produced by using "off-angle" conditions (less than perpendicular), and we would appreciate input from the Community regarding technical references discussing this topic. Of particular interest are papers discussing the inherent degradation of coating properties (increased porosity, etc), where due to the service environment, highintegrity coatings are required. Answer 7.1: References go back to at least 1972. The effects were described briefly in a chapter I wrote on "Advanced Thermal Spray Deposition Techniques" in the *Handbook of Deposition Technologies for Films and Coatings*, edited by R. F. Bunshah, Noyes Publications, 2nd ed., 1994 with references. Also see a paper by R.C. Tucker, Jr. and M.O. Price, "The Effects of Angle of Deposition on the Properties of Selected Detonation Gun Coatings," Proc. International Thermal *Spray Conference*, May 13-15, 1988, p 61-72.

Answer 7.2: There was some research carried out on this topic at Sandia National Labs. The following papers that I came across a few years ago might be interesting to you:

- M.P. Kanouff et al., Surface Roughness of Thermal Spray Coatings Made with Off-Normal Spray Angles, *J. Therm. Spray Technol.*, 1998, **7**(2), p 219
- M.F. Smith et al., An Investigation of the Effects of Droplet Impact Angle in Thermal Spray Deposition, *Proc. Seventh National Thermal Spray Conf.* (Boston, MA), June 1994, p 603