JTTEE5 16:185–188
DOI: 10.1007/s11666-007-9043-6
1059-9630/$19.00 © ASM International

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.

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Question 1

Bond strength in function of coating thickness. I was wondering if anyone has some data on the drop in measured bond strength as a function of coating thickness for APS coatings.

Answer 1.1: Take a look at the following references:

- R.T.R. McGrann, J. Kim, J.R. Shadley, E.F. Rybicki, and N.-G. Ingesten, Characterization of Thermal Spray Coatings Used for Dimensional Restoration, *Thermal Spray—Surface Engineering via Applied Research*, C.C. Berndt, Ed., ASM International, 2000, p 341-349 (*Proceedings of the ITSC 2000*, Montreal, Quebec, Canada).

This paper discusses different types of NiAl coatings that were sprayed via APS and HVOF. The coating thickness was varied from 400 to 1800 μm. Bond strength tests (ASTM C 633) were carried out. There is another reference where the bond strength of wire arc nickel-aluminum coatings (i.e., not APS) was measured in function of the coating thickness:

- D.J. Greving, J.R. Shadley, and E.F. Rybicki, Effects of Coating Thickness and Residual Stresses on the Bond Strength of ASTM C 633-79 Thermal Spray Coating Test Specimens, *Journal of Thermal Spray Technology*, Vol 3 (No. 4), 1994, p 371-378.

The thicknesses of the coatings varied from 250 to 1500 μm.

Question 2

Hafnia (HfO_2) oxidation. We are experiencing coating color difference (dark gray to light gray) from one plasma spray event to the next and believe it is due to the oxidation of particles via spray parameter and substrate temperature due to process variables. Why does powder particle oxidation and/or substrate temperature change cause a color difference in the resultant coating?

Answer 2.1: I would suggest that metallic oxides have different optical properties from their parent metals. Alumina for example is white, whereas aluminum is silvery/grayish white in color. Color is also due to how materials respond to light in the visible spectrum and their band structure. Metals typically do not have "band gaps," but have vacant energy states available above the highest filled shell (the Fermi level), whereas many insulators (most oxides fall into this category) and semiconductors have band gaps between the valence and conduction bands and, depending on the magnitude of the gap and the incident energy, will respond differently. The observed color differences may indicate varying levels of oxide content.

Answer 2.2: Would the resultant coatings perform differently? If so, in what ways?

Answer 2.3: Absolutely; in materials the "eternal triangle" is always structure (composition)-property-performance.
Oxides are typically harder and more brittle than metals, which are softer and (usually) more ductile. The wear, corrosion, and just about all the properties will vary to some extent as the oxide content changes. Hard oxide particles could "pull out" in a wear situation and roll around in the wear track/surface contacts and cause further damage. The same may not occur if the deposit was pure metal with no oxide content. Hardness will also vary. Some years ago we sprayed titanium by VPS. It had a microhardness of ~190 Vickers. The same material sprayed by APS had a hardness of around ~900, largely due to the presence of a significant amount of TiO_2 after spraying in air.

Question 3

Vickers diamond chipping. I am a user of Vickers diamond indenter for indentation test (for quantifying basic properties such as hardness and fracture toughness) of thermal spray ceramic coatings. To my understanding, the indenter gets chipped due to obvious reasons (e.g., hard metastable phases in ceramic coatings and high loads). I wonder if any of you face the similar "chipping" problem during the indentation testing procedures using Vickers or other indenters:

- During microhardness testing
- During macrohardness testing
- During measuring the indentation fracture toughness

The diamond should not chip during application at hardness testing load of 10-50 kgf.

Answer 3.1: I have never seen the diamond chipping from Vickers testing. I assume something is not correct, and you should check to ensure the load and machine mechanism are working properly.

Answer 3.2: In extension to my discussion, the machine is working as per standards and the system was tested for calibration before its use. The machine I am using is "macrohardness" tester, which has load range of 5-110 kgf. But I am using only 5-50 kgf. The microhardness testing (100-300 gf) could not generate fracture in coatings; this is the reason I am using macrohardness testing for fracture toughness determination. The chipping is very small (1~5 μm) along the any of the four ridges of the Vickers indenter, and it has happened quiet a few times during application. I cannot use the indenter if I find any chipping, is that correct? For conventional hardness testing (micro or macro) user "may" ignore the chipping, but I have found that those chippings are affecting the indentation fracture results considerably, and this was the concern. I hope you all would agree with this. I also assume that the nano-micro size (hair-like) cracks are bound to be ignored by the indenter manufacturers, as they might not be testing the indenter quality in SEM before it is sent to user. I would like to hear from the indenter manufacturers if they are member of this TSS forum.

Answer 3.3: We replaced our Vickers indenter on our microhardness unit a couple of years ago due to wide variation in the hardness values of our standard. The diamond had chipped. The diamond was used on the unit for about

20 years and with a wide range of loads, 50-1000 gf (300 gf the most common) and a wide range of materials; most are carbide composites. The technician who serviced the unit felt the diamond had been damaged by moving the turret while the load was still being applied. I have been guilty of doing this myself over the years, not waiting till the load was fully retracted. Typically this leaves a large scar on the sample, evidence the load had not fully disengaged prior to the movement of the turret. Some of the newer units lock the turret so movement is not possible until the load is retracted, which should prevent damage to the indenter and sample. If this is the case in for your unit, then I would say you may be on the right track considering flaws in the diamond. Another consideration would be if you are testing materials that contain large carbides; then the diamond may be damaged by sliding movement if the point is applied to the edge of carbide. We have had this experience with our Rockwell test unit, so we do not test carbide composites with Rockwell C; rather we use macrohardness scale and indenter 15N. I was not aware that a Vickers indenter was rated for loads up to 110 kg, even 50 kg seems to be an excessively high load.

Question 4

Thermal conductivity of arc sprayed 95MXC. I am looking to the group to see if anyone has any data on the thermal conductivity of the TAFA arc spray wire 95MXC. I cannot find any data in their published literature.

Answer 4.1: The thermal conductivity of arc sprayed 95MXC coatings is 5.11 W/m K, produced using a standard TAFA 8830 arc spray system.

Question 5

Coatings on large rotating parts. I am searching for information on repairing the main and connecting rod journals on crankshafts, especially of large diesel engines, with diameters approaching (190 mm) 7 in. plus. Questions:

- I have heard of arc spray using cored wire, HVOF with carbides, and even flame spray being used for the repair of worn journals. Which is the best method? Is this a common repair?
- If all the welding metallurgical considerations were understood and followed, would plasma transferred arc (PTA) welding be a good consideration.

Answer 5.1: For this application that has rotating stress/fatigue elements, any weld technique will require a post-weld heat treatment. There is probably no point loading on the sprayed coating, so my preference would be to use arc wire spray, as you can use a more economical feedstock (ferrous based). A sealer maybe necessary to inhibit corrosion (marine), but it may also help with reducing frictional wear. Before a full start-up, the crankshaft should be manually rotated to ensure the journals are fully lubricated.

Answer 5.2: The diesel crankshaft must have enough strength (80 to + 100 ksi tensile) and surface hardness to withstand high impact force created by firing of each cylinder plus forces produced by rotary motion. It cannot be rigid, but must be able to give a little, to twist and flex. Bond strength from thermal spray coating (even D-gun) are not strong enough to withstand bending, torsional, and alternative load fatigue produced by the firing impulses and rotating motion.

- We recondition worn-out diesel crankshaft by grinding worn journals undersize and then arc spraying to build up a hard shell bearing by babbitt (tin base) and machining to maintain original tolerance.
- Diesel crankshaft can be repaired by submerge arc welding, using two different wires. High tensile material (80-90 ksi tensile) on fillets area and hard face material (40-45 HRC) on bearing load area. Preheat, welding interpath, postheat, and cooling rate have to be closely monitored according to crankshaft base material.

Answer 5.3: I think from an industrial/cost/quality basis, arc and flame wire spray are the best methods to repair a crankshaft, unless a specific hardness specification is required (e.g., a crankshaft that was previously nitrided), which cannot be attained with arc spray. Then the recommended method of repair is HVOF. The first step for any process is cleaning and degreasing the part. The part must be thoroughly degreased. This is obvious, but it needs to be stressed to anyone attempting to repair a crankshaft via thermal spray. If at all possible, I would solvent degrease, and then heat the part to 150 °C for several hours, then solvent degrease again. Concerning HVOF:

1. After the crankshaft is cleaned, mask the areas adjacent to where the coating will be applied and grit blast. Due to the heat and abrasiveness of the HVOF process you may have to use sheet metal or high-temperature silicone masking. Also, if the crank is nitrided, the nitriding may need to be removed so that a good grit blast profile can be attained. If steel grit (chilled iron) cannot provide a sharp, angular blast profile, I suggest that silicon-carbide grit be used. The blast profile should be sharp and angular, with a 50-75 μm profile.
2. The crankshaft should be preheated to ∼200 F(100 °C) and rotated quickly, so that no more than 0.0005 in. (12 μm) of HVOF coatings are applied with each pass of the gun. The actual spraying temperature should not be allowed to exceed 320 F (160 °C). These steps may be difficult to achieve with a very large crankshaft.
3. Usually the bond coat/build up layer is 95/5 NiAl (Metco Diamalloy 4008), which is used to repair the crankshaft to about 0.020 in. (500 μm) undersize (4008 may be built up as high as 0.040 in., or 1 mm) followed by a light grit blast of coarse (40 mesh) aluminum oxide to obtain a 25-50 μm blast profile and then top coat with an iron-base hard coating (Fe 17Cr 11Mo 3Ni 3Si 3Cu 4B 0.4C, Diamalloy 1008) layer built up to 0.035 in. (890 μm). Of course, the condition of the crankshaft will determine the actual coating thicknesses.
4. Grinding is typically done with a 60 grit silicon carbide wheel.

Concerning Arc and Flame Spray: Basically follow the same general cleaning procedure as HVOF; however, rotational speed is not as critical. If you can, spin it fast, but if not, the arc and flame wire coatings are less prone to cracking due to slow rotational speeds and thicker per pass applications. I suggest that you use a 95/5 NiAl wire as a bond coat (such as Metco 8400) for arc spray, and either 1/8 in. 95/5 NiAl (Metco 405) or molybdenum (Metco SpraBond) wire for flame spray, followed by a topcoat of 13% chrome steel wire (Metco Metcoloy No. 2). I have a photo of a diesel crankshaft, as arc sprayed, with this coating system if someone would like to see it. I also have an old Metco process bulletin showing the steps required to repair a crankshaft with thermal spray flame wire coatings.

Answer 5.4: Usually PTA is not a good choice for a repair coating to a crankshaft. The temperatures that are inherent to the PTA process may damage the metallurgy of the part, and heat treating may not be able to bring the crankshaft back to its OEM specifications.

Answer 5.5: Regarding spraying soft Babbitt on the surface of a crankshaft, the surfaces of crankshafts are usually very hard, especially for heavy-duty power generation and marine diesels. It is these types of diesels that will usually require the HVOF coating system mentioned earlier. Babbitt is usually applied to bearing surfaces (crankshaft main bearing caps and engine block, connecting rod ends, etc.) on the engine block. This is a popular and successful coating application. Here is how it is typically done:

1. The old Babbitt is typically burned/melted off with a torch.
2. While the part is still hot, it is chemically and mechanically cleaned with a flux, a wire brush, and a cloth.
3. After it is clean, more flux can be added and tin powder or stick can be applied to it, tinning the entire surface you plan on applying Babbitt to.
4. Once tinned, carefully and thoroughly wash off all the flux (water based is best), making certain the part remains hot enough to keep the tinned area shiny and wet.
5. Immediately apply the thermal spray Babbitt coating via flame or arc wire to the desired thickness. The wet tinned surface will accept the Babbitt (a tin alloy), and the first spray pass will actually be wetted (melted) into the tinned areas, providing an excellent bond. I prefer to apply Babbitt coatings via the flame wire process, because it is easier to minimize the oxide content of the zinc by spraying with an O_2 reducing flame (very fuel rich). There is also much less dust generated during the flame wire application of Babbitt.

Answer 5.6: You can use to repair both rod journals and main bearing surfaces on crankshafts by undercutting surface area 0.030-0.040, 0.015-0.020 per side. Then apply a bond coat and topcoat with an HVOF wire spray application. When you use an HVOF wire spray your coating is much denser and your Rockwell hardness is approximately 20 points higher than that of a conventional twin arc system.

Question 6

Tensile strength data for WC-17Co. Does anyone have tensile strength data (i.e., not bond strength) for tungsten carbide + 17% Co that has been applied using hydrogen + oxygen HVOF? Actually, data for this material from any thermal spray process would be useful.

Answer 6.1: We may consider taking a look at this reference: F.R. Vandeput and N. Mastrantonis, A Comparison of the Strength of WC-Co Measured by Ring and Transverse Rupture Strength Specimens, *Materials Science and Engineering*, Vol A105/106, 1988, p 423-428. These authors measured the tensile strength of WC-Co cermets (bulk) via three-point bending method. The cobalt contents of the WC cermets were 3, 6, 9, 15, and 20 wt.%.

Question 7

The market size of the thermal spray industry. Can anyone tell me about (or point me toward an appropriate source for) the size of the thermal spray coating industry at present? I am talking in terms of revenue/business (in dollars) in the United States, European Union, as well as worldwide.

Answer 7.1: Please take a look at the following references:

- Peter Hanneforth, SpaCom LLC, The Global Thermal Spray Industry—100 Years of Success, So What's Next, *International Thermal Spray & Surface Engineering*, Vol 1 (No. 1), May 2006, R. Knight, Ed., TSS Publication, www.asminternational.org/tss
- Dr. Bruno Walser, Sulzer Ltd., The Importance of Thermal Spray for Current and Future Applications in Key Industries (Key Note Lecture, International Thermal Spray Conference and Exposition (ITSC), Orlando, FL, May 2003), *SprayTime*, Vol 10 (No. 4), Fourth Quarter 2003, International Thermal Spray Association (ITSA), Kathy M. Dusa, Ed., kathydusa@thermalspray.org

Question 8

Coating application on steam turbine blades (cavitation). We are helping a customer develop an application for steam turbine blades. At the low-pressure end of the turbine, the steam condenses and cavitation type wear occurs on the blades. What coating materials have been used successfully to protect the blades?

Answer 8.1: Take a look at the following references from the 1996 thermal spray conference proceedings:

- "Cavitation Erosion of HVOF Coatings" by R. Schwetzke and H. Kreye of the University of the Federal Armed Forces, Hamburg, Germany, p 153 of the proceedings
- One specifically on coating performance for steam turbines: "Chromium Carbide Coatings for High Temperature Erosion Resistance" by D.R. Sileski of the Tennessee Valley Authority, Chattanooga, TN, p 159 of the proceedings.

Answer 8.2: HVOF applied coatings of either chrome carbide or nickel chrome silicon boron are the suggested and widely used materials used in this application. Especially the latter is best for cavitation resistance. Both are available through Sulzer Woka or Praxair. Wall Colmonoy has three outstanding NiCrSiB alloys that you may find useful: Colmonoy 53HV, Colmonoy 63HV, and Colmonoy 88HV.

Question 9

Plasma spraying MgO. Does anyone know where I could find information regarding plasma spraying of MgO?

Answer 9.1: As far as I know this material is difficult to plasma spray, at least in pure MgO. The reason is the narrow gap between melting temperature and excessive evaporation temperatures. In the early 1980s we had a lot of interest in this material, but at least at that time all experiments were unsuccessful. These are some references:

- Kuno Kirner, Plasma Spraying of Free Standing Ceramic Bodies, *Proc. Ninth International Thermal Spraying Conference* (May 19-23, 1980, Hague); in a Table he wrote MgO: sprayability: good.

- Mentions better sprayability: K.T. Scott and J.L. Woodhead, Gel-Processed Powders for Plasma Spraying, *Thin Solid Films*, Vol 95, 1982, p 219-225. MgO-10 mol% ZrO_2 composition: DE only 15%.
- J.L. Besson, M. Vardelle, and P. Boch, Arc Plasma Spraying of Ceramic Deposits, *L'industrie Ceramique No 727*, 4/79, p 248-260. In this paper it was said that the material is difficult to spray due to the mentioned reasons.

Question 10

Coating graphite using HVOF. Is it possible to coat graphite through HVOF technology?

Answer 10.1: It is possible to coat materials onto a graphite substrate. However, if the material being applied is very hard or abrasive, then it would likely erode away the graphite. HVOF in this respect will behave like a high-temperature grit blaster. One way to mitigate this would be the use of a ductile metallic bond coat, such as Zn, NiCr, or maybe even Mo, onto which the topcoat could then be applied via HVOF.

Answer 10.2: I have seen copper wire arc sprayed as a bond coat to allow HVOF topcoat application without damaging the graphite.

Answer 10.3: Increased erosion and lower DE with higher HVOF velocity should not be surprising. High DE and low shot peening or particle (or partial particle) bouncing off effect is a balance of velocity and particle temperature (plasticity). Of course, there is the goal of achieving proper coating properties, i.e., quality, that makes the balance challenging. My experience with spraying onto brittle surfaces such as graphite or alumina with HVOF that it requires a soft, ductile overlay such as a thin layer of copper or aluminum has been achieved as a bond coat. Topcoats of carbides and some metals, however, still can erode or peen the bond coat till it fails. Therefore, the topcoat conditions often have to be modified compared to spraying on metallic parts. Thermal shock resulting into cracking or exploding of the substrate is another problem, especially if it is relatively thin. Some superconductive materials explored in the late 1980s and early 1990s were also deposited on graphite and alumina substrates as long as the velocity was fairly low and the coating was applied typically less than 0.005 in.