

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. Any further discussion can be submitted to the Editor of the JTST.

Question 1

Peak and Valley Contour. We have sprayed high-velocity oxyfuel (HVOF) cermet coatings on “APL rollers” using a HVOF CDS machine for years. Recently we found that the last one of the rollers showed exaggerated peak-and-valley contour with constant spacing. The difference in height is around 40-50 μm (nominal coating thickness are 120 μm) and the spacing between peaks is 5 cm. Could anybody offer advice on the conditions that may result in the above mentioned phenomenon?

Answer 1.1: Have your torch or part rotation speed changed?

Answer 1.2: Sounds like what is referred to as the “barber pole” effect. The relative speeds of the lateral torch traverse used and part rotation speed can result in the spray pattern taking on a spiral form. This phenomenon happens when the synchronization is such that the spray pattern overlaps itself on repeated horizontal passes. You need to break up the synchronization between the two motion axes involved.

Response to 1.2: That is what I initially thought, but why would it be a 5 cm period? Unless the index per revolution was on the order of 5 cm, but who would do that with HVOF cermet? Around 1/3 of the spray pattern width per revolution should be good.

Answer 1.3: If you have done this for years chances are that something changed in your system rather than in the way you sprayed. I would look at the torch, a change there can “split” the particle stream. According to my experience another source of such waviness is the change in the particle stream width (narrower or wider has the same effect). This effect is more pronounced when you have two materials with different heat capacity.

Answer 1.4: We use home-blended cermet powders. Since the flowability of the

powder is not good enough for DJ powder feeder, we can only use CDS system at the moment. The peak-and-valley patterns are not forming at a continuous spiral line, it is discrete instead. The waviness can be evident during finishing (grinding) since the top layer of our coating was always more porous than the bottom layer (please comment on this phenomenon too), so you get constant spacing black stripes corresponding to the porous region. I suspect the wavy coating has happened to all other rollers and was amplified in the last roller for unknown reasons. If you have tried most everything else, check if the air jets on either side of the torch meet or cross at a point that would be 1 in. (25 mm) past the surface of the roll.

Answer 1.5: If you do not have a spiral, then it is neither the way you spray nor the shape of the particle stream. A possible reason would be that you have some sort of standing wave on your roller due to the oscillation caused by the motor that rotates the roller. I used to spray a rotating target, and it sometimes oscillated up and down but rarely in a steady manner. I would look into the driving mechanism.

Answer 1.6: If I understand your comments, the ridges you see do not form a continuous helix, but do follow a somewhat helical pattern with interruptions in the circumferential direction. If my understanding is correct, powder pulsing may be the issue at hand. Powder pulsing or surging can be caused by several powder and powder feeder problems. First and foremost are powder carrier gas leaks. Carrier gas leaks are common at hose fitting, powder feeder fittings, and lid seal areas. Very small leaks are commonly known to cause powder pulsing or surging, which would be evidenced by a discontinuous helical pattern on a rotating part. Remember that carrier gas flows are relatively low, such that small leaks are significant. While leaks are the number one cause of powder-feeding problems, followed closely by poorly classified powders, there are several other potential causes including, hose ID, moisture, manipulation speeds, hose dress, etc. As you are probably aware, blended powders do segregate or classify during transport through the feed system, at the point of injection, and along the length of the jet.

Answer 1.7: How do you measure the porosity in the top and bottom layer of the coating? If you measure the porosity on

the cross section of the polished sample, this difference could be due to an inappropriate polishing procedure as well.

Answer 1.8: The top layer (depending on the material composition and particle size) may tend to always be more porous due to the fact that the very last spray pass did not receive the “shot-peening effect” from subsequent coating passes. We have seen “wavy” coatings too, and changing of the powder injector and nozzle assembly has corrected the problem.

Question 2

Hydrofluoric-Resistant Coating. I am looking for a coating that will resist hydrofluoric (HF) acid (70%) at room temperature. The HF solution may contain solids smaller than 50 μm .

Answer 2.1: I believe HF comes in a fluoropolymer bottle. Teflon or PPS coatings are candidates for this type of application.

Answer 2.2: HF acid is commercialized in high-density polyethylene (HDPE) bottles. Glass is highly corroded by HF acid. The great majority (if not all) of metal oxides are attacked by HF acid.

Answer 2.3: Acids such as HF come in some type of plastic. Materials suited to handle HF include tetrafluoroethylene, fluoroethylene propylene, perfluoroalkane, and monochlorotrifluoroethylene (*ASM Handbook of Corrosion Data*, page 321).

Answer 2.4: A 94% W_2C -6% (Ni 63-70, C 0.3 max, Mn 2 max, Fe 1 max, Cu bal) overlay has been very successful in this sort of application.

Answer 2.5: Teflon coatings are porous and allow aqueous materials to weep through to the base metal in a coating. It is well documented that unless you have a highly corrosion-resistant material beneath the coating delamination will ultimately occur. If one were to use ETFE (ethylene tetrafluoroethylene) instead of Teflon (ETFE is nonporous as a coating and may be hot flocked up to 1/8 in. (3.2 mm) in thickness) then permeation will not occur.

Answer 2.6: We field apply ETFE and have found it to be quite effective in addressing low-temperature corrosion (<500 $^{\circ}\text{F}$, or 260 $^{\circ}\text{C}$). The only downside of using it in a field environment with flame spray equipment is the hydrofluoric acid that evolves during flame spray ap-

plication. We “envelope” our people so they have no contact with the HF, but this significantly slows the surface area coverage.

Answer 2.7: If the HF is evolving from the ETFE, then it is likely being overheated and degraded. This can be minimized with HVOF and control of the particle dwell time.

Question 3

Molten Sulfur. I have a customer that is having corrosion problems in a molten sulfur storage tank. Corrosion is occurring only in the first 20 mils of the walls and a 2 mils annular ring around the floor. We are looking for a metallic coating that will provide either sacrificial protection or corrosion protection without developing a galvanic corrosion cell with the existing carbon steel floor.

Answer 3.1: Along the Gulf Coast a lot of the refineries are having the floor and the first few feet up of the tank walls, steam coil, steam coil clips, and supports coated with aluminum. Most of this sort of work is done with wire spray systems, and the user then seals up the porosity in the coating with a nonmetallic sealer. This is not only used in storage tanks, but also in some rail cars. The coating system has a finite life that can be extended several orders of magnitude by using an HVOF system with a 0.007-0.010 in. (0.18-0.25 mm) thickness unsealed coating.

Question 4

Deep-Ocean Corrosion. I have a question concerning deep-ocean and low-temperature (35 °F, or 1.7 °C) corrosion. I am working with deep-ocean cables, and in several areas there are screws that hold down small steel plates (1018) coated with 8 mils thermal sprayed aluminum, top coated with a 3 mils silicone aluminum sealer. The present method is to fasten the plates with 302 stainless steel screws. An alternate method is to use zinc-coated steel screws with neoprene washers. This method needs to have a service life of 20 years. The question: can either method last 20 years in a deep ocean and what concerns should be of interest to me?

Answer 4.1: Due to the lack of oxygen in the deep ocean, carbon steel resists corrosion more than stainless steel or other high-alloy materials.

Answer 4.2: It is correct that oxygen content decreases with depth; however, this phenomenon only occurs up to a point,

and after this depth is reached the oxygen content starts increasing again. In the Gulf of Mexico the lowest oxygen content occurs at approximately 1800 ft (550 m). Wave action throughout the oceans increases the oxygen level, whereas the biological oxygen demand of decomposing organisms will reduce it. In some oceans the oxygen content at the bottom is similar to the surface because of the movement of the current. The solubility of oxygen in seawater also increases with decreasing temperature. For steels, the presence of oxygen greatly accelerates rates of attack. On the other hand, the presence of oxygen generally reduces rates of attack of corrosion-resistant materials, such as stainless steels and titanium, by promoting passivation. However, where the oxygen supply to a passive metal surface is limited locally, such as at crevices, the presence of oxygen on the boldly exposed surfaces may promote localized attack. For your application I would not recommend the use of neoprene washers. This will create crevices. For most deep-water applications, cathodic protection (CP) is utilized. CP is adequate to protect bare metal. In cases where this is not an option, the best recommendation is to coat the plates with thermal spray aluminum and zinc coat the screws. Omit the neoprene washer with the 302 screws as the stainless steel screws will corrode away.

Answer 4.3: A 3% BeCu has been used in deep-ocean service since the first transatlantic telegraph cable was laid over a century ago. In the 1960s, some of the old cables were raised and inspected. There was no significant corrosion of the beryllium copper connectors. This alloy age hardens to a range similar to that of 302 stainless steel. It is available as wire and would probably be a good candidate for arc wire spraying as a corrosion-resistant overcoat as long as the toxic dust was controlled. The material is readily machinable and has been used for screws. It is also available in sheet, plate, and cast form. If your application needs to last a long time, I highly recommend this alloy.

Answer 4.4: Beryllium copper is a good material for deep-ocean service; however, I would be careful with its use in an arc weld process. The fumes of this material are very toxic.

Answer 4.5: We have done some titanium-clad subsea components for several of our customers who claim that this material is vastly superior to aluminum or

zinc. The titanium-clad coating is 1/8 in. (3.2 mm) thick, and we are braze-bonding it to the components for maximum durability. I believe that these components are being utilized in deep-water applications. I do not know the depth, but the equipment is rated for 20 ksi (140 MPa) service in H₂S bearing crude.

Answer 4.6: What is the ductility of the coating? For thickness of 1/8 in. (3.2 mm), either the coating has excellent ductility or the part has no deflection. Titanium has excellent corrosion resistance in seawater and many fluids. It is resistant to most fluids. It is not resistant to HCl or HF. For most subsea applications, titanium is adequate.

Question 5

Metals Resistant to H₂SO₄. Can anyone recommend metals that have particularly high etching resistance to sulfuric acid?

Answer 5.1: Titanium, zirconium, and tantalum when subjected from ambient temperature to 250 °F (120 °C) in nonoxidizing environments.

Answer 5.2: Be careful, if you spray a noble metal over a less noble material you will have a galvanic cell and form a corrosion cell. Check the potentials of the alloys before.

Answer 5.3: A galvanic cell will not be generated if the less noble metal is encapsulated or if the more noble metal is a small percentage of the total surface area available for galvanic reaction.

Answer 5.4: Yes, you are right. However, the thermal spray coatings have defects such as microcracks and porosity. If the acid can penetrate into the coating and reach the substrate, you will have a galvanic cell. That is why is important to seal the coatings.

Answer 5.5: This is correct. As difficult as it is to accept, in mating materials exposed to seawater, it is common practice to coat the more noble material to minimize the galvanic effect.

Question 6

Rust Spots on a CrC-NiCr Coating. Has anyone ever experienced this condition: rust spots on the surface of a CrC-NiCr alloy coating sprayed by high-velocity oxyfuel (HVOF) onto titanium substrates? The spots occur after the part is rinsed in deionized water. The spots are rust colored and scanning electron microscopy (SEM) analysis detects iron.

The powder manufacturer specifies iron content between 0.33 and 0.55. The rust spots do not appear to go beyond the surface.

Answer 6.1: I would verify if your powder does not contain any free iron. Also talk with your vendor about possible contamination during manufacture. Any non-alloyed iron could give you this problem based on my experiences.

Answer 6.2: We also have experienced this phenomenon, but almost exclusively in field-applied coatings. Due to the dirty environments (free iron from sand blasting) we operate in, the iron dust is in the air and is caught up in the jet stream and deposited with the coating. I believe that you will find traces of free iron throughout your deposit if you have this sort of problem.

Question 7

Impact Testing for Coatings. Can anyone recommend a good testing lab for impact testing of coatings?

Answer 7.1: Impact testing is usually done (meaning how it is done for bulk materials) with the aid of a notch. This

procedure can seldom be done on a coating. There is another problem. If the coating is adhered to a substrate, it is very difficult to estimate the real value of the energy absorbed by the coating before it cracked or failed, since the substrate will absorb part of it.

Answer 7.2: Impact testing can be done on small samples using a miniature impact tester. This is a bench-top machine whose size is around 12 in. (305 mm) high and 6 in. (150 mm) wide. I have used this setup for testing epoxy and its particulate composites many years ago. Talk to mechanical testing labs and they may be able to help you.

Answer 7.3: You can machine the backing substrate or make a free-standing coating with maximum thickness possible. Since the samples are very thin, there is no need to make any notch. If your material chemistry and microstructure are such that they give a very high value, you may want to either put a notch or reduce sample dimension accordingly.

Question 8

Pistons and Mating Materials. For hydraulic applications, when pistons are

coated with hard coatings, how should we change the mating materials? Are there any generalized coating design principles?

Answer 8.1: In applications where the coatings have hardness in range of 50 HRC, it is possible to use the same mating materials. In applications where this is not possible, it is necessary to have a hardness variation between the two coatings. I am not aware if anything is published for this hardness variation between coatings.

Answer 8.2: We have provided 94% WC-6% Ni high-velocity oxyfuel (HVOF) overlays to customers for carbide-to-carbide mating surfaces that have proven to be extremely effective for mechanical sealing and bearing purposes. These "superfinished surfaces" have to be held to very tight geometric tolerances (± 0.0003 in., or 0.008 mm) to be effective in >3500 rpm service. One drawback is that a vacuum may be formed after "wear in," necessitating the use of high-pressure lubricators to keep the bearing from "locking up" after shutdown or startup.