

# Thermal Spray Coatings

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THERMAL SPRAY COATINGS are a versatile and well-established means of protecting metals from corrosion in a wide variety of environments (Ref 1, 2). Many different materials can be used to produce thermal sprayed coatings, thereby providing effective solutions to diverse corrosion problems. These materials—including metals, ceramics, polymers, and combinations thereof—may be used to give reliable long-term corrosion protection to substrates. Another use of thermal sprayed coatings is production of anodes for cathodic protection of steel reinforcement in concrete. Thermal spraying is virtually unlimited in scale and complexity of applications, ranging from small fasteners to structures. Production of coatings is rapid and can be automated. Other advantages of thermal sprayed coatings include portability, ability to seal or top-coat, abrasion and erosion resistance, and lack of curing requirements.

## Thermal Spray Processes

Thermal spray (TS) is a generic term used to describe a group of processes, including flame spraying, plasma spraying, arc metallization, detonation gun (D-gun), high-velocity oxyfuel (HVOF), and cold spray, that can be used to apply a variety of different coating materials for corrosion protection (Ref 3). Although these processes encompass a wide range of equipment needs, costs, materials selection and application, they can all be treated as belonging to the same family since the processing variables that are being altered are temperature and particle velocity. Figure 1 depicts the temperature-velocity processing envelope that allows materials engineers to create a vast array of coatings for applications that include coatings for orthopedic hips, thermal barrier coatings for aerospace hardware, rebuilding of original equipment manufacturer components, and coatings to protect against corrosion.

Besides temperature and velocity, another obvious variable is the nature of the material that is used to form the coating. The material can be a powder, rod, wire, or liquid. The material that is fed into the TS process is termed feedstock, with the most common forms being powder and wire (Ref 4, 5). The feedstock morphologies are

selected according to the process. Arc metallization and the wire flame processes require wire as the feedstock, whereas the most common renditions of the gas flame, plasma, and HVOF processes require powders.

Table 1 lists thermal spray processes. Those that are based on similar technological principles or that have equivalent names are grouped onto the same lines. The choice of process or material depends on the engineering application. Ceramic TS coatings generally require processes with higher velocities and temperatures than lower-melting point materials. Therefore, plasma, D-gun, and HVOF are the preferred techniques for deposition at high rates. The deposition of ceramics is more sensitive to spray parameters than is the deposition of metals.

Generic figures that demonstrate the principles behind TS processes are shown in Fig. 2. Wire flame, powder flame, electric arc, and plasma spray processes are depicted. The same principle applies in all cases; a feedstock is rapidly heated and then accelerated toward a suitably prepared substrate where on impact it consolidates to form an adherent coating.

The coating structure is often nonuniform and an example of an HVOF-sprayed Inconel 625 coating and the remelted condition of Fig. 3 (Ref 7).

Coatings applied by the same technique can exhibit a wide variability (Ref 8–10) that arises from processing variables such as gas flow rates, the rate of coating deposition, the coating thickness, substrate preparation (e.g., preheat, post-heat, and surface preparation schedules), type of spray material used, and the torch-to-substrate distance. These thermal spray parameters influence the quality of the adhesion to the substrate and the material properties such as electrical conductivity, density, and porosity. It is incorrect to assume that all thermally sprayed coatings of a particular material are identical in performance. The process must be "optimized" for each particular application.

Coatings are suited to specific applications because they retain some intrinsic material characteristics of the original coating powder. However, it must be emphasized that "bulk" material performance cannot be directly correlated to any property of the coating. The structure of a coat-

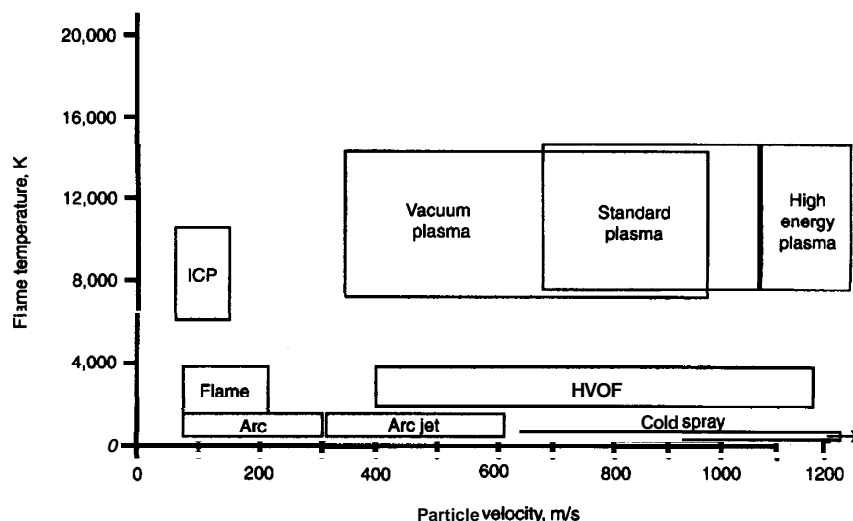


Fig. 1 The temperature-velocity distribution envelope of thermal spray processes. HVOF, high-velocity oxyfuel; ICP, impressed current protection

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ing is quite dissimilar to that of a material produced by a bulk-fabrication process. Properties of the coating that may limit its utility include the physical, mechanical, thermal, electrochemical, and electrical properties. An additional property of great interest is adhesion to the substrate, since good adhesion is crucial for the coating to retain functionality throughout its intended service life.

### Controlling the Structure, Properties, and Performance of Coatings

**The Microstructural Character of Thermal Spray Coatings.** It is the structure and chemistry of TS coatings that ultimately define their utility. Thermal sprayed coatings are produced from the repeated deposition of particles that are in the diameter range of 10 to 120  $\mu\text{m}$  (0.4 to 4.7 mils). The coating structure is of lamellar morphology, much the same way as cards stacked on top of each other. Distinctive processing advantages of TS technology include the ability to coat most materials with an almost unlimited range of other materials, be they metals, ceramics, polymers, or combinations thereof. It is also possible to produce thick coatings from 0.1 to 2 mm (0.004 to 0.08 in.) routinely and to precisely control the coating formulation and chemistry.

The performance of a TS coating is directly related to this lamellar morphology. The resultant lamellar dimensions are about 60  $\mu\text{m}$  (2.4 mils) in diameter and from 1 to 2.5  $\mu\text{m}$  (0.04 to 0.1 mil) thick. Every coating structure is highly oriented with the lamellae parallel to the surface of the substrate.

Important microstructural artifacts, especially for corrosion-control applications that require a barrier to conducting and corrosive liquids, include porosity and microcracks.

It has been estimated (Ref 11,12) that the real contact area of lamellae with the substrate and within the coating is 30% of the available boundary area. Direct measurements of interlamellar porosity have shown that the porosity is about 10 to 100  $\mu\text{m}$  (0.4 to 4 mils) in size. Unmolten particles become incorporated into the coating and these, along with the interlamellar boundaries and porosity, constitute regions of poor bonding that may lead to failure of the coating system. The control of porosity is critical to the performance of any corrosion-control coating. Any defects that allow ingress of aggressive species will accelerate the coating-degradation process. Much attention has been paid to the control and modification of porosity that is inherent to the majority of conventional TS processes.

In one study (Ref 13), the porosity of thermal spray coatings was classified according to the potential mechanism of formation (Fig. 4). Type 1 porosity was exhibited between lamellae and was caused by the stacking of separate particles. This porosity can be directly related to the particle size and distribution characteristics of the spray material. Type 2 porosity was distin-

guished as trapped gas pockets caused by the turbulence of the gas flow during the TS process. Type 3 porosity was manifested in the form of gas bubbles caused by the dissolution of gas into the molten metal that evolved upon freezing of the metal. Type 4 porosity was caused by the disintegration of spray particles upon impact during the coating-deposition process. Type 5 porosity evolved from the condensation of partially evaporated particles and could be identified very often by containing powdery residues. Type 6 porosity arose due to solidification shrinkage, as observed between dendrites. Type 7 porosity results in microcracks regardless of their formation origin. Thus, although there may be some differences of opinion concerning the precise formation mechanism of porosity, there is general agreement that it can be controlled in a quite reproducible fashion by selection of appropriate TS parameters. Therefore, as mentioned previously, the control of temperature and velocity during the TS process is distinctly related to the deformation mechanism of the impacting lamellae and the formation of porosity.

**Process Optimization and Parameterization.** Optimization involves the study and analysis of operational parameters and their influence on a particular property. Single-wire arc spraying and powder flame spraying are two processes for manufacturing a corrosion-control coating.

When spraying a new material, the processing parameters are developed by taking the powder/wire manufacturer's recommendation or that of an experienced TS engineer. Much of the TS industry uses such an experience base. This type of experience is valuable, but a trial-and-error method is not time or cost effective in spraying new materials or developing new microstructures. It is necessary to understand the relationship between properties and parameters for a given process and to present this relationship in a form that can be easily understood. Simple experiments can be set up to map a region of interest (Ref 14, 15). The map is referred to as a response over a region of parameters that needed evaluation.

Six primary process variables are:

- Enthalpy input into the particular TS process, whether it be gained from a combusting gas, the transfer of particle momentum to kinetic energy on impact against a substrate, or the use of direct-current electrical energy
- Feedstock delivery rates and the corresponding coating buildup per pass and the appli-

cation rate in quantities of "mils per square foot per hour"

- Gas pressures and flow rates used for the combustion or arc processes
- The standoff distance between the TS device and substrate
- The surface preparation of the substrate
- Pre- or postconditioning of the substrate by heating or cooling

Control of these spray variables leads to the design of the **microstructure** and control of physical properties such as tensile adhesion strength, coating density, and surface roughness. **They** also relate to the deposition efficiency of the process, and this is directly correlated to the process economics. The role of these variables in the control of bond durability is often measured by a bond-strength technique, such as ASTM C 633 (Ref 16).

**Surface Preparation.** The most critical step is the preparation of the surface to be sprayed. The ideal surface is one that is roughened by grit blasting and that is contaminant free, that is, no oil, water, or blast media residues. The specifications given in this article detail these requirements. It is recommended that the coating process take place within several hours of the surface preparation so atmospheric oxidation of the highly energetic surface will not cause formation of a poorly bonded coating.

#### Coating Sealers and Surface Treatments.

The material properties of coatings are a direct consequence of their complex **structure** and determine the overall coating behavior. Not all coatings are used in their as-sprayed condition. Metallic and ceramic coatings are often sealed to extend the protective **properties** and service life, particularly in immersed or severe environments. Sealers are typically low-viscosity liquids that penetrate and seal the coating pores. Commonly used sealers include vinyls, epoxies, epoxides, polyurethanes, **phenolics**, and **silicones**. Sealers are also used to produce decorative and smooth surface finishes. Other postprocessing surface treatments such as laser glazing and hot-isostatic pressing have been used to **densify** coatings and improve corrosion resistance. More information on sealers and surface treatments can be found in Ref 7 and 17 to 20.

### Criteria for Coating Selection

**Selection According to the Corrosion Environment.** Table 2 lists engineering compo-

Table 1 Thermal spray process parameters

Process	Temperature		Velocity	
	°C	°F	m/s	ft/s
Oxyacetylene gas flame spraying, flame spraying	3,000	5,430	150	490
Atmospheric plasma spraying, APS	12,000	21,630	900	2,955
Low-pressure plasma spraying, LPPS, VPS	1,200	2,190	900	2,955
Detonation gun spraying, D-gun	300	570	1,000	3,280
Ceramic rod process, Rokide process	3,000	5,430	150	490
Hypersonic plasma spraying, diamond jet gun (DJ gun), JetKote, High-velocity oxyfuel process (HVOF), J-gun, Topgun, Nova-jet, Plazjet	3,000	5,430	800	2,625
Arc metallization, wire spraying	1,500	2,730	200	655

Thermal spraying processes at a glance

Particle formation & environment

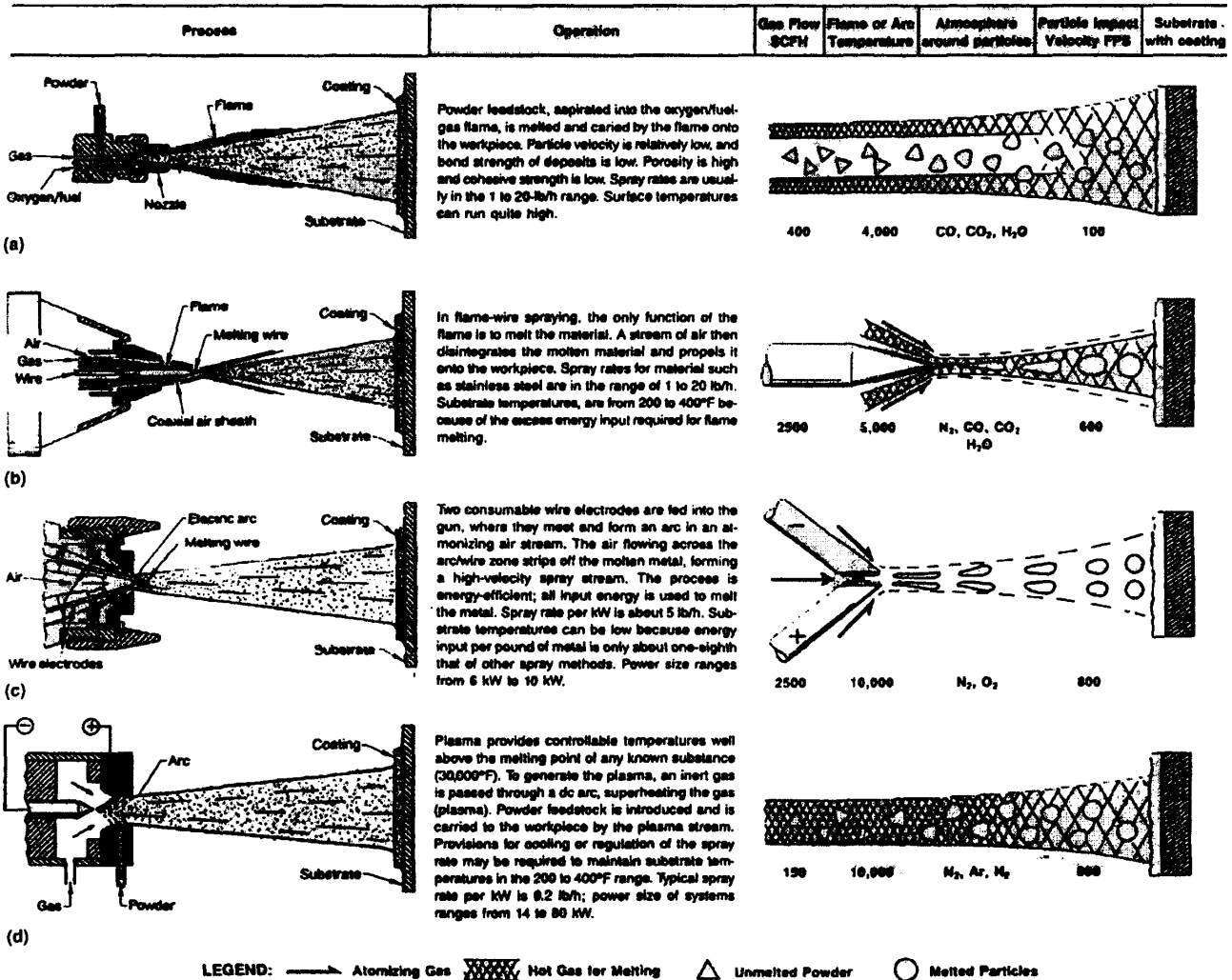


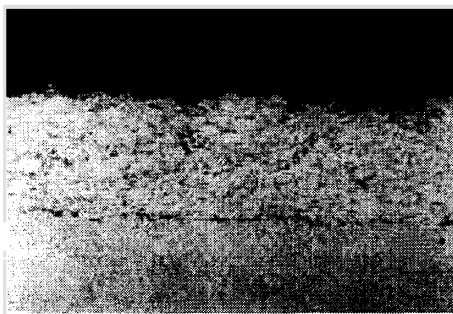
Fig. 2 Generic process schematics for (a) flame powder, (b) flame wire, (c) wire arc, and (d) plasma spray. Gas flow SCFH, standard cubic feet per hour; temperature, Kelvin; impact velocity FPS, feet per second. Source: Ref 6

nents that have benefited in mitigating the stated corrosion-related environment. It is difficult to specify one coating for any one set of operational

conditions since the coating choice will be dictated by the environment, temperature, component dimensions, any requirement for postpro-

cessing of the coatings such as reduction of surface roughness, and other practical factors.

Common atmospheric and immersion service environments with typical TS coatings for cor-



(a)



(b)

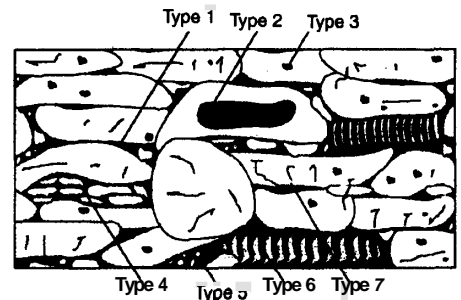


Fig. 4 Forms of porosity can be categorized within a thermal spray coating. Explanation in text. Source: Ref 13

Fig. 3 Optical micrograph of high-velocity oxyfuel sprayed, Inconel 625 coating in (a) as-sprayed and (b) laser-remelted conditions. Coating thickness is 300 and 400 μm (12 and 16 pin.), respectively. Source: Ref 7

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rosion protection are given in (Table 3) (Ref 21) and elevated-temperature service is addressed in Table 4.

**Applications for Metallic Coatings.** Uses of metallic coatings for corrosion protection include bridges, buildings, marine vessels and structures, pipelines, chemical-processing equipment, power plants, exhaust flues, water-storage tanks, and boilers. Specific examples for use of HVOF nickel alloy C-276 and 316L stainless steel in petrochemical applications are given in Ref 22 and 23. Table 5 (Ref 6) details other TS applications in this highly demanding petrochemical environment.

Thermal sprayed metallic zinc and aluminum alloys coatings are commonly used for corrosion protection of steel substrates. Such coatings are sacrificial. It is also possible to thermal spray many other protective coatings such as nickel-base alloys, stainless steel, bronze, tin, and more exotic materials. These coatings are cathodic to the steel substrate, and it is important that they act as a barrier. For this reason, cathodic coatings are often sealed or surface treated to prevent penetration of corrosive species to the steel substrate. Furthermore, it is preferable that cathodic coatings are applied using a process that minimizes coating porosity such as HVOF. Selection of coating thickness depends on the severity of the environment and typically ranges between 50 and 500  $\mu\text{m}$  (2 and 20 pin.).

Experience with metallic TS coatings for infrastructure applications extends back to the 1940s. Sluice gates and canal lock gates that have been zinc coated have remained in perfect condition with virtually no maintenance for decades: the St. Denis Canal Lock Gates in France, coated in the early 1930s, are an outstanding example. The locks of the Panama Canal have also been zinc sprayed. In the United Kingdom, the suspension chains and other components of the Menai Straits Bridge were zinc sprayed just before World War II. During the war, the bridge received no maintenance. When it was inspected after the end of the war, the sprayed areas of the bridge were found to be in excellent condition. The steel deck structure, on the other hand,

which had been painted but not sprayed, was rusting. The obvious reduction in required maintenance of the bridge prompted the British to apply sprayed metal coatings to numerous other road and railway bridges over the past 40 years. In the United States, metal sprayed coatings are presently being specified and used by departments of transportation (DOT) in Florida, Connecticut, California, Oregon, and Ohio.

The use of TS metallization makes it possible to achieve fully effective, maintenance-free protection of corrosion and corrosion-enhanced mechanical failure of steel structures for more than 30 years. Fifty-year protection effectiveness has been documented in rural environments and more than 20 years in harsh industrial, urban, and coastal regions. On an overall cost basis that includes maintenance, TS metallization has long been competitive with comparable corrosion-protection systems. Recent studies indicate that TS is now competitive on an initial cost basis alone. The conservative lifetime for a 255  $\mu\text{m}$  (10 mil) thickness of zinc (or zinc-aluminum alloy) is approximately 25 years, which can be extended 15 years by the application of a vinyl paint as a topcoat to seal any porosity. Initial application costs of TS zinc (in 1998 U.S. dollars) are \$10 per square foot or \$0.40 per square foot per year for 25 years. Further examples and

information on TS coatings for protection of steel structures can be found in Ref 24 to 27.

In the case of cathodic protection (CP) of steel reinforcement in concrete, the TS coating is used as an anode. Zinc is the most common material for this purpose, although titanium has also been used. The coating is applied directly to the concrete substrate. The type of connection to the reinforcement depends on the CP system. It is more common to use impressed-current systems, although galvanic systems with zinc may also be effective in low concrete resistivity situations. Advantages of thermal sprayed anodes include ability to cover complex surfaces, uniform current distribution, and redundancy of an overlay as required with alternative mesh systems. Methods used to TS zinc onto concrete include oxy-acetylene wire flame spraying, twin-wire arc spray, and single-wire arc plasma spraying. These methods may form coatings that display different properties and process economics. Plasma and arc spraying have been used to produce titanium anodes.

Early applications that detailed the modern development of these coatings by regional DOTs in the United States are documented in Ref 28 to 31. Updates of this area are covered in Ref 32 and 33 and field applications and the practical experience gained from the thermal spraying of

**Table 2 Categorization of engineering components by anticipated type of corrosion**

Corrosion type	Component
Cavitation	Water turbine buckets, wear rings in hydraulic turbines, impeller pump housings
Particle erosion	Exhaust fans, cyclone dust collectors, exhaust valve seats
Heat and oxidation resistance	Tuyeres for liquid metal, continuous casting molds, heat treating fixtures and brazing jigs, exhaust mufflers
Atmospheric and immersion corrosion	Electrical conduits, bridges, transformer cases, steam-cleaning equipment, ship superstructures, ship holds and tanks, storage tanks for oils, fuels, and solvents, power-line hardware, heat exchangers

**Table 3 Thermal spray coatings for atmospheric and immersion service**

Exposure environment	Thickness of coating systems for 20-year expected service							
	Unsealed zinc		Sealed zinc		Unsealed aluminum		Sealed aluminum	
	$\mu\text{m}$	mils	$\mu\text{m}$	mils	$\mu\text{m}$	mils	$\mu\text{m}$	mils
Atmospheric								
Inland (nonpolluted)	150	6	150	6	150	6	100	4
Inland (polluted)	150	6	150	6	150	6	150	6
Coastal (nonpolluted)	250	10	150	6	150	6	150	6
Coastal (polluted)	350	14	250	10	250	10	150	6
Immersion								
Seawater splash zone	NA	NA	250	10	NA	NA	150	6
Seawater immersion	NA	NA	250	10	NA	NA	150	6

**Table 4 Table 4. Thermal spray coating for elevated-temperature service**

Service temperature, °C (°F)	Coating metal or alloy	Coating thickness	
		$\mu\text{m}$	mils
Up to 550 (1020)	Aluminum	175	7
Up to 550 (1020) in the presence of sulfurous gases	Ni-43Cr-2Ti	375	15
550-900 (1020-1650)	Aluminum or aluminum-iron	175	7
900-1000 (1652-1830)	Nickel-chromium or MCrAlY	375	15
900-1000 (1652-1830) in the presence of sulfurous gases	Nickel-chromium(a)	375	15
	Aluminum(a)	100	4

(a) Coating system consists of aluminum layer deposited on top of a nickel-chromium layer.

**Table 5 Petrochemical application of thermal spray coating**

Component	Coating use	Process	Coating
Ball valves	Wear/corrosion	HVOF	Tungsten carbide
Gate valves	Wear/corrosion	HVOF	Tungsten carbide
Piston rods	Wear	Flame spray	Chrome oxide
Offshore oil rigs	Corrosion	Flame spray	Aluminum
Pump housings	Restore dimension	Arc spray	Aluminum bronze
Compressor cylinders	Restore dimension	Arc spray	420 stainless steel
Processing tanks	Corrosion resistance	Flame spray	Aluminum

zinc are described in Ref 34 to 37. The development of new materials, especially titanium, is covered in Ref 38 and 39, while specific attention to bond strength, or adhesion, studies is the focus of the work reported in Ref 40 and 41. Reference 42 specifically discusses process development and the parameterization of the thermal spray variables in order to obtain the best coatings.

**Applications for Ceramic Coatings.** Ceramic coatings are used from 200 to 1150 °C (390 to 2100 °F). In such instances a metal-based "bond coat" (Ref 43-45) may be used as a compliant layer to compensate for thermally induced stresses that arise from the ceramic overlay. A 0.1 to 0.2 μm (0.004 to 0.008 mil) thick metallic layer is applied to the substrate by conventional TS methods prior to the ceramic coating. Such layers improve the bonding property of any subsequent thermal spray layer that is deposited. Bond coatings are based on alloys of nickel, chromium, molybdenum, and aluminum, with some additions of yttrium in special cases.

**Applications for Polymer Coatings.** Polymer spraying (Ref 46-49) has gained significant commercial attention within the United States since the mid-1990s. Its acceptance as a replacement for paint is due to:

- No need for a primer
- A one-step process with no need for multiple passes
- No need for a topcoat
- Virtually zero volatile organic compounds (VOCs)
- Improved weathering resistance
- Excellent impact resistance

Thermal spray technology is also well suited for automation and can be adapted to existing robotic and automatic applicators. Polymer spraying is a one-coat process that acts as both the primer and the sealer, with no additional cure times, unlike the traditional multicoat painting processes. Thermal spraying is ideally suited for large structures that otherwise could not be dipped in a polymer suspension. Thermoplastic coatings can be repaired by simply remelting or applying additional material to the desired location. In addition, reports have shown that functionalized polyethylene polymers such as ethylene methacrylic acid copolymer (EMAA) and ethylene acrylic acid (EAA) can be applied in high humidity as well as at temperatures below freezing.

Polymer powders are specified by their chemistry, morphology, molecular weight distribution or melt-flow index, and particle size distribution. Spray parameters must be selected to accommodate each particular polymer formulation. A narrow particle size distribution is preferred to produce a homogeneous coating structure. A larger thermal input is required to melt larger particles and higher molecular weight organics. A large particle size or molecular weight distribution will facilitate the formation of numerous heterogeneities within the coating microstructure, creating voids, a range of splat aspect ratios,

and degraded material. A processing window therefore exists for each polymer where poor particle coalescence defines the lower limit and pyrolyzation defines the upper limit. It is also important to note that the polymer may also cross link, undergo chain scission, and/or oxidize during processing.

Polymer powder is axially fed into the combustion zone via a carrier gas. The polymer particulates are propelled through the flame where, upon melting, they become droplets and are transported to the preheated substrate. As the molten particles impinge on the substrate, they deform and solidify, **forming** an interlaced network of splats. Porosity within the coating depends on the nature of the substrate surface, polymer melt viscosity, and decomposition products. The thickness of the coating is governed by the number of repeated passes of the spray gun across the substrate.

The heat source of the TS torch can be a plasma, combustion flame, or combustion exhaust as in the HVOF process. The technique is chosen on the basis of the polymer-melting characteristics. A simple combustion torch is well suited for low-melting-point polymers with a large processing window, such as polyethylene. High-melting-point polymers may require plasma deposition for maximum quality to melt the polymer without causing oxidation. Therefore, processing parameters must be selected for each polymer chemistry and deposition technique.

Two sets of distinct processes illustrate two fundamentally different spheres of polymer coatings. Both processes can generically be referred to as thermal spray; however, one process relies on a propane torch and the other class of processes uses the heat source of either a direct-current (dc) plasma torch or a HVOF gun. Thermal spraying of polymer powder is a 100% solids process. Polymers that can be applied using this process are listed in Table 6 and also include polyaryletherketone (PAEK), **fluoropolymers**, polyesters (Ref 51), and others.

Intrinsic properties of the polymers of interest include melt processibility, high chemical and impact resistance, electrical insulation, low co-

efficient of friction, ductility, and high toughness. Certain polymers also exhibit stability at elevated temperatures up to 300 °C (570 °F). Examples of thermal spraying of polymers are described in Ref 51 to 54, while the thermal spraying of composites is detailed in Ref 56 to 58.

Thermal spraying of polymers is receiving increased attention in military and civil engineering sectors. The ability to apply thin (about 0.13 mm, or 0.005 in.) and thick (up to 6.4 mm, or 0.25 in.) coatings of polymers onto a variety of metals, ceramics, and composites of complex geometry provides solutions to component manufacture and on-site or factory rehabilitation. The development of complex coating chemistries then may be dual phase; for example, composites of plastics and metals or plastics and ceramics is an area that needs further research.

Applications of polymer coatings currently include snowplow blades, pump impellers, tank linings, external pipe coatings, structural steel coatings, transfer chutes, and vacuum systems. Here the intrinsic properties of polymers—such as high chemical resistance, high impact resistance, and high abrasion resistance—are used to advantage. One study has focused on incorporating recycled polymers in the feedstock (Ref 59).

## Costs of Thermal Spray Coatings

Experience with the Oregon DOT in the rehabilitation of the Cape Creek, **Depoe** Bay, and Yaquina Bay bridges indicated an expense of \$19.1 million (in 1995 U.S. dollars) compared to a replacement cost of \$70 million (Ref 60).

Reference 31 specifically details financial aspects of a **ConnDOT** bid. It is stated that the bid price for the field metallizing of five bridges comprising a total area of 5866 m<sup>2</sup> (62,950 ft<sup>2</sup>) amounted to \$110/m<sup>2</sup> (\$10/ft<sup>2</sup>) in 1995 U.S. dollars. The bid price for class 3 containment of waste generated during the rehabilitation contract was \$50/m<sup>2</sup> (\$4.50/ft<sup>2</sup>), and the disposal of this debris was \$3.30/m<sup>2</sup> (0.30/ft<sup>2</sup>).

A detailed cost analysis indicates that the most expensive item in either the twin-wire arc (to spray zinc) or a gas flame technique to spray polymer is the feedstock. The materials used during an arc wire process will constitute ~73% of the total running cost, while the polymer feedstock is ~93% of the total cost (Table 7). As well, a polymer coating process (by a gas flame

**Table 6 Selection of polymers applied as coatings via thermal spray processes**

Polymer	Maximum temperature resistance	
	°C	°F
Ethylene methacrylic acid copolymer (EMAA)	40–60	105–140
Polyethylene (PE)	40–80	105–175
Polypropylene (PP)	70	160
Nylon 6,6 (PA)	65	150
Polyphenylene sulfide (PPS)	110	230
Polyethylene-tetrafluoroethylene copolymer P(E-TFE)	160	320
Polyetheretherketone (PEEK)	125	255
Liquid-crystal polymers (LCPs)	250	480
Phenolic epoxy	130	265
Polyimide (PI)	300	570

Source: Ref 50

**Table 7 Percent costs of twin-wire arc and polymer spray methods**

Cost factor	Cost, %	
	Zinc by twin-wire arc	Polymer by gas flame process
Power	2	0.5
Labor	18	5.5
Materials	73	93
Equipment	7	1
Total cost	100	100
Relative total cost, \$	1	3.3

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thermal spray method) is about 330% more expensive than zinc sprayed by two-wire arc. Table 7 also indicates the relative startup costs with polymer spraying being about one-half that of two-wire arc. The prorated power and labor costs for both of these processes are approximately equivalent.

Case Studies

Example 1: Adhesion of Polymer Coatings.

This case history of EMAA applied to steel does not constitute a recommendation for a specific application, but it does demonstrate the unique characteristics of TS polymeric coatings applied by a gas flame process with fluidized powder feed.

The coating was studied for application in an environment involving biochemical treatment of geothermal sludge. An Atlas cell (ASTM C 868) arrangement was used. The test solution was hypsersaline brine with composition of:

Compound	Content, ppm
NaCl	58,000
CaCl <sub>2</sub>	25,000
KCl	15,000
FeCl <sub>2</sub>	1,000
MnCl <sub>2</sub>	930
SrCl <sub>2</sub>	430
LiCl	410
ZnCl <sub>2</sub>	370
H <sub>3</sub> BO <sub>3</sub>	300
BaCl <sub>2</sub>	130

The pH of the brine was 4.15. The test temperature was 55 °C (130 °F), and the duration was 12 weeks.

At the completion of the tests, the coated panels were visually examined for signs of deterioration such as blistering, discoloration, and loss of gloss. The residual adhesion was determined for EMAA coatings by measuring the peel strength (ASTM D 3167). The plates were cut into strips 25 mm (1 in.) wide, and the orientation was vertical so that the strip traversed the vapor and immersion-exposed zones. The strips cut from the outer edges of the plates were beyond the exposure zone. The coatings were peeled back approximately 40 mm (1.6 in.) using a razor blade to enable the coating to be gripped. An Instron tensile testing machine was used, and the crosshead speed was 152 mm/min (6 in./min).

Figure 5 depicts the peel force versus displacement curve for a strip cut from the edge of one of the panels (Ref 61). The coating in this location was not exposed to brine. The peel force was relatively constant, and the failure mode was adhesive. The average peel strength was 4.33 Pa (0.0006 psi) Figure 5 also shows the results for a strip cut through an exposed area. The peel force was low in the initial region, and this corresponded to the presence of corrosion products at the interface. The increase in peel force at higher displacement occurred outside the exposed area. Peel strength varied from 1.97 to

6.97 Pa (0.0003 to 0.001 psi). Plastic deformation of the coatings occurred during peeling, and this was concentrated in the areas outside the test cell where greater force was required to remove the coating.

Fracture surfaces from the EMAA mild-steel peel tests were examined under a scanning electron microscope (SEM). An example of mixed adhesive/cohesive failure in an uncorroded area is shown in Fig. 6. The dark areas are polymer adhering to the steel surface. Spherical pores, 100 to 200 μm (4 to 8 mil) diameter, in the polymer are evident, and failure often has occurred through these pores. Ductile tearing, indicative of a well-formed coating, may be observed around the edges of a pore (Fig. 6).

Example 2: Thermal Spray Process to Remove Lead-Base Paint. An alternative means of

surface preparation, patented by the U.S. Army Corps of Engineers, is on-site vitrification of hazardous waste. Thermal spraying of specially developed molten glass is used to encapsulate and chemically stabilize lead-base paint and rust (Ref 62). The encapsulant is then removed by chipping off relatively large chunks, which are readily removed for disposal. The objective has been to develop technology and guidance for maintenance where work will involve the removal of a coating material containing lead-base paint or other hazardous waste. Spray techniques, glass deposit chemistries, and encapsulation effectiveness are being testing and optimized.

The U.S. Environmental Protection Agency (EPA) regulations have necessitated the removal and containment of toxic lead from lead oxide

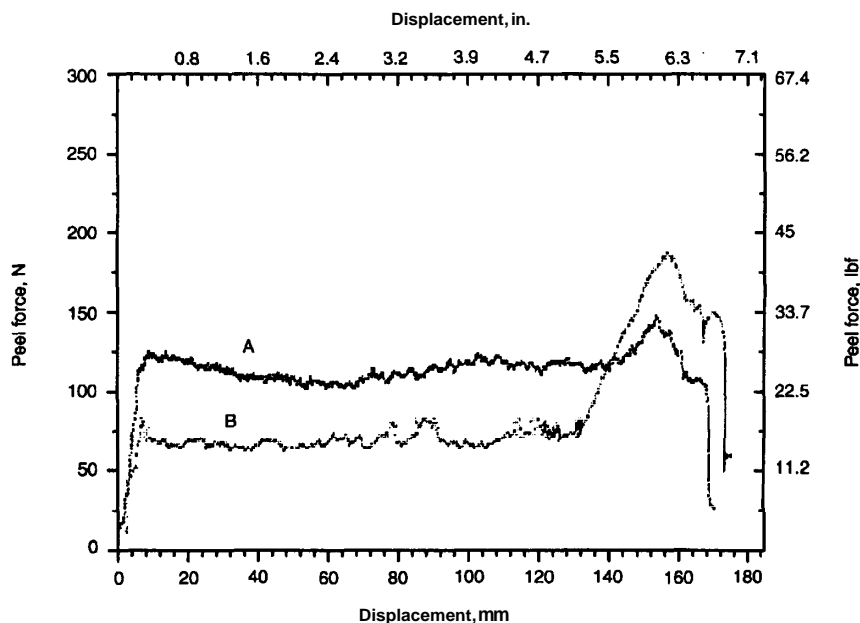


Fig. 5 Peel-force measurements for thermal spray coatings applied to as-received (curve A) and environmentally exposed (curve B) polymeric coatings. Courtesy of J. Brogan, SUNY at Stony Brook

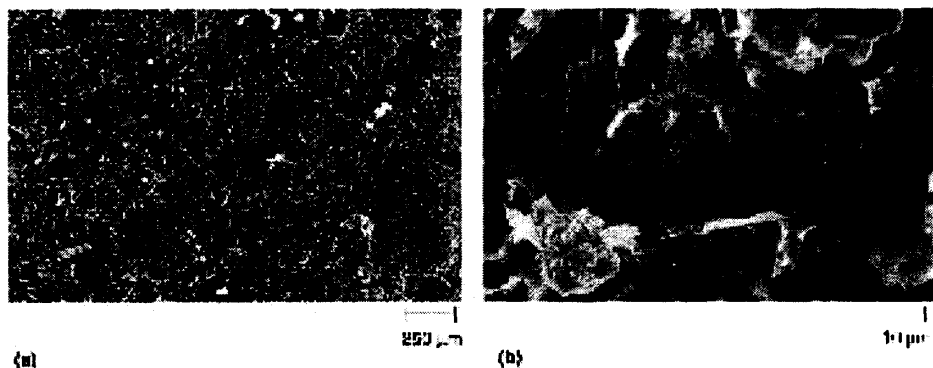


Fig. 6 Fracture surface morphology of a polymeric coatings that exhibits (a) porosity artifacts and (b) ductile tearing. Courtesy of J. Brogan, SUNY at Stony Brook

containing organic paints. Traditional grit blasting of hydraulic structures and highway bridges potentially involves the wide distribution of lead contaminant some distance from work sites and inflicting unacceptable health risks. The thermal spray vitrification process (TSVP) is an elegant technique that has been proposed to alleviate this problem. The TSVP is a "green technology" that seeks to provide an economic solution to the maintenance of existing structures, for example, bridges and other infrastructure. In this process, glass powder is melted in a high-temperature flame and sprayed onto the lead painted surface. On impact of the molten glass droplet, lead diffuses and dissolves from the paint into the glass and forms a stable glass network that is resistant to lead leaching by acid attack.

When a molten droplet of glass strikes a lead painted surface, the following phenomena occur. First, the droplet will spread, splatter, and deform to form an intimate contact layer between the glass and the painted surface. The molten glass will penetrate and fill the pores and cavities in the surface by capillary transport. Mass transport rates and extent of reaction will depend on the properties of the molten glass such as surface tension, kinematic viscosity, and heat-transfer coefficient and on the properties of the coated surface. Next, there is diffusion, dissolution, and natural and forced convection of lead into the molten glass. The kinetics of this reaction will be controlled by the diffusivity of lead in the paint. The temperature and vapor pressure of the lead as well as the pore structure of the glass are the deciding factors for this phenomenon. There may also be solid-state interdiffusion of cationic species at the interface between the glass and painted surface, and the reaction layer will grow into the glass and the substrate surface. The cation with the lowest diffusivity will be the rate-limiting species for this reaction. In summary, the lead can be absorbed into the glass by gas-phase transport, dissolution into liquid slag, and solid-state interdiffusion of cationic species.

Dissolution and diffusion of lead into the glass are determined by the time duration for which the glass particles remain molten and at high temperatures, respectively. In thermal spray processes, the coating material is melted in a flame and then quenched on impact onto a cold underlayer. The heating and cooling of the particles depend on the thermophysical properties of the particles in their liquid and solid states and their processing environments.

The composition of the glass basically decides its thermophysical properties. Selection of the glass composition for the lead-vitrification application should follow the following three criteria:

- Lead dissolution into the glass should follow the congruent path of the phase equilibrium diagram.
- The kinematic viscosity should be low.
- The glass should be stable in the desired range of lead concentrations.

Glass modifiers such as alkali oxides break the glass network and thereby reduce the melt vis-

cosity. However, breaking of the network also weakens the glass structure and affects the stability of the glass. Intermediate oxides such as alumina, titania, and lead oxide, for example, increase the stability of the glass, but since they increase the surface energy of the melt, the kinematic viscosity of the glass melt also increases with the addition of the intermediate oxides. Thus, the composition of the glass should be optimized so that it will have high lead absorptivity and lead-leaching resistivity.

The processing environment that decides the rate at which the heat and momentum transfer to and from the particle occur are controlled by a large number of spray-process parameters such as the operating power level, stand-off distance, powder feed rate, gas flow rates, carrier gas flow rate, and gun traverse. Considerable amount of information already exists on the effect of spray variables on the properties of the coatings.

## Specification and Quality Control for Coatings

**Specifications and Guidelines for TS Applicators.** Several professional and industrial organizations in the United States have developed guidelines with the intent of assisting those people who need to specify coatings for a particular application as well as helping practical TS operators accomplish a particular task. The listing below indicates the organization that generated the particular document as well as a very brief description of the content of the document. It should be noted that several of these documents are still "works in progress" that are still being refined.

- AWS C2.16-92, "Guide for Thermal Spray Operator Qualification." This guide recommends thermal spray operator qualification procedures. It covers applicable documents relating to thermal spray equipment, consumables, and safety. It also contains operator qualification and coating system analysis forms. Note: this standard is being revised; see **C2.16A** standard in preparation.
- AWS C2.18-93, "Guide for the Protection of Steel with Thermal Sprayed Coatings of Aluminum and Zinc and Their Alloys and Composites." This guide sets forth recommended thermal spray operator qualification procedures. It covers applicable documents relating to thermal spray equipment consumables and safety. It also contains operator qualification and coating analysis forms. Note: this standard is being revised; see **C2.18A** Part A and Part B standard in preparation.
- AWS **C2-18A**, NACE (designation to be determined), and SSPC CS **23.00A**, Part A, "Specification for the Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc, and Their Alloys and Composites for the Corrosion Protection of Steel," Draft **No.3**, 2001-05-22 (45 pages). This standard is a **procedure** for the **application** of metallic
- TS coatings of aluminum, zinc, and their alloys and composites for the corrosion protection of steel. Required equipment, application procedures, and in-process quality-control (QC) checkpoints are specified. This standard may be used as a procurement document. **Appendices** include a "model procurement specification." Note: this standard is the update that will be the permanent standard to replace the interim standard SSPC CS **23.00(I)** (1999–present).
- AWS **C2-18A**, NACE (designation to be determined), and SSPC CS **23.00A**, "Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc, and Their Alloys and Composites for the Corrosion Protection of Steel, Part B: Guide," Draft **No.2**, 2001-10-10 (47 pages). This guide presents additional information and recommendations on safety, selection of TS coatings, inspection guide and checkoff list, bend testing, thermal spray operator qualification, thermal spray equipment qualification, and the maintenance and repair of TS coatings (1993–present).
- AWS C2.19-XX, "Machine Element Repair with Thermal Spray Coatings," CD **No.3**, 5 May 2000 (52 pages). This standard covers thermal spray processes for machinery element repair of ferrous and nonferrous substrates. Included are requirements for the qualification of thermal spray procedures and operators, requirements and guidance for use of thermal spray material and equipment, quality assurance requirements, and descriptions of applicable qualification tests. Note: the Navy (Charles Null, NAVSEA Code **05M2**) requested AWS incorporate **MIL-STD-1687A(SH)** into an AWS standard, April 1998 (1998–present).
- AWS C2.20-XX, "Specification for Thermal Spraying Zinc Anodes on Steel Reinforced Concrete," CD **No.3**, 16 Jan 2001 (25 pages). This AWS standard is a specification for thermal spraying zinc anodes on steel reinforced concrete. The scope includes: job description, safety, **pass/fail** job reference standards, feedstock materials, equipment, a step-by-step process instruction for surface preparation, thermal spraying, and quality control. There are three annexes: job control record, operator qualification, and portable adhesion testing (1995–present).
- AWS C2.21-XX, "Specification for Thermal Spray Equipment Acceptance Inspection," WD-4, 15 May 1998 (19 pages). This standard specifies the thermal spray equipment acceptance requirements for plasma, arc wire, flame powder, wire, rod, and cord, and HVOF equipment. The equipment supplier shall provide proof of suitability. Example inspection reports are provided in four nonmandatory appendices.
- AWS C2.25-XX, "Specification for Solid and Composite Wires, and Ceramic Rods for Thermal Spraying," DS 1; 7-11-2001 (25 pages). This specification defines the **as-manufactured**, chemical-composition **classifica-**

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tion requirements for solid and composite wires and ceramic rods for thermal spraying. Requirements for standard sizes, marking, manufacturing, and packaging are included. 100 materials are listed (1985–present).

- SSPC-QP 6, "Standard Procedure for Evaluating Qualifications of Thermal Spray (Metallizing) Applicators," Draft No.2, 2001-21 (23 pages). This standard describes a method for evaluating the qualification of thermal spray (metallizing) applicators to apply thermal spray coatings per SSPC CS 23.00(I), "Interim Specification for the Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc and Their Alloys and Composites for the Corrosion Protection of Steel," (latest edition), that is, the surface preparation, thermal spraying, and sealing or sealing and topcoating of **components/assemblies** in the shop and complex structures in the field. These procedures are applicable to a fabricating shop, shipyard, or other entity that applies coatings in the shop, even though providing coating application services is not the primary function (2001–present).
- SSPC CS 23.00(I), "Interim Specification for the Application of Thermal Spray Coatings (Metallizing) of Aluminum, Zinc and Their Alloys and Composites for the Corrosion Protection of Steel," 1 March 2000. This interim specification covers the requirements of thermal spray metallic coatings, with and without, sealers and topcoats, as a means to prevent the corrosion of steel surfaces. Types of metallic coatings include pure zinc, pure aluminum, and **zinc/aluminum** alloy, 85% Zn/15% Al by weight. Note: this standard is being incorporated into AWS C2.18A/NACE (designation to be determined) SSPC CS 23.00A Part A, standard in preparation.

The AWS C2.18 documentation recommends guidelines for the TS of zinc and aluminum wires and powders (Table 8). The prime **quality-control** checkpoints are stated as measurement of substrate temperature; measurement of air temperature, dew point, and humidity; appropriate measurement of the TS coating thickness; measurement of the TS coating ductility; and evaluation of representative bend coupons, companion coupons, and other samples.

**Standards for Coatings.** A great challenge for TS coatings is their specification and standardization since, as described previously, the character of a TS coating is controlled greatly by their manufacturing method. Much of the history of TS coatings has relied on internal company specifications so that reproducible coatings might be produced, and the out growth of such documentation now constitutes accepted practice. With regard to testing practices, the standard methods developed by ASTM (or equivalent organizations) are a good basis on which to recommend procedures that rank coatings or different materials. Table 9 lists those ASTM standards that are most appropriate to TS coatings, but it should be kept in mind that these often

provide only quality, ranking data rather than quantitative, life-prediction, and performance data.

**Adhesion of Coatings.** Adhesion is a property of major concern for thermal sprayed coatings since it is necessary for the coating to adhere to the substrate throughout the design life of the system. Numerous adhesion tests can be used to evaluate the adhesion strength of TS coatings and thereby ascertain the utility of coatings. For example, bond-strength measurements allow optimization of different grit blast media and the angle of grit blasting, as well as establishing the best coating thickness for **aluminum coatings** (Ref 63). Other workers (Ref 64, 65) have **optimized** plasma spraying parameters with respect to strength. In recent years, with the adoption of design of experiment methods, bond strength measurements along with other physical measurements, such as roughness and porosity, have been used to select coatings for industrial specifications.

**Adhesion** is a property of major consideration when thermal spraying coatings since it is necessary for the coating to adhere to the substrate throughout the design life of the system. Numerous adhesion tests can be used to evaluate the adhesion strength of TS coatings. The most

common test is the tensile adhesion test (TAT), which, being simple to perform, is a widely used method as a quality-control tool (Ref 66). **ES**

The TAT has been standardized, and there are four main standards: ASTM C 633-79 (United States), AFNOR NF A91-202-79 (France), DIN 50 160-A (Germany), and JIS H8666-80 (Japan). The test configurations of these standards are essentially the same; however, each standard specifies a different design and dimensions of substrate; that is, the diameter varies from 25.4 to 40 mm (1 to 1.57 in.) and the length is from 25.4 to 50 mm (1 to 1.97 in.).

The TAT arrangement involves attaching a support fixture to the coated specimen with an epoxy so that a tensile force may be applied. The stress at failure is called the **tensile adhesion strength** or **bond strength** and is an important property to characterize coatings. However, there are some shortcomings of the TAT procedure, such as variations in the penetration of epoxy and in the alignment of test fixtures. The mixed mode of failure may also occur, and this makes the interpretation of results difficult.

The adhesion strength or cohesion strength can be influenced by many factors. Some of them are intrinsic; that is, related to the spray variables, such as powder characteristics, spray pa-

**Table 8 AWS Guidelines for thermal spraying of zinc and aluminum**

Feedstock	Flame spray		Arc spray	
	Deposit efficiency, %	Material required, lb/ft <sup>2</sup> /0.001 in.	Deposit efficiency, %	Materials required, lb/ft <sup>2</sup> /0.001 in.
Aluminum wire	80-85	0.014	70-75	0.017
Aluminum powder	85-90	0.014	NA	NA
Zinc wire	65-70	0.050	60-65	0.054
Zinc powder	85-90	0.039	NA	NA
85/15 wire	85-90	0.036	70-75	0.049
90/10 MMC wire	80-85	0.014	70-75	0.017

(a) MMC, metal matrix composite

**Table 9 ASTM standards related to thermal spray**

ASTM designation	Title
<b>Corrosion</b>	
B 117-95	Practice for Operating Salt Spray (Fog) Testing Apparatus
G 3-89 (1994)	Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing
G 5-94	Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
G 15-97	Terminology Relating to Corrosion and Corrosion Testing
G 78-95	Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments
G 85-94	Practice for Modified Salt Spray (Fog) Testing
<b>Wear</b>	
G 40-96	Terminology Relating to Wear and Erosion
G 65-94	Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus
G 73-93	Practice for Liquid Impingement Erosion Testing
G 76-95	Test Method for Conducting Erosion Tests by Solid Particle Impingement Using Gas Jets
G 77-93	Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test
G 81-97	Practice for Jaw Crusher Gouging Abrasion Test
G 98-91 (1996)	Test Method for Galling Resistance of Materials
G 99-95	Test Method for Wear Testing with a Pin-on-Disk Apparatus
G 105-89	Test Method for Conducting Wet Sand/Rubber Wheel Abrasion Tests
G 115-93	Guide for Measuring and Reporting Friction Coefficients
G 119-93	Guide for Determining Synergism between Wear and Corrosion
G 132-96	Test Method for Pin Abrasion Testing
G 133-95	Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear
G 134-95	Test Method for Erosion of Solid Materials by a Cavitating Liquid Jet

rameters, substrate preparation, and so forth. The others are extrinsic, which include posttreatment and service conditions. However, adhesion tests are usually performed at room temperature under laboratory conditions on "witness samples" and do not consider in-service conditions that may decrease the adhesion strength. It is important for materials designers to keep in mind that the adhesion strength is highly related to service conditions. As well, the confidence-interval estimation for such coatings enables the reliability of the so-determined property to be ascertained.

The measurement of adhesion of thermal spray materials is, at least on the conceptual level, a routine operation. The tensile adhesion method as detailed in ASTM C 633 is simple and often used in industry for ranking different coatings. However, the major shortcoming of this test is that it does not promote any understanding of coating performance; that is, how coatings can be designed to be more functional.

## Summary

The coating should be considered as part of the overall component system and, therefore, current trends are to design the coating as an integral part of the component assembly rather than as an add-on to the substrate. Whereas the property of coating adhesion to the substrate is of principal interest, there is still no single measurement which can satisfy all the requirements for determining material properties. Standardization of measurements, which may be achieved by improving existing experimental techniques or the combination of two or more techniques, will aid future coating development. Finally, a coating design encompassing both **microstructural** and mechanical engineering designs, which is based on lifetime modeling should be forthcoming from any test method. Such designs will increase the knowledge-base and understanding of thermal sprayed materials and coatings so that their reliability and application will grow.

The use of thermal spray coatings makes it possible to achieve fully effective, **maintenance-free** protection of steel and concrete structures for more than 30 years in rural environments and more than 20 years in harsh industrial, urban, and coastal regions. On an overall cost basis, with the expense of maintenance factored in, thermal spray coatings have long been competitive with comparable corrosion protection systems. Studies over the last 2 decades indicate that this is now often true even on an initial cost basis alone.

## Further Literature Sources for Thermal Spray

The major forum for thermal sprayers and technologists to meet since 1956 has been at the International Thermal Spray Conferences. The first seven of these meetings up to 1973 were known as International Metal Spraying Confer-

ences. Since the **mid-1980s**, several other meetings have been convened: the National Thermal Spraying Conferences (organized by ASM International), the Plasma-Technik (Ref 67) meeting (a former Swiss company), and the Advanced Thermal Spraying and Allied Coatings Symposium (Ref 68) (organized by the High Temperature Society of Japan). The ITSC-2002 was convened in Essen, Germany, in March 2002 (Ref 69) and ITSC-2003 was held in Orlando, FL, in May 2003 and organized by the Thermal Spray Society of ASM International.

Other organizations such as the National Association of Corrosion Engineers (NACE International) and the American Welding Society (AWS) (Ref 70) have also convened focused conference sessions that specifically address TS under corrosive environments. The SSPC often documents TS coatings within their publication *The Journal of Protective Coatings and Linings*, JPCL.

- Online Resources. Thermal spray information is available at the following websites:  
ASM—The Materials Information Society (<http://h.asminternational.org/>)
- The DVS, Deutscher Verband für Schweißen, The German Welding Society (<http://www.dvs-ev.de/en/main.htm>)
- ASM Thermal Spray Society—An affiliate society of ASM International (<http://www.asminternational.org/tss/>)
- NACE—The Corrosion Society (<http://nace.org/nace/index.asp>)
- AWS—Gateway to the World of Welding (<http://www.aws.org/>)
- The SSPC—The Society for Protective Coatings (<http://www.spsc.org/>)

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