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THERMAL SPRAY COATINGS FOR MODERN TECHNOLOGICAL APPLICATIONS

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Abstract: A variety of mechanical and chemical cleaning and pre-treatment techniques are used prior to coating. The thermal spray techniques to deposit coatings consist of atomization and deposition of molten or semi-molten droplets of the coating material on substrates. Industrial thermal spray techniques differ from one another in the type of energy source used for melting the feed material and associated hardware. The feed material is melted by using energy from fuel combustion, electric arc, or plasma. Flame spray, plasma spray (atmospheric plasma and vacuum plasma), HVOF (high velocity oxy-fuel), and detonation gun are some of the most common thermal spray techniques for depositing a wide range of coatings.

1. INTRODUCTION

Thermal sprayed coatings have been produced for at least 40 years, but the last decade has seen a virtual revolution in the capability of the technology to produce truly high performance coatings of a great range of materials on many different substrates. This enhancement of the technology has been achieved largely through the introduction of new spray techniques, the enhancement of spray process controls, by employing state-of-the-art methods of feedstock materials production, and through the use of modern techniques of quality assurance [1].

Thermal sprayed coatings are used extensively for a wide range of industrial applications. Industrial thermal spray techniques differ from one another in the type of energy source used for melting the feed material and associated hardware. The feed material is melted by using energy from fuel combustion, electric arc, or plasma. Flame spray, plasma spray (atmospheric plasma and vacuum plasma), HVOF (high velocity oxy-fuel), and detonation gun are some of the most common thermal spray techniques for depositing a wide range of coatings [2]. Thermal spray processing is a well established means of forming coatings of thicknesses greater than about 50 micrometers: so-called thick coatings. A wide range of materials can be thermal sprayed for a variety of applications, ranging from gas turbine technology (heat engines) to the electronics industry.

Although the use of advanced thermal spray coating methods has largely occurred within the aircraft industry, newer, extended applications of the technique have demonstrated its versatility. Applications include protection from wear, high temperatures, chemical attack, and the more mundane uses of environmental corrosion protection in infrastructure maintenance engineering.

Of greatest importance, and making thermal spray processing uniquely important to an ever increasing engineering community, are:

- improved spray foot-print definition versus wide spray beam;
- high through-put versus competitive techniques;
- significantly improved process control;
- lower cost-per-mass of applied material, together with overall competitive economics. In the following will be given an overview of thermal spray coatings, as well as the fundamentals and application areas for the technology [3].

2. THERMAL SPRAY PROCESSES

Before a coating can be applied to a surface, the latter must be cleaned to remove physical and chemical impurities and structural defects such as surface micro-voids and cracks, sand, scale, flux residues, oil, grease, soil, and other chemical impurities. A variety of mechanical and chemical cleaning and pre-treatment techniques are used prior to coating. Abrasive cleaning is used to remove sand inclusions and oxide scale. Sand, steel grit, and steel shot are used as abrasives. Pressurized air and abrasive particles from a centrifugal pump impact the work piece at a high velocity [4].

Barrel finishing or tumbling is used to descale and derust parts. Tumbling is a low-cost, mass finishing operation, usually done in dry condition. Sand, granite chips, slag, and alumina pellets are used as abrasives. A barrel of mild steel plate lined with hard wood, or natural synthetic rubber, is filled with the abrasive and the parts to be cleaned. The lining material increases tumbler life, improves surface finish, and reduces metal contamination. Rotary motion the tumbler leads to "landsliding" action, which causes cutting, scrubbing, and polishing, and removes fins, scales, and sand particles. Only a small fraction of parts is finished at any time because most of the cleaning action is confined to a surface layer where agitation and landsliding most intense. Higher speeds lead to faster processing but also part damage by impingement.

The thermal spray techniques to deposit coatings consist of atomization and deposition of molten or semi-molten droplets of the coating material on substrates. The various thermal spray processes are distinguished on the basis of the feedstock characteristics (wire/powder) and the heat source employed for melting. In the following are described the various thermal spray processes in use today.

2.1. Vapor-Phase Deposition

Vapor-phase techniques deposit thin or thick films and coatings of a variety of materials from the vapor phase. Among the widely used vapor-phase deposition methods are vacuum-metallizing, sputtering, chemical vapor deposition, and ion-nitriding. In vacuum-metallizing, the coating material is evaporated from a source and condensed on work piece under vacuum (<0.001 torr). Thin metal coatings of Zn, Al, Cd, and other metals are readily deposited from the vapor phase on a variety of substrates. [5]. Figure 1 shows the basic approach of batch type vacuum-metallizing process.

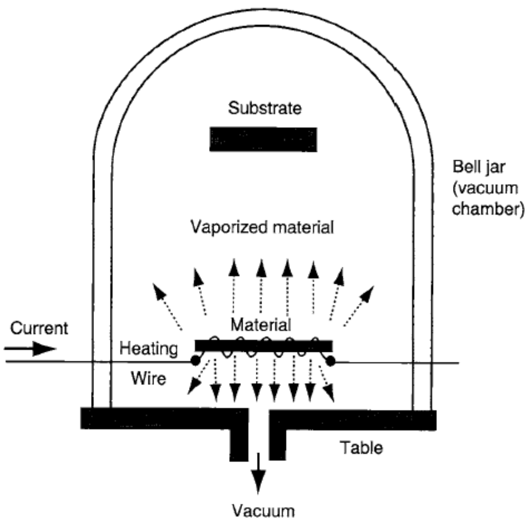

***Fig. 1 Vacuum metallizing of a substrate via evaporation and condensation of the coating material* [6].**

The equipment for vacuum-metallizing includes vacuum chamber, vapor source, vacuum pumps, control valves, etc. Usually, a tungsten filament is heated by passing an electric current, and chips or wires of coating material are fastened to the filament. Alternatively, a ceramic crucible containing the metal to be evaporated is heated either by induction power or an electron beam. Pre-cleaning of the substrate is necessary to form adherent coatings. Generally, parts to be metallized are first cleaned by ionic bombardment using the glow-discharge technique. Aluminum has a high vapor pressure and is easy to deposit, followed by Se, Cd, Ag, Cu, Au, Cr, Pd, Ti, Pt, and other metals.

A wide variety of coatings are deposited using vacuum-metallizing. These include decorative coatings of Al or Au on molded plastics, metal parts, and paper rolls; optical coatings of Al, Cu, Cr, and Pt over-coated with thin SiO and MgF films for optical systems such as mirrors, headlamps, microscope and telescope lenses, sunglasses, filters, and beam splitters; corrosion-resistant coatings of Cd and Al on steels to prevent hydrogen embrittlement, and electrical and electronic thin film components such as resistors (NiCr, PtAu, CrAl), capacitors (metal films on dielectric ribbons of plastic or glass), and magnetic memory devices (FeNi coatings on nonmagnetic plastic tapes for computer storage memory). Hundreds of diodes, triodes, transistors, resistors, and capacitors are deposited on small (~1 cm^2) Si wafers using this process.

3. THERMAL SPRAY COATING

The thermal spray techniques to deposit coatings consist of atomization and deposition of molten or semi-molten droplets of the coating material on substrates. Coating grows by rapid solidification of droplets that coarsen and sinter to cover the substrate. Multiple (up to a few hundred) passes may be needed to build up the desired deposit thickness. The feed material for thermal spray can be in the form of powder, wire, and rod. Industrial thermal spray techniques differ from one another in the type of energy source used for melting the feed material and associated hardware. The feed material is melted by using energy from fuel combustion, electric arc, or plasma. Flame spray, plasma spray (atmospheric plasma and vacuum plasma), HVOF (high velocity oxy-fuel), and detonation gun are some of the most common thermal spray techniques for depositing a wide range of coatings. The basic approach of *flame-spray technique* is illustrated in Figure 2.

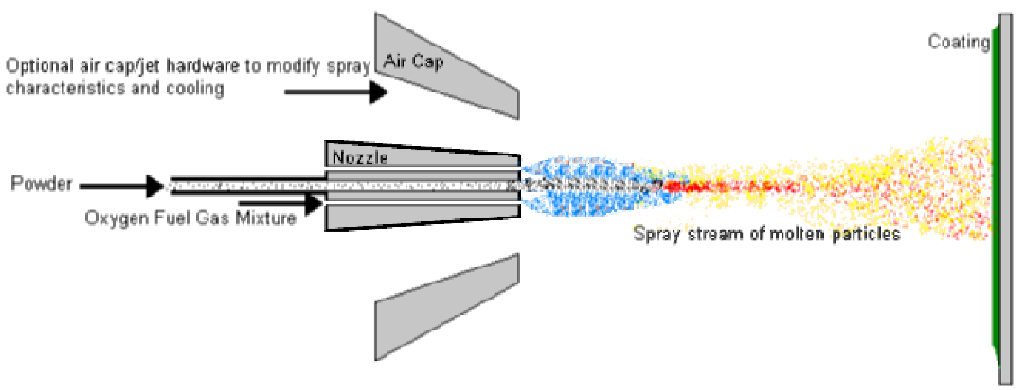

Fig.2 Schematic Diagram of Combustion Powder Thermal Spray Process **[7].**

Combustion flame spraying employs compressed air or oxygen, mixed with one of a variety of fuels (e.g., acetylene, propylene, propane, hydrogen), to both melt and to propel the molten particles. Generally (with an exception to be noted shortly), the process yields low performance coatings, and it is not employed where high density, well-bonded coatings are required. The reasons for these deficiencies have to do with the relatively low flame velocity of about 50 m/s and the low temperature achieved within the combustion flame, well below 3000^0C. Combustion flame spraying uses either powder, wire or rod as the feedstock material and has found widespread usage around the world for its relative simplicity and cost effectiveness.

High Velocity Oxy-Fuel Spraying (HVOF), a novel variation on combustion spraying, has had a dramatic influence on the field of thermal spray. This technique is based on special torch designs, in which a compressed flame undergoes free-expansion upon exiting the torch nozzle, thereby experiencing dramatic gas acceleration, to perhaps over Mach 4. A schematic of a typical HVOF torch is shown in Figure 3.

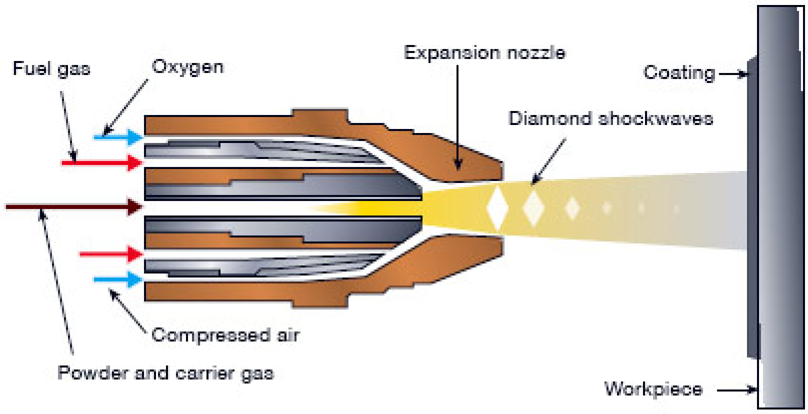

Fig. 3 Schematic cross-section of a typical High Velocity Oxy-Fuel spray gun (HVOF) **[8].**

By properly injecting the feedstock powder from the rear of the torch, and concentrically with the flame, the particles are also subjected to velocities so high that they will achieve supersonic values. Therefore, upon impact onto the substrate, the particles spread out very thinly, and bond well to the substrate and to all other splats in its vicinity, yielding a well adhered, dense coating, comparable, if not superior to plasma sprayed coatings.

It should be noted, however, that the powder particles are limited in the temperature they can achieve due to the relatively low temperature combustion flame. It is, therefore, not currently generally possible to process refractory ceramics using this technique. However, of particular importance is the fact that HVOF hard facings (e.g., WC/Co, Stellite) have hardnesses and wear resistances superior to such materials plasma sprayed in air.

Two-Wire Electric Arc spraying involves two current-carrying electrically conductive wires fed into a common arc point at which melting occurs Figure 4 [9]. The molten material is continuously atomized by compressed air, forming a spray of molten metal with a very high material throughput, as high as 40 kg/hr. This rate, which is the highest in standard industrial level thermal spray guns, yields highly cost effective processing, allowing the competitive spraying of corrosion resistant zinc and aluminum in the marine industry and for infrastructure applications. Modern developments have led to electric arc guns which can operate in inert atmospheres, using argon or nitrogen atomization and spraying reactive metals such as zirconium and titanium for corrosion protection in the chemical industry.

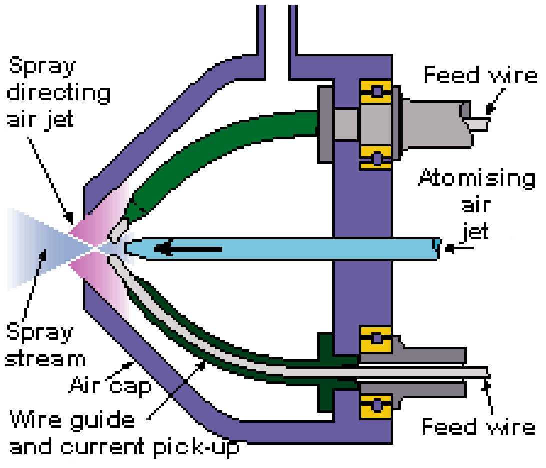

Fig. 4 Two-Wire Electric Arc spraying process **[9].**

These coatings can survive harsh service conditions, particularly in wear and many corrosion applications, which greatly increase component service life. The smooth, as-sprayed surface, uniform chemistry and low porosity of the coating can be finished to very smooth surface profiles.

Plasma spraying is relatively straight forward in concept but rather complex in function. The gun, as pictured schematically in Figure 5, operates on direct current, which sustains a stable non-transferred electric arc between a thoriated tungsten cathode and a annular water-cooled copper anode [10].

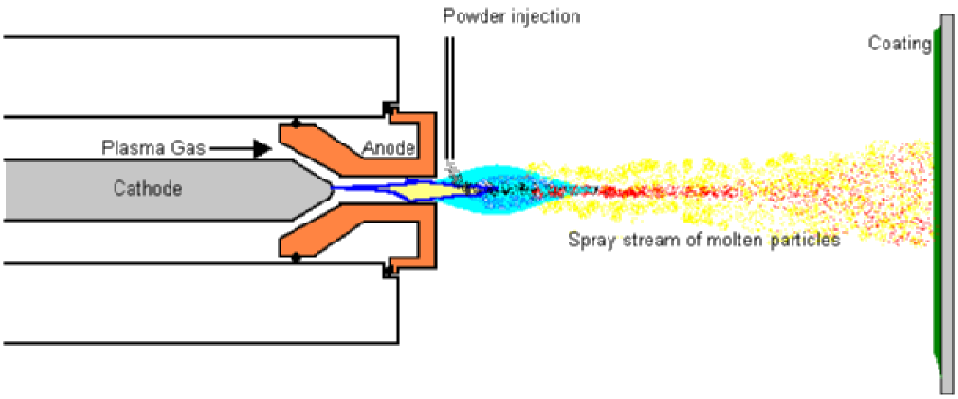

Fig. 5 Schematic of the plasma spray process.

A plasma gas (generally, argon or other inert gas, complemented by a few percent of an enthalpy enhancing gas, such as hydrogen) is introduced at the back of the gun interior, the gas swirling in a vortex and out of the front exit of the anode nozzle. The electric arc from the cathode to the anode completes the circuit, generally on the outer face of the latter, forming an exiting plasma flame which axially rotates due to the vortex momentum of the plasma gas. The temperature of the plasma just outside of the nozzle exit is effectively in excess of 15,000 K for a typical dc torch operating at 40 kW. The plasma temperature drops off rapidly from the exit of the anode, and therefore the powder to be processed is introduced at this hottest part of the flame. The powder particles, approximately 40 micrometers in diameter, are accelerated and melted in the flame on their high speed (100-300 M/sec) path to the substrate, where they impact and undergo rapid solidification (106 K/sec). Plasma spray is used to form deposits of greater than 50 micrometers of a wide range of industrial materials, including nickel and ferrous alloys, refractory ceramics, such as aluminum oxide and zirconia-based ceramics [11].

It is useful to list the key features of plasma spraying:

- Deposits metals, ceramics or any combinations of these materials
- Forms microstructures with fine, equiaxed grains and without columnar boundaries
- Produces deposits that do not change in composition with thickness (length of deposition time)
- Can change from depositing a metal to a continuously varying mixture of metals and ceramics (i.e., Functionally Graded Materials)
- High deposition rates (>4 kg/hr)
- Fabricate free-standing forms of virtually any material or any materials combinations

Vacuum Plasma Spray (VPS): The low pressure plasma spraying process was developed by Muehlberger in the early 1970^{s} and gained widespread commercial use in the mid-1980^{s}, to a large extent displacing EB-PVD (electron beam - physical vapor deposition) for the production of high quality metallic (CoNiCrAlY) coatings (figure 6). The compositional flexibility afforded by VPS and the high coating rates achieved though liquid droplet transfer versus the limitations of evaporation in EB-PVD caused a major shift to VPS during the 1980^{s}. As with all thermal spray processes, VPS is limited to line-of-sight. With the VPS process, individual parts are fixtured on a manipulator within a load-locked transfer chamber. The load-lock is pumped down and the parts are preheated to about 900-1000^{0}C before being transferred to the coating chamber. Prior to initiation of the plasma spray, the part is usually treated through reverse transferred arc sputtering to remove any traces of oxide that may have formed during preheat. The part is then plasma sprayed in a non-transferred mode.The coating distribution is determined by computer controlled gun and part motion [12].

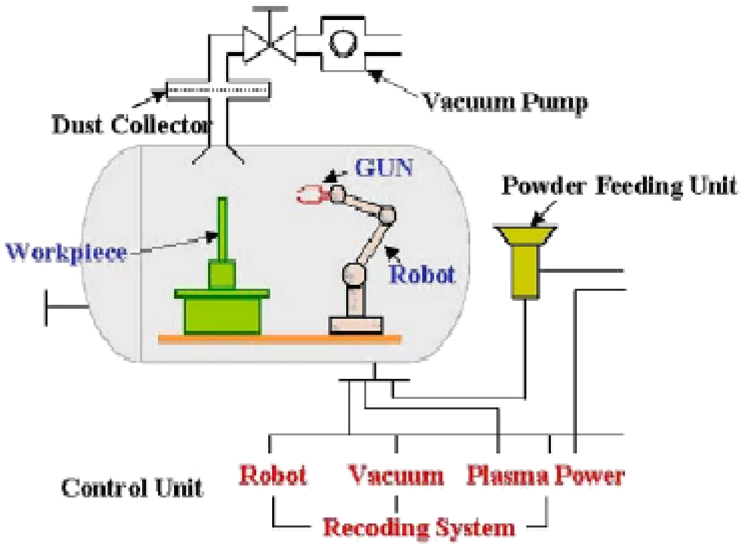

Fig. 6** **Vacuum plasma spray system for CoNiCrAlY coating **[12].**

Typical parameters for turbine blade coating would have a gun-to-substrate distance of ~ 4 - 7 cm at a chamber pressure of 30-60 torr and a gun power of 80 kW [12]. For example, considerable work has been carried out on the VPS processing of nickel aluminides and molybdenum disilicide, which have potential uses in the aerospace industry. It was demonstrated that the VPS process was capable of producing dense, free-standing forms which showed impressive mechanical properties. The deposits were ultra-fine grained and illustrated the capability of VPS in manufacturing of rapidly solidified intermetallics. Some studies have been published on the VPS processing of composites based on Ni3Al and MoSi2. High density deposits are obtained and some promising toughness increases are found. There is a clear important potential for VPS in the processing of intermetallics as both protective coatings and as free-standing forms.

Multiple vapor sources in the chamber allow successive coatings of different metals to be deposited on the same work piece. The work piece is initially at room temperature but heats up due to vapor condensation; however, the part should not vaporize, excessively outgas, or undergo structural changes. Vaporization is difficult for metals with low vapor pressure, in which case better vacuum and higher temperatures are needed for metallizing.

4. CONCLUSIONS

Coatings and surface engineering are used to protect manufactured components from thermal or corrosive degradation, impart wear resistance and hardness to the surface while retaining the toughness and ductility of the bulk component, and enhance the aesthetic and decorative appeal. The process of selecting coatings must consider the operating conditions, material compatibility issues, nature and surface preparation of substrate, time or speed of application, cost, safety, environmental effects, coating properties, and structural design. Generally, coatings used in complex high-technology areas are application specific and cannot be transferred to other applications. One challenge for the designer of the coatings is to create multilayer, multifunctional coatings in which the synergy of the properties of different layers determines the combination of functions that can be performed.

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