

Vékonyrétegek előállítása és alkalmazásai

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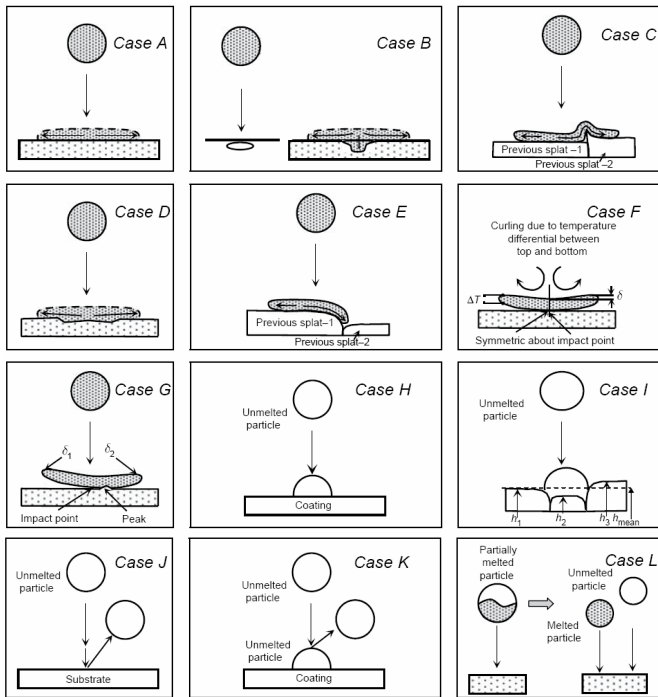
Thermal Spray deposition

Thermal Spraying, TS is a process in which molten, semi-molten or solid particles are deposited on a substrate. Powder is heated to near or above its melting point, accelerated and directed at the substrate to be coated. On impact, the process forms a coating consisting of many layers of overlapping thin lamellar particles or splats.

Coatings can be generated if the particles can plastically deform at impact with the substrate, which may only happen if they are molten or solid and sufficiently rapid. Almost any material that can be melted without decomposing can be used to form a coating. The substrate, for most applications, is not heated above 150°C, so its metallurgical properties remain unchanged. Typical coating thicknesses range from 50µm to 0.5mm, but in a few applications may exceed several mm.

The materials used in thermal spraying are principally powders, rods and wires. The wires are made of metals or alloys and are used mainly in flame-spraying (FS-wire) and arc-spraying processes (AS).

Particle landing



- A The splat is formed on the surface, following one of the equations given in Table 6.1. The shape of the underlying surface is maintained
- B The porosity under the splat below the uppermost layer, under the impact region, is 'hammered down' to the uppermost layer below it. The pore is destroyed and the splat follows the surface
- C The splat encounters a 'dead-end', fills the space available and then flows over the outer surface above (interlocking mechanism)
- D The splat 'covers' the roughness created by other splats
- E The splat comes to a 'vertical drop' and then falls straight down until the surface is 'found' again
- F The splat 'curls-up', provided that it is in the topmost layer
- G The underlying region contains a large peak, the splat is 'pinned' by the peak and curling occurs with respect to the peak
- H The unmelted particles form hemispheres on the coating
- I The hemisphere is assumed to lie on the 'mean-line' of the surface and the cavities below are filled
- J The unmelted particles do not adhere to the substrate surface. On impact, they bounce off
- K The unmelted particles do not adhere to other unmelted particles. If they "hit" one of them, they bounce off
- L A partially melted particle is divided in two parts: the molten part follows rules A to G while the unmelted part follows rules I, J and K

Types of spray techniques

Classification of spray techniques is based on the way such streams of particles are generated.

Thermal spraying methods

Energy input to gas	Variation	Spray technique
Electric discharge	DC arc	AS, APS, VPS
	Pulsing arc	Torches described by Vollrath <i>et al.</i> (1992) or by Whitterspoon <i>et al.</i> (2004)
	HF (RF) glow discharge ^a	RF plasma spraying (Mailhot <i>et al.</i> , 1998; Bouyer <i>et al.</i> , 2003) ^b
Combustion	Continuous	HVOF, FS
	Explosive	D-gun TM
Decompression of gas	—	CGSM

Plasma spray process

Detonation gun process

High velocity oxy-fuel (HVOF) Deposition

Arc spraying

In arc spraying two wires, being consumable arc electrodes, are drawn from spools and form a liquid droplet due to arc heating. The droplet is blown by the atomizing gas. The gas atomizes the molten droplet and propels fine particles towards a substrate. If the wires are made of different metals, a 'pseudo-alloy' coating can be produced.

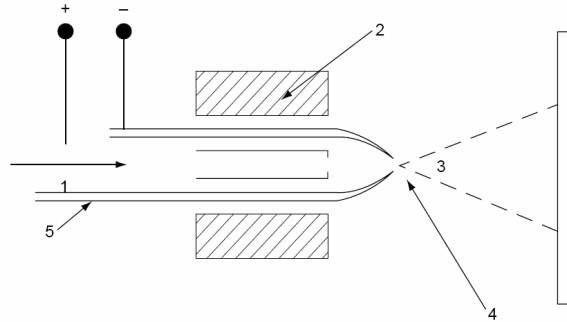


Figure 3.7 Schematic of an arc-spraying installation: (1) atomizing gas flow; (2) torch outer shield; (3) stream of molten particles; (4) electric arc; (5) consumable arc electrodes

Flame spraying

Flame spraying (FS) is chronologically the first spraying technique. It was developed by Schoop (a Swiss engineer) at the beginning of the last century (Schoop and Guenther, 1917). This process was used initially for low-melting point metals, such as tin or lead, and was later extended to more refractory metals and even ceramics.

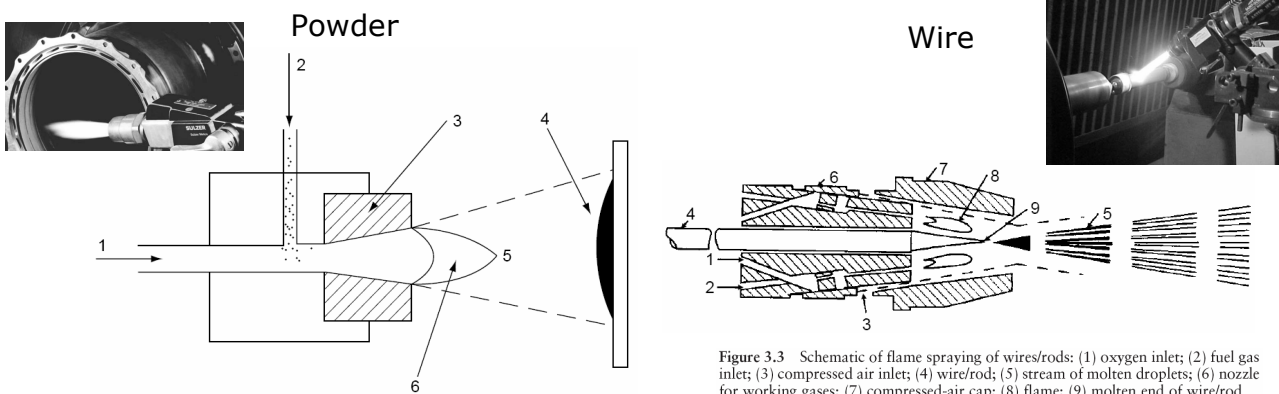


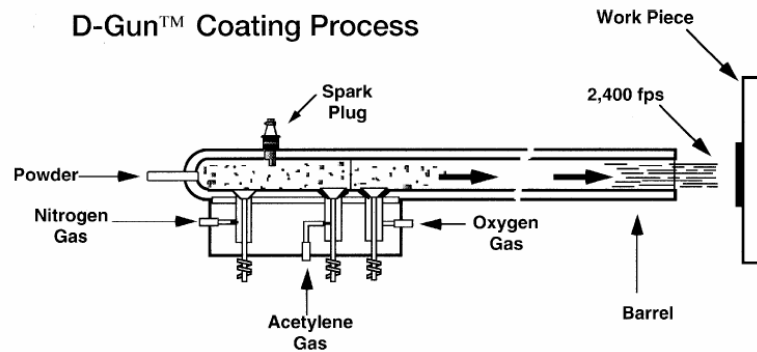
Figure 3.1 Schematic of flame spraying of a powder: (1) working gases (fuel and oxygen); (2) injection of powder; (3) torch body; (4) sprayed coating; (5) stream of particles; (6) combustion flame

Figure 3.3 Schematic of flame spraying of wires/rods: (1) oxygen inlet; (2) fuel gas inlet; (3) compressed air inlet; (4) wire/rod; (5) stream of molten droplets; (6) nozzle for working gases; (7) compressed-air cap; (8) flame; (9) molten end of wire/rod

In a flame spraying, the chemical energy of combustion of the fuel gas in oxygen is used to generate a hot flame. The gas inlet is axial and powder or wire can either be introduced axially or perpendicularly.

Detonation gun spraying

The D-gun™ includes a long, watercooled barrel with an ID of about 25mm. A mixture of oxygen and acetylene is fed into the barrel, together with a charge of powder. The gas is ignited, explodes and its detonation wave accelerates the powder. In order to avoid 'backfiring', i.e. explosion of the fuel gas supply, an inert gas, such as nitrogen, is used between the portions of exploding mixture. Nitrogen also purges the barrel. There are 1–15 detonations per second with purges of nitrogen between them.



Super D-Gun particle velocities (up to 900 m/s) are higher than traditional thermal spray processes. The coatings have a lamellar microstructure with a density very close to theoretical. Typical coating thicknesses range from 50 to 500µm, but both thicker and thinner coatings are possible.

Plasma spraying

The plasma generator consists of a circular anode, usually of copper, and a cathode of thoriated tungsten. The cathode is made of graphite in a water-stabilized torch. The electric arc discharge heats up the working gases, which expand in the atmosphere, forming a jet. The powder, suspended in a carrier gas, is injected into the jet. The particles of the powder after being melted and accelerated in the jet impact the substrate and form the coating.

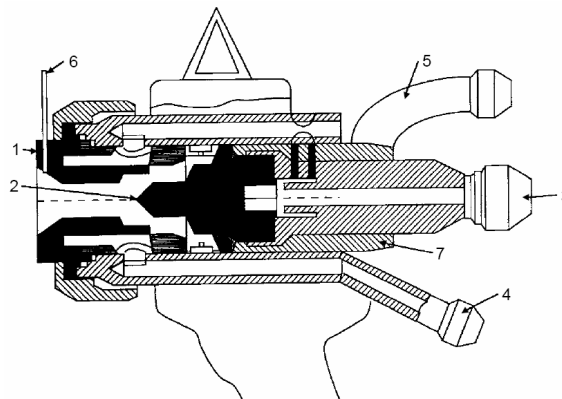
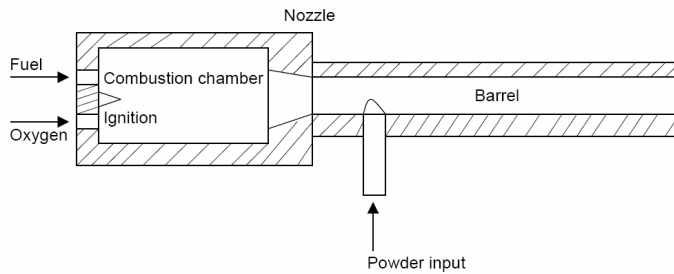


Figure 3.5 Schematic of a section of a plasma torch: (1) anode; (2) cathode; (3) water outlet and cathode connector; (4) water inlet and anode connector; (5) inlet for working gases; (6) powder injector; (7) electrical insulator

High velocity oxy-fuel spraying

The principles of this technique are similar to that of the D-gun,TM with the difference in the way of burning the fuel medium in oxygen. The burning is continuous for HVOF and repetitive for D-gun.

In the HVOF process, the fuel gas or liquid is introduced into the combustion chamber together with oxygen. An ignition initiates the combustion and the exhaust gas, formed by a nozzle, passes through a barrel and emerges into the open atmosphere. The powder is introduced radially or axially into the jet. The combustion chamber, nozzle and barrel are intensively cooled by water.



Presently, this technique has become a standard in the spraying of carbides and many applications in the aeronautical industry that have been previously realized using electrolytic chromium are now being replaced by carbides and alloys sprayed by the HVOF process.

Vacuum or Low-Pressure Plasma Spraying

Vacuum plasma spraying (VPS) sometimes called Low-Pressure Plasma Spraying (LPPS) is an alternative of atmospheric plasma spraying (PS or APS) performed in a reduced pressure environment. A vacuum plasma spraying installation is composed of a plasma torch with a nozzle supplied by the working gases and an electric arc generator. Powder is introduced by a port to a plasma jet working in a vacuum. An additional transferred arc is used to clean up and heat the surface prior to spraying.

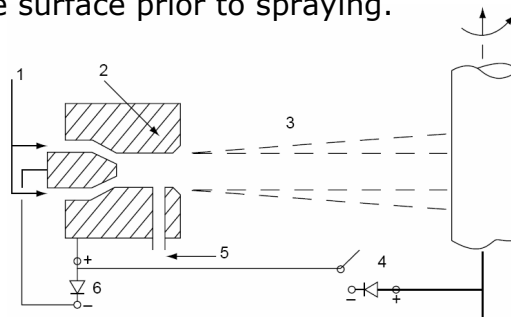
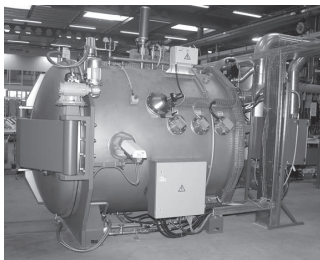


Figure 3.13 Schematic of the vacuum plasma spraying process: (1) working gases inlet; (2) anode; (3) vacuum environment; (4) transferred arc generator (if the substrate is negatively polarized, the arc cleans up the surface, while if the substrate is positively polarized, the arc heats the surface); (5) powder injection port; (6) plasma generator

VPS installations are used mainly to spray hot corrosion-resistant coatings onto gas turbines blades. LPPS-ed coatings with thicknesses lower than 50 μ m have become an alternative to gas-phase deposition methods, such as PVD and CVD.

Powder properties

As the properties of powders considerably influence the quality of the coatings, they should be characterized very carefully.

The physical characteristics include the following:

- grain-size (granulometry);
- internal and external morphology;
- apparent density and flowability (measuring the time necessary to 'flow out' a 50 g sample of powder from the calibrated orifice funnel $d = 254\mu\text{m}$);
- thermal properties (differential thermal analysis (DTA) and thermogravimetric analysis (TGA)).

The following chemical properties determine the quality of the coatings:

- chemical composition;
- phase content;
- element distribution.

Comparison

FS The bond strength can reach 60MPa for flame-sprayed NiAl alloys or even 70MPa for self-fluxing ones. Typical values are in the range of 15MPa for ceramics coatings to 30MPa for metals and alloys. Porosities are in the range of 10 to 20% (self-fluxing coatings are, after heat treatment, virtually 'pore-free') and typical thicknesses are in the range of 100 to 2500 μm .

PS The bond strength of plasma-sprayed ceramics on metallic substrates is in the range 15 to 25 MPa. Plasma-sprayed bonding alloys (NiAl or NiCrAl) or metals (Mo) may reach a strength of 70MPa or even higher. The porosity of APS coatings is usually in the range 1–7%, but might be intentionally greater. The thicknesses of these coatings are typically in the range 300 to 1500 μm .

AS The tensile bond strength is in the range 10 to 30MPa for Zn and Al coatings, but can reach a value of 70MPa for NiAl coatings or for NiCr+SiC composites sprayed by using Sonarc™. The porosity is in the range 10 to 20%. The thicknesses of the coatings are in the range 100 to 2000 μm .

D-gun The porosities of D-gun™ coatings are very small: the reported values are 0.5% for WC–Co coatings and about 2% for Al₂O₃ ones. The tensile bond strengths were 83 and 70 MPa, respectively. The thicknesses of the detonation gun-sprayed coatings do not exceed 300 μm .

HVOF The tensile bond strengths of HVOF-sprayed carbide composites might be as high as 90MPa – this value exceeds the maximum strength of most of the resins. The porosity of HVOF-sprayed coatings is lower than 1%. Typical thicknesses are in the range 100–300 μm .

VPS The tensile bond strength of alloys coatings, which are most frequently deposited by using the VPS technique, is greater than 80MPa. The porosities of the coatings are usually lower than 1 or 2% and a careful choice of the operational spray parameters enables the deposition of coatings without any pores. VPS deposits have typical thickness ranging from 150 to 500 μm .

Liquid phase film formation

The growth of inorganic thin films from liquid phases by chemical reactions is accomplished primarily by electrochemical processes.

These processes are either driven externally:

- Electrolytic anodization
- Electroplating

or internally, like

- Electroless plating
- Immersion plating
- Electrophoretic deposition
- Chemical reduction plating

In the external processes the electrons are supplied from outside the cell while the internal mechanisms generate themselves the charge carriers necessary for the chemical reaction.