

Characterization of surfaces and gases dynamics in HVOF thermal spray systems

Ion Aurel Perianu, Dan Ionescu

Natioanl R&D Institute for Welding and Material Testing - ISIM Timișoara, România

E-mail: aperianu@isim.ro

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1. Introduction

The thermal spraying process is one of the most successful processes because it has a high versatility due to the very wide range of materials that can be used as coatings and the substrates that can be processed belonging to many types of applications in different fields.

The high-velocity oxy-gas spraying (HVOF) is one of the most common thermal spraying technologies being used in many fields because of its flexibility and superior coating quality compared to other thermal spraying techniques.

High technology applications and the emergence of new powder-like materials have made major advances in this area. The need to select the substrate and the corresponding coating materials and the possibility of determining optimal spraying parameters together with substrate surface preparation methods are the main research directions of the HVOF spraying process.

2. Surface properties

Surface engineering involves designing, evaluating and operating the totality of a system, including the substrate from the interface to the coating layer [1]. It is a branch of science dealing with the methods of realizing the desired surfaces and evaluating the behaviour of the surfaces in operation, for mechanical components [2]. The behaviour of a material is largely dependent on its surface, shape of the contact surface, environment and operating conditions.

Surface properties for certain applications can also be selected after a subjective choice, for example after a particular colour or texture usable for decoration. However, the surfaces define not only the outer boundaries of the components but also the role of having a variety of functions, often quite different from the possibilities of the basic materials. Modern process environments that contribute to the wear of machinery / equipment / machinery in the industry can be very complex, usually involving a combination of chemical and physical degradation.

The surface properties of components used in a particular work environment must be designed in accordance with that working environment. Different surface properties that are relevant to the behaviour of different components are shown schematically in Figure 1.

Surface properties are presented, with an important role in the analysis of thermal spraying processes.

Physical adsorption refers to a process in which the electron structure of the atom or molecule is insignificantly disturbed when the adsorption phenomenon occurs.

The fundamental interactive force of physical adsorption is caused by the van der Waals force. Physical adsorption plays an important role in nature [3] even if the interaction energy is very poor (~ 10 - 100 meV).

Chemical adsorption is an adsorption reaction involving a chemical reaction between the surface of the material and the adsorbent, and thus new chemical bonds are generated on the surface of the adsorbent. Examples include macroscopic phenomena that can be very obvious, such as corrosion phenomena. Due to the specificity, the nature of the chemical adsorption can vary greatly depending on the chemical identity and the surface structure of the material. The strong interaction between the adsorbate and the surface of the substrate thus creates new types of electronic bonds [4].

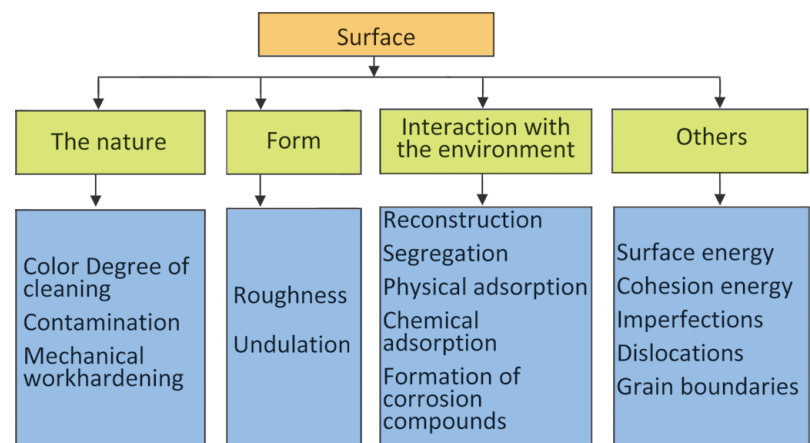


Figure 1. Different surface properties.

A comparison of physical and chemical adsorption reveals the following:

- physical adsorption is a general phenomenon that occurs in any solid / liquid or solid / gas system; chemical adsorption is characterized by chemical specificity;

- in the case of physical adsorption, the disturbances of the electronic states of the adsorbent and of the adsorbate are minimal; for chemical adsorption, changes in electronic states may be detectable by appropriate physical processes;

- the typical binding energy in the case of physical adsorption is approximately 10-100 meV; In the case of chemical adsorption, the binding energy is usually 1-10 eV;

- the elementary phase in the physical adsorption phase to a gas does not involve an activating energy; chemical adsorption usually involves activation energy.

Surface energy, or interface energy, quantifies the disruption of intermolecular bonds that occurs when a surface is created. In the physics of solids, the surfaces must be intrinsically less energetically beneficial than most of a material (surface molecules have more energy compared to molecules in most of the material) otherwise, in the opposite case a driving force would appear to generate surfaces that will remove most of the material. Therefore, surface energy can be defined as an excess of energy at the surface of a material as compared to the rest of the material.

Cohesion energy is the energy required to break all the links associated with a molecule constituted by a system. A link system typically has less potential energy than the sum of its component parts, which is the phenomenon that keeps the system together. This means that energy is released with the creation of a bonding layer. This definition corresponds to a positive link energy.

Connecting energy is the mechanical work to be done and is opposed to the forces that maintain an object compact and which is necessary for structuring the object in separate components at a sufficient distance where the separation is carried out with a negligible mechanical work. The surface properties of a component's material may change visibly due to the environment in which it operates. The outer surface of the base material consists of several areas with different physical and chemical characteristics for that material [5]. The structure of a metal surface is shown schematically in Figure 2.

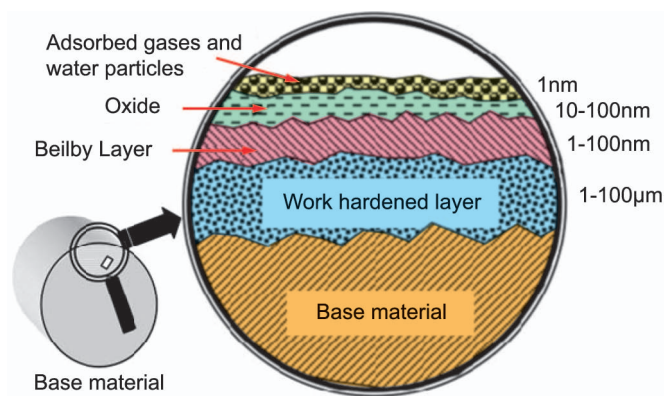


Figure 2. Schematic representation of a metal surface.

Above the mechanically work hardened layer there is a region of amorphous or microcrystalline material called the Beilby layer resulting from melting and creeping of the surface during work hardening. Above it there is an oxide layer, forming this layer depending on the environment and the surface oxidation mechanism. At the top end is a layer of adsorbate which is generally a layer of water or hydrocarbons from the environment that can become condensed and physically adhere to the surface.

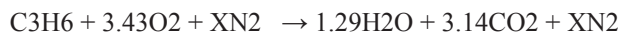
3. Combustion and gas dynamics in a HVOF system

The HVOF process is based on the use of a combination of thermal and kinetic energy for melting and accelerating the powder particles to deposit the desired coatings. Hydrocarbons

(propane, propylene, acetylene) or pure hydrogen are mainly used as combustible gases, and the temperature of the gas depends on the choice of fuel gas and the ratio of the oxygen and fuel gas flows. The powder particles of the desired coating material are fed axially in the hot gas jet being melted and propelled to the surface of the work piece to be coated. During operation, the spray system is cooled by air or water. Fuel and oxygen are mixed by coaxial jets and then guided into the firing zone where a pilot flame or external ignition initiates the combustion.

During combustion the gas expands into the nozzle in which it is accelerated. The powder is accelerated by the carrier gas and injected into the flame. The powder has the same flow direction as the direction of the dilatant gas inside the nozzle. Upon entering the combustion zone in the nozzle the powder particles are heated and are further accelerated. Due to the high velocity and the high impact of the powdered powder, the coating produced has a reduced porosity and has an anchoring strength higher than that produced by other methods [6], [7], [8].

Oxygen and fuel gas are at certain pressures, usually recommended by the equipment manufacturer, are mixed in the gun mixing zone and then directed to the combustion zone. After ignition there is a chemical reaction that releases thermal energy from the combustion process. As the firing continues, the pressure inside the combustion chamber increases and the hot gas flows at high speed. Propylene, propane or acetylene and oxygen are the gases used for combustion. When spraying using propylene and oxygen with nitrogen as a powder carrier gas, according to Kovalsky et al. [9], the simple gas chemical reaction to stoichiometry (theoretically necessary for complete combustion) in terms of mass is as follows:



The stoichiometric ratio between fuel and oxygen is 4.5 to 1. The energy released by the chemical reaction of the combustion gases is used for heating and accelerating both the exhaust gases and the powder used for spraying. The resulting gas velocity is a function of variables such as gas composition, pressure, temperature, density and area through which the gas circulates. However, the maximum velocity that can be obtained by the gas over the minimum cross-sectional area is proportional to the local sound velocity.

The local speed of a perfect gas is defined by the formula:

$$C = \sqrt{KRT} \tag{1}$$

Where,

C = sound speed

K = the specific ratio of heat emitted by the oxygen-fuel mixture

R = gas constant

T = local temperature

The Mach number is defined as the ratio of local gas velocity (V) and local sonic speed:

$$M = \frac{V}{C} \tag{2}$$

Basic flow patterns are defined by Mach numbers as:

- Subsonic $M < 1$
- Sonic mode $M = 1$
- Supersonic mode $M > 1$
- Hypersonic Mode $M > 5$

The condition in which the gas velocity is equal to the sonic speed, where $M = 1$ is called the “critical state”. The critical condition is associated with the critical condition of the gas condition, the critical mass flow rate and the critical area. When the local gas velocity is equal to the sonic velocity through the nozzle, a maximum rate of mass flow can be evolved, m . The critical mass flow rate can be defined as:

$$m = \rho VA \tag{3}$$

Where,
 ρ = critical density
 V = critical gas speed
 A = critical area

This equation can be written from the point of view of the total pressure and temperature, as:

$$m = \left[\frac{K}{R} \left(\frac{2}{K+1} \right)^{\frac{K+1}{K-1}} \right]^{\frac{1}{2}} \cdot \frac{P_0 A}{T_0^{\frac{1}{2}}} \tag{4}$$

Where,
 P_0 = the total pressure at the critical state
 T_0 = total temperature at critical condition
 At the critical situation, the flow is considered to be over-saturated. From the above equation we can see that by increasing

then turbulently mixed and accelerated at high speed and heated in the hot gas environment. The powder and gas mixture comes out of the spray gun as a high-velocity jet. Since the particles are injected at supersonic speed, each particle will pass through shock waves.

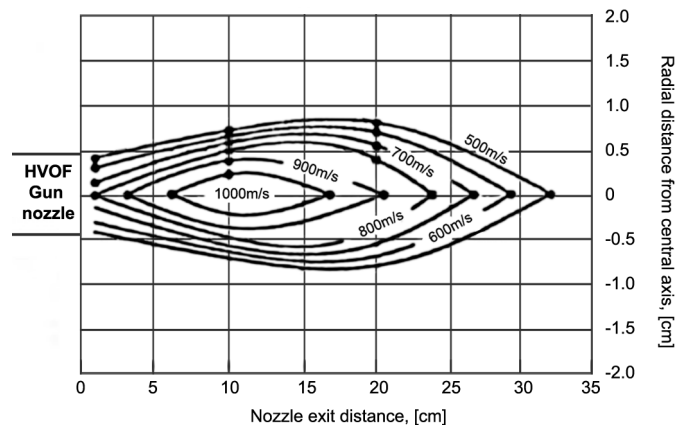


Figure 4. The particle velocity distribution schematically represented.

From the measurements made on the velocity of the powder particles of different sizes and different materials (Figure 4) it results that the velocities with the highest values are found in the central axis and they decrease radially outwards. This decrease is determined by the interaction of the forces acting between the flame jet and the ambient air.

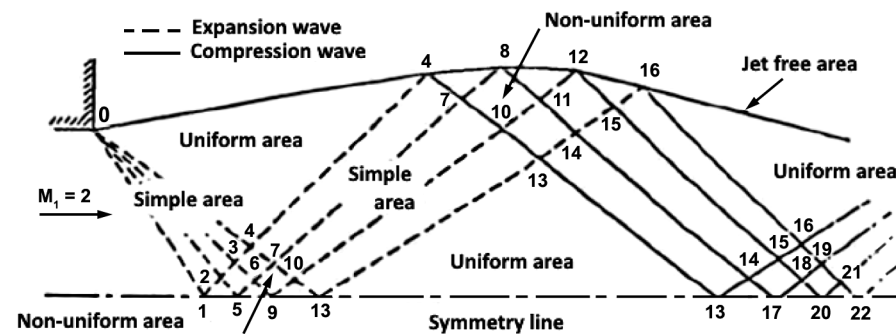


Figure 3. Shockwave formation for a sub-expanded jet.

the gas pressure the critical mass of the flow increases, while the increase of the critical temperature decreases the mass flow. Figure 3 shows the variation of the gas flow velocity according to the pressure of the combustion chamber [10]. The combustion chamber enclosure is usually maintained at a certain pressure that varies according to the HVOF.

Beyond the combustion point, the combustion gases are expanded into a convergent / divergent nozzle to achieve supersonic velocity. The adiabatic flame temperature of the combustion gases is about 2,900 °C (if the gas used is propylene). The jet and flame temperature also varies with the oxygen / fuel ratio as seen from the schematic in Figure 4 [10]. In the HVOF device, the heat obtained both from gas combustion and from friction along the inner nozzle surface tends to obstruct the flow at the outlet of the nozzle. At the exit of the combustion product nozzle the jet expands because the static pressure in the nozzle is higher than the ambient pressure, thus exposing and compressing the free jet. The intersection of these waves forms the light regions in the flame jet stream, known as shock waves [11].

During combustion, the spray particles are injected into the centre of the combustion chamber by means of a carrier gas,

The choice of gaseous fuel is mainly governed by economics, by the coating material itself and by the resulting coating properties. Propane is the gas mainly used as fuel gas. The classes of materials that are commonly used using the HVOF method, including the recommended combustion gases as well as the hardness of the coatings are presented in Table 1 [12].

Table 1. Materials and gases usable for HVOF spraying

Material type	Spraying material	Combustible gas	Hardness HV 0.3
Metal	Cu	Propane	150 – 250
	Al	Propane	>120
	Mo	Propane, acetylene	600-900
Metallic alloy	Steel	Propane, hydrogen	160-500
	Ni alloy	Propane, hydrogen	400-750
	Co alloy	Propane, hydrogen	400-750
Hard alloy	Ni alloy	Propane, hydrogen	250-800
	Co alloy	Propane, hydrogen	400-700
Hard metals	WC 12 Co	Propane	1200-1700
	WC 10 Co 4 Cr	Propane	1000-1100
	WC 13Ni	Propane	1000
	Cr ₃ C ₂ 25NiCr	Propane	900
Ceramic oxides	Cr ₂ O ₃	Acetylene	1200-1700
	Al ₂ O ₃	Acetylene	1200-1400
	Al ₂ O ₃ 40TiO ₂	Acetylene	950

Conclusions

HVOF thermal spraying, compared to any other coating process, has almost no limitation on the number of options available for the substrate as well as the materials and combinations of powdered coating materials used. As a result, HVOF thermal spraying is suitable for a wide range of applications, both for new components and for repairs.

The coating characteristics can be varied over a wide range to suit the application-specific requirements. This requires, however, many years of experience and know-how of specialists in the field.

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 tagungen@dvs-hg.de
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Fachliche Information
 Jens Jerzembeck
 T +49 211 1591-173
 jens.jerzembeck@dvs-hg.de