METALLIC COATINGS DEPOSITED BY COLD GAS SPRAY ONTO LIGHT ALLOYS

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A mi familia

'Por mucho que recorramos el mundo detrás de la belleza, nunca la encontraremos si no la llevamos con nosotros'

Louis Audobert

La verdadera ciencia enseña, por encima de todo, a dudar y ser ignorante"

Miguel de Unamuno

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CHAPTER 0.OBJECTIVES

This thesis focuses on the use of Cold Gas Spray technology (CGS) to spray different nature powders onto light alloys with the aim of increasing their wear resistance. The growing industrial interest for costs reduction (fuel consumption, machinery lifetime, or personal security) has emphasized the necessity to investigate the potential applications that light alloys can offer.

Weight reduction is a reason why light metals and its alloys have been associated with strong industries as transport or aerospace.

Nevertheless, weight saving aspect should not opaque the fact that light metals possess other "relevant technological" properties like the high corrosion resistance and high electrical and thermal conductivity of aluminium, the machinability of magnesium and the extreme corrosion resistance of titanium.

It must be taken into account that despite these technological importance properties, due to their density, among some other physical properties, aluminium and magnesium have a low hardness and low wear resistance, which provokes the need of improving its surface properties.

The main objective has been the obtention and optimization of Ti6Al4V and 316L stainless steel coatings onto light alloys, by means of Cold Gas Spray technology, a thermal spray technique which provides a dense and with no oxidation traces coatings, keeping the original microstructure of the spraying powders.

Ti6Al4V and SS316L coatings have been produced onto Al-7075-T6 and AZ31 substrates and Ti6Al4V coatings have been also produced onto Ti6Al4V substrate. Actually industrial machinery made of titanium alloy Ti6Al4V, that due to use has been damaged, needs repair and it will be easily repairable through this technique leading to a reduction in costs and repair times.

Schedule

Thesis document has been divided according to the different coatings production with their corresponding results on characterization and properties evaluation. Some of these results have already been published in different journals. These have been referenced and enclosed in the corresponding part of the study along with related results and discussion.

Following the introduction, presented in chapter 1, the experimental procedure used for the evaluation and analysis of powder and coating properties is described in chapter 2. Chapter 3 includes the entire raw materials characterization; the obtention. Characterization and optimization of the coatings onto the different substrates is developed in chapter 4 and 5. A discussion based on the comparison among the different systems, specifically in view of results as wear properties, porosity, adherence, and hardness is given in chapter 6. Finally, chapter 7 includes the conclusions of the present study.

CHAPTER 1.INTRODUCTION

CHAPTER 1

1. GENERAL CONSIDERATIONS

In surface engineering, one of the most important branches to protect the structures against any kind of external damage is the coating production technologies.



Figure 1 : Surface engineering processes scheme

From those, thermal spray processes are one of the most cost-effective and high quality technologies.

Conventional thermal spraying technologies are production processes in which molten or semi-molten particles are deposited on a substrate ^[1].

Powder particles or wires injected into flames or plasma jets are subjected to rapid acceleration and intense heating before being in contact with the substrate surface. Properties and microstructure of the sprayed coatings depend of the occurring phenomena during particle flight.

These techniques require pre-spray treatments as well as after-spray treatment. Prespray treatments consist mainly of surface cleaning as well as activation of the substrate surface to allow the adhesion of the particles to the surface.

Post-spray treatments are the key to the optimization and finishing of the coating. The main existing post-treatments are:

• Heat treatment.

- Electromagnetic treatment which involves microwave sintering and laser treatments.
- Hot isostatic pressing (HIP).
- Combustion Flame re-melting.
- Impregnation treatment to close the porosity of the sprayed coatings.
- Finishing.

But like any other technique, thermal spray technologies have limitations. The main ones are:

- Oxidation of metallic feedstocks.
- Chemical modification at flight of sprayed particles, like decarburization, oxidation or reduction.
- Particles in liquid state can evaporate and reduce their size.
- Increase of tensile stresses.
- Substrate microstructure modification due to heat and impact.

These existing limitations in thermal spray processes has prompted the development of spraying techniques where low costs and high deposition efficiencies, are essential when a coating technique is chosen, in industries increasingly specialized and demanding development

Material costs reduction, decrease in surface treatments (pre-and post-spaying), possibility of increasing the life cycle of the equipment, reduction of problems associated with material melting (oxidation, corrosion, tensile stresses, microstructure change), have made of cold gas spray (CGS) an efficient, clean and cost competitive technique.

The main objective of CGS technology, as well as thermal spray techniques, is the coating obtention to improve material's surface, for the desirable application. Deposition efficiency, adhesion, the final structure of the sprayed material depends upon many factors that, at the same time, depend on the spraying material and the substrate.

CHAPTER 1

INTRODUCTION

1.1. Coating obtention technologies

As it has been seen in figure 1, there are several coating obtention techniques. These techniques are divided in:

- Vapour processes.
- Electrochemical processes.
- Melting processes.

Each one of those, subdivided into multiple methods.

1.2. Thermal spray processes (TS)

TS are a group of processes that use thermal energy generated by chemical or electrical methods to melt or soften an intake material and accelerate fine dispersions of particles or droplets to speeds in the range of 50 to 1000 m/s. The high temperature and achieved speed by the particles, results in a high deformation when impact on the surface producing the often called *splats* which adhere to the substrate surface. A continuous stream of molten or semi-molten particles impact onto the substrate surface, solidifying and producing layers. After impact, particles cool down at very high rates to form an uniform, very fine-grained, polycrystalline coatings or deposits^[2].



Figure 2: Thermal spray coating obtention

The major advantage of these processes is the wide variety of materials that can be used to produce coatings. Other advantages are the ability to produce coatings onto substrates with a very low heat input or the capability of recoat damaged coatings without changing properties or dimensions.

Figure 3 shows the three major categories of thermal spray processes. Each category has subsets that have their own characteristic: range of temperature, velocity and enthalpy. Each process develops certain specific properties in the coatings such as bond strength, porosity, oxides and hardness.



Figure 3: Thermal spray processes

Table 1 shows a comparative between the main TS processes in terms of jet, feedstock material and coating attributes

Attribute	Flame spray	High-velocity oxyfuel	Detonation gun	Wire arc	Air plasma	Vacuum plasma	Radiofrequency plasma
Jet							
Jet temperature, K Jet velocities, m/s (ft/s)	3500 50–100 (160–300)	5500 500–1200 (1600–4000)	5500 >1000 (>3300)	>25,000 50–100 (160–300)	15,000 300–1000 (1000–3300)	12,000 200–600 (700–2000)	10,000 20–80 (70–300)
Gas flow, sLm Gas types Power input, kW equiv.	100–200 O ₂ , acetylene 20	400–1100 CH ₄ , C ₃ H ₆ , H ₂ , O ₂ 150–300	N/A O ₂ , acetylene N/A	500–3000 Air, N ₂ , Ar 2–5	100–200 Ar, He, H ₂ , N ₂ 40–200	150–250 Ar, He, H ₂ 40–120	75–150 Ar, He, H ₂ 40–200 (plate)
Particle feed							
Particle temperature (max), °C (°F)	2500 (4500)	3300 (6000)	N/A	>3800 (>6900)	>3800 (>6900)	>3800 (>6900)	>3800 (>6900)
Particle velocities, m/s (ft/s)	50-100 (160-300)	200-1000 (700-3300)	N/A	50-100 (160-300)	200-800 (700-2600)	200–600 (700–2000)	20-50 (70-160)
Material feed rate, g/min	30–50	15-50	N/A	150-2000	50-150	25-150	20–50
Deposit/coating							
Density range (%)	85-90	>95	>95	80-95	90-95	90-99	95-99
Bond strength, MPa (ksi:)	7-18 (1-3)	68 (10)	82 (12)	10-40 (1.5-6)	<68 (<10)	>68 (>10)	>68 (>10)
Oxides	High	Moderate to dispersed	Small	Moderate to high	Moderate to coarse	None	None

Table 1: Thermal Spray Processes comparative

In general, only those materials which are stable at elevated temperatures are suitable for thermal spray processes, these include most metals and its alloys, ceramics, cermets and some polymers.

The most common applications of thermal spray coatings are:

- Wear protection coatings.
- Thermal insulation.
- Corrosion resistance.
- Abradables and abrasives.
- Electrically conductive coatings.
- Electrically resistive/insulating coatings.
- Dimensional restoration coatings.
- Medical coatings.
- Polymer coatings.

One of the biggest engaging of CGS is the possibility of obtaining coatings with unique properties, which are not achievable through conventional thermal spray techniques. This is due to the fact that the deposition of material onto the substrates to form the coating takes place in the solid state. Material is not exposed to high temperature so it does not reach its melting temperature. As a result, undesirable decomposition or oxidation reactions are virtually eliminated ^[3-4]. Moreover CGS is not limited to industries with large budgets like military or aviation, but because of its affordability and wide range of materials that can be used, has allowed its application in industries such as transportation or service.

Material's costs reduction (raw materials, gas), surface treatments decrease (pre-and post-spraying), the possibility of increasing the service life time, reducing the problems associated with the spraying material melting (oxidation, corrosion, residual tensile stresses), maintaining the starting microstructures, have made of CGS an efficient, more ecological and economically affordable technique than the conventional ones^[5,6].

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2. COLD GAS SPRAY PROCESS (CGS)

Cold gas spray (CGS) is a solid-state spraying technique that produces coatings by exposing a powder, with a certain size distribution, to a high-pressure gas stream (nitrogen or helium). These particles acquire high kinetic energy, thus allowing them to reach speeds between 300 and 1200 m/s, depending on several parameters, namely pressure and temperature of the streaming gas, powder composition, particle size and morphology, and the geometry of the nozzle.



Figure 4: Cold Gas Spray system

There is a basic difference between conventional thermal spray techniques and cold gas spray. While the first technologies require high thermal and kinetic energy to form the coating, in the case of CGS, kinetic energy acquires a major role in the process.

A comparison of particle velocity vs. temperature for the different spraying techniques is shown on Figure 5. It can be seen than CGS leads to higher particle velocities obtained at lower temperatures

The mechanism on how the particles adhere is still not clear, although is based on high kinetic energy, localized plastic deformation of impinging particles and substrate (depending on its properties), and adiabatic shear instabilities^[7]. The study and control of the parameters involved in CGS, namely pressure, temperature, particle speed, standoff distance, powder morphology, feedstock rate, gun angle and substrate roughness, allows the production of a coating from particles in solid state ^[8].



Figure 5: Particle velocity vs. Temperature graphic^{19]}

Given that high temperature is not involved in CGS, this technique is appropriate for the deposition of temperature-sensitive materials, such as nanophased and amorphous substances. Furthermore, many deleterious phenomena caused by high temperatures, such as grain growth, which happens during thermal spraying, or oxide formation, are minimized or even prevented by CGS. Therefore the potential to produce nanostructures by Cold Spray technology using nanostructured powders is much higher than when using other methods. Other typical advantages of coatings obtained by this technique include compressive rather than tensile stresses, wrought-like microstructure, near theoretical density, oxides, and other inclusion-free coatings ^[4].

The oxygen content of coatings is dramatically reduced or even absent when high oxygen reactive materials like titanium, aluminium or copper are deposited by CGS, as shown by N. Cinca et al. for titanium grade 2 coatings on aluminium alloy ^[10].

Upon impact of these particles with the substrate surface, plastic deformation occurs. Depending on substrate and powder characteristics, this deformation can take place just in the powder, in the substrate, or in both. Only when the impact velocity of the particles reaches a critical value, particles can adhere producing a coating ^[11].

CGS allows material cost reduction, minimization of surface treatments, possibility of increasing machinery lifetime, and reduction of problems associated with material melting. These features make it an efficient, environmental friendly and economically more affordable than conventional thermal spray and deposition processes.

The main advantages that the process involves are ^[13-20].

- Reduction of the porosity of the coatings. The compressive effect of the particles impacting at high velocity against the substrate, tend to close the small pores and voids present in the underlying layers of material.
- High deposition efficiency, with the possibility of obtaining coatings with high density and hardness.
- Reduction of oxides in the coating. By not melting the particles, the surface reactivity is smaller than in case of conventional techniques.
- Compressive instead of tensile stresses, mainly because the particles are not melted when impact onto the substrate.
- The composition and microstructure of the starting materials is retained.
- Minimum substrate preparation
- Possibility of obtaining coatings with high electrical or thermal conductivity
- Possibility of spraying heat sensitive materials
- Possibility reuse the particles which are not adhered to the substrate (100% recycling)
- Operational safety increased due to the absence of a high temperature gas beam, combustion, radiation or explosive gases.

2.1. Process variables

Spraying conditions depends on physical and chemical properties of the spraying powder material and substrate, and the desired final application for which it is desired to generate the coating.

As it has been said before, the mechanism on how the particles adhere is still not clear but is influenced by various factors. These factors range from the geometrical parameters, such as surface roughness and impact zone, to thermo-mechanical parameters as plastic deformation, yield stress, pressure and temperature at the interface.

In addition, should be taken into account physicochemical properties of the materials themselves as hardness, plasticity and surface reactivity.

The main variables that must be taken into account when performing a spraying are ^{[21-} ^{32]}

INTRODUCTION

2.1.1. Particle velocity

The first particles impacting onto the substrate increase the reactivity of the surface due to the creation of a high concentration of dislocations and the elimination of impurities which can decrease the contact surface between particles and substrate.

A high number of initial impacts cause activation and cleaning of the surface (mainly removing the passivation layer or existing oxide in most of the metals) and generates favourable conditions for the adhesion of these particles. The elapsed time since the first impacts onto the substrate surface occur, until the first particles begin to adhere, is called the "induction time (t_i)". This t_i will increase as the speed of impinging particles onto the substrate decrease, because kinetic energy of the arriving particles is higher as higher the speed is. The characteristic activation degree of the surface can be expressed as the number of impacts in a known section of the surface before adhesion occurs.



Figure 6: Time delay vs. deposition. Impact speed [22]

For any pure material, it is possible to calculate the theoretical value of the activation energy based on the statistical physics laws. Experimentally however, the surface status of most materials is far from ideal, so there is a difference between the experimental and the theoretical value of the activation energy. This experimental value also depends on the stresses or strains applied on the material, as well as physicochemical properties of particle and substrate. The behaviour of a particle impacting on the surface of the substrate is very dissimilar. It can bounce off the surface, adhere to it or sink into. Often, the impact of a particle causes a deformation onto a surface or on both, the particle and the solid body. The result of the impact will depend mainly on the speed of the particle and its physical properties such as hardness, ductility or thermal conductivity.

There are three main areas of interaction between particle and substrate according to the particle velocity at the moment of impact ^[22]

Low velocity (speed) particle impacts

At low impact velocities (1-100 m/s), small particles (0.1-1.0 μ m) may become attached to the surface mainly by Van der Waals and electrostatic forces. Larger particles (1 to 50 μ m), which impact up to about 40 m/s, usually bounce without being destroyed but leaving plastic marks both the particle and substrate surface. The rebound is part of the initial kinetic energy that is stored as elastic energy in the interacting bodies, and is then is transformed back into kinetic energy of the bounced particle. The size of the marks increases with increasing impact velocity.

Ballistic impacts

When the impact of large particles (1 to 50 μ m) occurs at higher speeds (50 to 2000 m/s) the so-called "ballistic impacts" are produced. Due to the high kinetic energy of the particles, the values of plastic strain and tensile strength increases strongly during impact. This leads to a hardening and an increase of the temperature of the material. This temperature increase generates a softening. It should be taking into account the competition between hardening due to impact and softening due to thermal influence

Hyper-velocity impacts

At impact velocities above 2000 m/s the tensions in the material due to impact exceed significantly the elastic limit thereof. Under these conditions solids behave as fluids. Generally, particles penetrate into a substrate reaching depths of 2 and 3 times the diameter of the particle.

These three types of behaviour can be summarized in the following scheme:



Figure 7 Particle impact on a solid surface: Influence of impact velocity and particle size on features of the interaction

"Isentropic unidimensional theory" makes possible to calculate approximately the velocity of the particles under given spraying conditions

$$v_p = M_a \sqrt{\gamma RT} \sqrt{\frac{C_D A_p \rho_g X}{m_p}}$$

Equation 1: particle velocity

Where:

M_a: Mach number dependant of the streaming gas.

 $\boldsymbol{\gamma}:$ constant proportional to the heat capacity of the gas at constant pressure and volume,

R: specific gas constant.

C_D: drag coefficient.

A_p: area of the particle.

 ρ_g : gas density.

X: distance travelled by the particle inside the nozzle.

m_p : mass of the particle.

In cold spraying, successful bonding of an impacting particle requires localized deformation and adiabatic shear instabilities. For every impact particle/substrate and particle/particle, there is a so-called critical velocity, dependent mainly on the characteristics of the spraying material and the substrate, from which particles can deposit to produce a coating.

The critical velocity increases with the yield strength and the melting temperature, whereas decreases with the increase of density and temperature of the particle. For a typical range of material properties and process parameters, the yield and the melting point has a minor effect on the critical speed in comparison with the density and the temperature thereof.

The overall effect of these parameters can be summarized in the following equation obtained by Assadi et al ^[24]

 $V_{critical} = 667 - 0.014\rho + 0.08(T_m - T_R) + 10^{-7}\sigma_u - 0.4(T_i - T_R)$

Equation 2: Critical velocity

Where:

p: Density

- T_m: Melting temperature
- T_R : Reference temperature
- σ_u : Yield strength
- T_i : Impact Temperature

This equation does not take into account the size of the impacting particle, so Tobias Schmidt et al. from Helmut Schmidt University has developed after numerical simulations and experimental tests and taking into account other properties of the particles like its sizes or specific heat, other equation where the critical velocity was calculated as^[25]:

$$v_{crit}^{th,mech} = \sqrt{\frac{F_1 \cdot 4 \cdot UTS \cdot \left(1 - \frac{T_i - T_R}{T_m - T_R}\right)}{\rho}} + F_2 \cdot c_p \cdot (T_m - T_i)$$

Equation 3: Critical and erosion velocity of CGS particles

Nomenclature for calculations:

F₁: Calibration factor 1 (Constant) F₂: Calibration factor 2 (Constant) UTS: Ultimate Tensile Strength T_i: Impact temperature T_R: Room temperature T_m: Melting temperature ρ : Density cp: Specific heat

Calibration factors ($F_1 = 1.2$, $F_2 = 0.3$) were obtained combining the calculated critical velocities with experimentally determined critical velocities. If these calibration factors F_1 and F_2 are calculated by relating theoretical calculations with experimental results obtained by particle penetration on impact tests the erosion limit can be determined. The calibration factors for erosion are $F_1 = 4,8$ and $F_2 = 1,2$.

Closely related with the velocity and the energy of the particles at the moment of impact, is the nature of the bonding between particles and substrate.

As it has been said before, it is generally believed that bonding is result of extensive plastic deformation and associated phenomena at the interface (adiabatic shear instabilities). However, the mechanism by which the solid particles are deformed and are bonded is still not fully understood ^[24]



Figure 8: Simulated impact of a copper particle on cooper substrate for initial velocities of 500 and 600 m/s

According to the simulation of figure 8, spraying particles and substrate are subjected to extensive localized deformation during impact. This causes the rupture of the thin oxide surface layer and allows a deep contact between particles and substrate or previously deposited materials.

The kinetic energy that particles contain at impact moment is often less than the required energy to cause local melting, but this depends on the spraying conditions as well as particles and substrate nature as it will be explained later.

At impact moment, plastic deformation energy is dissipated as heat, which will cause a softening of the material. This heat, depending on the thermal conductivity of substrate and particle's composition, is generally very focused at the contact point, because, specific heat and existing defects of the material difficult heat dissipation. Still possible melted zones are too small by what may be considered that the bond of particles with the substrate, or particles between themselves, is primarily a solid-state process.

During bond formation, atomic diffusion is not taken into account since the period of time that the interface particle/substrate remains at enough temperature to trigger diffusion processes, is very short.

CHAPTER 1

Although this diffusion is not necessary to produce bonding, surfaces must be free of passivation layers or oxides, and contact pressures should be relatively high.



Figure 9: Simulation of particle impact in solid state

Taking into account the quick impact process (tens of nanoseconds) it is assumed that the kinetic energy of the particle becomes a source of thermal energy.

There is a second theory sustained by numerous investigations, which support the existence of a possible localized fusion at the interface particle/substrate and particle/coating, under certain conditions. This melting at local level will favour the formation of a metallurgical bond between the deposited particles and the substrate-coating, and therefore, improved adhesion ^[15,36]A low melting point, low thermal conductivity, high particle velocity, a specific morphology or particle size distribution , are factors that influence this possible localized melting due to impact during CGS.

2.1.2. Spraying distance

Before determining the optimal distance between the nozzle exit and the substrate, it should be taken into account a phenomena that has a high influence on the deposition efficiency, and it is influenced by the spraying distance: "BOW SHOCK"

Shock waves are produced as result of the adaptation of a supersonic flow to perturbations. In a CGS spraying system, the perturbation is the substrate. When gas molecules impact onto the substrate, there is a change of momentum and energy that is transmitted to other regions of the flow through pressure waves. These pressure waves moves perpendicular to the substrate surface and in the opposite direction to the

beam current. Thus, the waves that are attached to a short distance from the substrate surface by generating a normal shock wave, indicate the presence of the substrate. The "Bow Shock" encloses a recirculation region, high speed and low density which is characterized by high gradients and abrupt changes in the properties of the flow. The characteristics of this region may affect the speed and path of the particles entrained by the gas stream^[37].



Figure 10:Bow Shock formation

The "Bow Shock" effect plays a fundamental role in CGS process, not only slows down the gas but also the dragged particles.

Therefore, at small spraying distances, when the strength of the "Bow Shock" is high, the deposition efficiency should be reduced. While at large distances, when the effect is gone, the deposition may still occur.

Many authors have demonstrated that deposition efficiency is very dependent on the spraying distance, mainly due to the "Bow Shock", and the relative gas velocity outside the nozzle, which determines particle velocity ^[33,38]

There are three regions of deposition as a function of spraying distance ^[38]:

- 1. Short spraying distances, where the presence of the "Bow Shock" adversely affects the deposition efficiency
- 2. Middle spraying distances, where the "Bow Shock" effect has disappeared, and if the gas velocity is above the particle velocity (positive drag force), the deposition efficiency is still increasing.

3. Long spraying distances, where the gas velocity is lower than the velocity of the particle (negative drag force), and therefore, the particles begin to decelerate.



Figure 11: Deposition efficiency depending on the spraying distance

Where:

- Vg.: Gas velocity.
- V_i: particle impact velocity.
- V_p: in flight particle velocity.

F_d: drag force.

M_c: Match number.

For optimal deposition efficiency, the spraying distance should be established within Region 2

2.1.3. Spraying powder size and morphology

In general, smaller particle size, have in average a higher particle velocity. This is because the acceleration which prints the gas to the particles is inversely proportional to the particle diameter (taking into account Newton's laws and assuming spherical
particle). Theoretically this implies that at smaller diameter, higher is the acceleration experienced by the particle and therefore higher is the velocity of the particle at impact time. However, in the same way that the smaller particles are accelerated more easily, also their deceleration is faster, while with larger particles, speed is maintained for a longer period of time. As V. Champagne et al. have studied, small particles exit the nozzle at higher velocity than the bigger ones but their velocity at impact can be significantly lower. Modelling efforts showed that the low gas velocity following the bow shock wave decreases particle velocities, especially for the smallest particles. Impact velocity increases until a certain decrease in particle diameter. Up this size, impact velocity decreases as the particle diameter is further reduced ^[39].

Other important aspect is the powder morphology ^[40]. Non-spherical particles with irregular and roughened surfaces have a different flight and impact behaviour than spherical particles. Non-spherical forms generate a greater contact area, helping to bond formation.

An irregular morphology increases the stresses concentration during the impact due to the fact that the load is not uniformly distributed as in the spherical particles. This stresses concentration can facilitate the emergence of deformations which lead to the break of the thin oxide layer present on the material surface and therefore causing a greater contact between the particle and the substrate.



Figure 12: Optimum particle size distribution for cold spraying.^[12]

INTRODUCTION

2.1.4. Powder feeding rate

Varying the powder feed rate, it is possible to change directly coating's thickness. In Cold Gas Spray the thickness increases linearly with an increase of the feeding rate (Figure 13), until a maximum that indicates that there are too many particles impacting on the substrate surface, creating excessive residual stresses, which can cause coating detachment ("peeling effect")^[41].



Figure 13: Coating thickness vs. Powder mass flow rate

2.1.5. Spray angle

All authors agreed that the angle at which the particles impact onto the substrate has a significant influence on the properties of the coating and deposition efficiency.

Below certain angle, no material deposition occurs. The relationship between spraying angle and deposition efficiency can be divided into three ranges (Figure 14)

Maximum deposition Range

Transition Range

No deposition Range

When particles are sprayed with an angle that is not in the normal direction of the substrate surface, the *normal* component of the particle velocity will be lower in comparison with those sprayed perpendicularly to the surface. Since the deformation of the particles at the moment of impact depends primarily on the impact velocity, can be

considered that spraying angle will influence the deposition and the coating microstructure ^[42].



Figure 14: Schematic diagram of spray setup and effect of spray angle on the relative deposition efficiency^{[9].}

When the spraying angle is reduced approximately 40°, almost no particles are deposited onto the substrate and the relative deposition efficiency tends to zero. This result suggests that there is an angle below which no deposition occurs.

As it is shown in figure 14b, deposition efficiency is maximum in the range of 80° to 90 (normal impact direction). However, by decreasing the spraying angel, the relative deposition efficiency decreases dramatically.

Since only those particles which speed is above its critical velocity can adhere to the substrate surface, it can be speculated that the normal component of the particle velocity is one of the main factors influencing the deposition. As the spraying angle decrease, the normal component of the velocity is reduced. When the normal component of the particle velocity is lower than the critical velocity, the particle will not adhere to the substrate (Figure 15).



Figure 15: Decomposition of particle impact velocity at spray angle of θ .

INTRODUCTION

2.1.6. Particle, substrate and carrier gas temperature

Temperature influences cold spray process in different ways. First, increasing the initial temperature, carrier gas velocity increases, and as result, particle velocity and therefore its impact velocity.

Secondly, the elastic and plastic properties of materials are temperature dependent. At higher temperature the elasticity and plasticity of the material increases, and it may cause softening, which is important for the appearance of adiabatic shear instabilities which influence on bonding mechanism.

When the propellant gas front arrives to substrate surface, is slowed down, compressed and deflected due to the impact. This interaction, besides inducing the phenomenon described above as "Bow Shock" (depending on the spraying distance), it produces a blockage near the substrate surface resulting in an increase of the gas temperature. Since the propellant gas is usually heated to achieve higher speeds, the gas temperature in this region may be high enough to increase the substrate temperature significantly. Temperature increase in addition to material softening, may cause an oxidation of the substrate and the deposited particles, affecting the adhesion, purity and properties of the coatings. The temperature of the substrate surface can also modify the coating formation process^[43].

2.1.7. Surface Roughness

One of the existing theories to explain the bonding mechanisms is based on mechanical anchoring that is formed between the particle and the substrate, therefore, it is expected that higher substrate roughness will increase particle/substrate bond formation due to the existence of a larger specific surface where particles can adhere [44.45]

For surfaces with low roughness, the first particles have am smaller contact area surface where they can adhere, leading to fewer bonding or these will be weaker due to the smaller contact area. In this case, since particles have a greater difficulty to bond to the substrate, deposition efficiency is lower than in the previous case. Numerous publications suggest that higher substrate roughness may be beneficial for the efficiency of the process; although once the first layers of material has been deposited, this influence disappears ^[46,47]



Figure16: Substrate roughness

As S. Kumar et al has demonstrate contact time, contact area and interface temperature are higher for impacting on roughened substrates. Bond strength values for grit blasted substrates are higher than that of planar substrates as the mechanical interlocking plays an important role in bonding mechanism.^[48]

2.1.8. Starting material.

Numerous publications claim that bonding of the particles to the substrate is intrinsically linked to the deformability of both, particle and substrate. Hence, the best deposition efficiencies are obtained with metallic materials with medium/high plasticity. Materials with high rigidity, in general, must be sprayed with other materials which act as matrix and embed the rigid material particles allowing deposition. Otherwise, in general, high rigidity particles tend to destroy the substrate.

Still, there are some publications where the authors have sprayed high stiffness materials without the need for a second powder serving as a matrix.^[49]

With soft substrates and hard spraying materials, first impacts deform the substrate and after an initial layer of not deformed particles, the following impacts will result in a deformation of the deposited material and the impacting particles.

INTRODUCTION

2.1.9. Deposition efficiency

One of the main properties to evaluate the quality of a coating process, and not only in CGS but in all deposition technique is the deposition efficiency.

Deposition efficiency is a function of many variables, but experimentally it can be determined by the following equation:

$$DE = \frac{\Delta S_w}{\sum P_w}$$

Equation 4: Deposition efficiency calculation

Where:

DE: Deposition efficiency ΔS_w : Substrate weight change P_w: Total impacting particles weight

Deposition efficiency gives an indication about the number of particles that have been adhered to the substrate. François Raletzet et al. assume that the curve of particle size distribution is equivalent to the curve of deposition efficiency (Figure 17). The value of this efficiency is directly related to the diameter of the largest particle that can be adhered to the substrate, which means that this particle will have a velocity equal to the critical velocity. Since the spraying parameters are known, the critical velocity of the particle can be calculated using Equation 1 previously described.



Figure17: Determination of the diameter of the particle that has a velocity equal to the critical one^[50]

INTRODUCTION

2.2. Economics of cold gas spray process.

Apart from the technological advantages, another major characteristic of CGS is the greatly costs and deadlines reduction. To achieve these objectives (goals), it is necessary to consider all the aspects that are involved in the manufacture of specific components. Most of the engineering works come from casting. The costs involved in different processes of manufacture of a casting is shown in Figure 18.



This analysis of the value chain shows that a large amount of cost reduction should be achieved through the cost reduction in all areas of the chain and not on a single one

The analysis value model was developed by Pratt & Whitney company as part of a laser powder deposition project, using titanium as feedstock. This cost model was then applied to the CGS process of titanium.

Reduction in the input material, Removal of the mold and the cost of pouring (tipping out) the molten material Reduction in the recasting Finishing

Increase in the use of materials (CGS has a deposition efficiency between 60 and 95%).

A simple calculation based on the results of the value chain showed that the raw material income can be reduced by 50%, reprocessing and finished by 75% and the mold, casting/ pouring and casting costs, eliminated. About 70% of the cost of the value chain could be reduced or eliminated. To this cost reduction, the direct costs involved in CGS manufacturing must be added. The estimated costs were subsequently used in the development of real cases to demonstrate the advantage that CGS technique have for manufacturing of certain pieces.

Furthermore, M. Grujicic et al from the International Research Center for Automotive, in partnership with BMW Group, performed an economic study on the feasibility of producing a polymer-metal hybrid piece of a car with different spraying techniques. During the last decade, the polymer-metal hybrid structures (PMH) have been used in a variety of applications in the automotive field, from the instrument panel to the bumper^[52].

The main idea of this type of materials is to combine the structural and nonstructural functions of a number of components in a single piece (usually consisting of a metal core covered by molding with a plastic material).

The total cost of production of one piece can be divided into:

Cm = Cmat + Ccap + Ctool + Ccons + Cpower + Cop + Cmaint *Equation 5: Production cost*

Where:Cm-manufacturing costs, Cmat-material costs, Ccap-capital costs, Ctoolequipment cost, Ccons- consumables cost, Cpower-power cost, Cop-operational cost and Cmaint-maintenance costs.

Based on the obtained results, it was found that cold spray process was the optimal method for obtaining structural parts. Table 2 shows a comparison of the costs associated with every coatings obtention techniques and can be observed that for CGS costs are the lowest ^[53]

Cost component (\$)	Powder coating process			
	1. Cold-gas spray	2. Flame spray	3. HVOF spray	4. Plasma-arc spray
Material cost, C _{mat}	0.3365	0.3883	0.3365	0.3883
Capital cost, C _{cap}	0.0356	0.0148	0.0238	0.0445
Consumable cost, C _{con}	0.2138	0.1438	1.027	0.0476
Power cost, Cpower	0.0107	0.0296	0.0170	0.0391
Operational cost, Cop	0.2524	1.1649	0.5048	0.7766
Total cost	0.8490 ± 0.1274	1.7415 ± 0.2612	1.9068 ± 0.2860	1.2961 ± 0.1944

Table 2: Comparative cost analysis

The evolution and maturation of this technology will set the CGS technique as a viable technique to produce coatings with high performance at an affordable price for many industries.

INTRODUCTION

3. LIGHT ALLOYS

Traditionally light alloys referred to aluminium and magnesium because they have low density values and they are used to reduce the weight of components and structures. On this basis, titanium also qualifies as one of them although it has a higher density. Their densities are in a range from 1.7 g/cm³ (magnesium) to 4.5 g/cm³ (titanium). Other materials are lighter than titanium and could be consider as light alloys, but with the exception of boron, none is used as a base material for structural purposes^[54].

The property of lightness translates directly to material property enhancement for many products since by far the greatest weight reduction is achieved by a decrease in density. This is an obvious reason why light metals have been associated with transportation, notably aerospace, which has provided great stimulus to the development of light alloys during the last 50 years.



Figure 19: Ashby diagram Strength vs. Density

The advantages of reduced density become even more important in engineering design, when parameters such as stiffness and resistance to buckling are involved.

Weight saving should not obscure the fact that light metals possess other properties of considerable technological importance, e.g. the high corrosion resistance and high electrical and thermal conductivities of aluminium, the machinability of magnesium, and extreme corrosion resistance of titanium.

INTRODUCTION

3.1. Ti6Al4V (R56400)

Titanium has a density 45% lower than steel, and its alloys are extensively used for aerospace components that work till moderately elevated temperatures like airframe and jet engine components. Titanium has the ability of forming a protective oxide layer which is the base of its corrosion resistance. This oxide layer allows to use this material in chemical equipments or prosthetic implants.

The main characteristics that make titanium a wanted element are:

- 1. At 882.5 °C, titanium experiences an allotropic transformation from hexagonal close-packed structure (α phase) to a body-centred cubic phase (β phase) that remains stable up to the melting point which is 1650-1670°C
- 2. Titanium is a transition metal which forms solid solutions with most substitional elements due to its incomplete shell in its electronic structure though metallic, covalent or ionic bonding
- 3. Titanium and its alloys react with several interstitial elements including the gases oxygen, nitrogen and hydrogen. This property, depending on the application, could be detrimental

Based on the phases present, titanium alloys can be classified as either α -, β -, or α + β alloys.

Alpha alloys contain elements such as aluminum and tin. These α -stabilizing elements work by either inhibiting change in the phase transformation temperature or by causing it to increase. Alpha alloys are characterized by satisfactory strength, toughness, and weldability, but poorer forgeability than β alloys. The absence of a ductile-to-brittle transition, a feature of β alloys, makes α alloys suitable for cryogenic applications.

Alpha - beta alloys contain transition elements which tend to decrease the temperature of the α to β phase transition and thus promote development of the bcc β phase. They have compositions that support a mixture of α and β phases and may contain between 10 and 50% β phase at room temperature. The most common $\alpha + \beta$ alloy is Ti-6Al-4V, which will be later explained.

Beta alloys contain transition elements such as vanadium, niobium, and molybdenum, which tend to decrease the temperature of the α to β phase transition and thus promote development of the bcc β phase. They have excellent forgeability, hardenability, and respond readily to heat treatment.

Alloying of titanium is dominated by the ability of elements to stabilize either α - or β phase. Alloying elements with electron/atom ratios of less than 4 stabilize the α -phase, elements with a ratio of 4 are neutral, and elements with ratios greater than 4 are β stabilizing. Compared with β , α phase is characterized by the following properties:

- High resistance to plastic deformation.
- Low ductility.
- Significant anisotropy of physical and mechanical properties.
- Diffusion rates are lower by at least two orders of magnitude.
- High creep resistance.

In titanium alloys, the main effect of an alloying element is the change on alpha-to-beta transformation temperature. The elements which stabilize the alpha structure raise the alpha-to-beta transformation temperature, while beta structure stabilizers decreases this transformation temperature.

Alloying element	Range (approx wt%)	Effect on structure
Aluminum	2-7	α stabilizer
Tin	2-6	α stabilizer
Vanadium	2-20	β stabilizer
Molybdenum	2-20	β stabilizer
Chromium	2-12	β stabilizer
Copper	2-6	β stabilizer
Zirconium	2-8	α and β strengthener
Silicon	0,05 to 1	Improves creep resistance

The most important alloying elements are shown in the following table

Table 3: α , β *stabilizers*

Ti6Al4V is an α/β alloy which contains a 6% aluminium as alpha phase stabilizer and a 4% vanadium which stabilizes beta phase. At equilibrium and room temperature, microstructure is mainly α phase with some retained β phase. Figure 20 shows the evolution of the Ti6Al4V microstructure with the temperature variation.



Figure 20: Ti–6Al phase diagram

Microstructure determined by α and β phase proportion and its respective size, defines the mechanical properties of this titanium alloy. Table 4 shows the main properties of this alloy with standard composition.

Ultimate Tensile Strength,	950 MPa
Yield Tensile Strength,	880 MPa
Elongation at Break	14%
Modulus of Elasticity	113,8 GPa
Compressive Yield Strength	970 MPa
Poisson Ratio	0,342
Fracture Toughness	75,0 MPa-m ^½
Shear Modulus	44 GPa

Table 4: Ti6Al4V mechanical properties

When α -phase colony decreases, yield strength, ductility and crack propagation resistance are improved, while with a big α -phase colony, macro crack propagation and fracture toughness are then improved.

Regarding to Ti6Al4V applications, aerospace industry hoards most of the Titanium alloys applications due to their high specific strength ratio. These applications goes from structural components to jet engines.

There are other industries which are also using titanium and its alloys. Consumer applications (Cameras, jewellery, musical instruments or sports equipment) and also in:

- Chemical processing
- Paper industry
- Marine applications
- Energy production
- Storage
- Biomedical applications for use in surgical implants and prosthetic devices.
- Special applications that exploit unique properties such as superconductivity (alloyed with niobium) and the shape-memory effect (alloyed with nickel).
- Automotive industry.

INTRODUCTION

3.2. Al-7075-T6 (A97075)

Aluminum has a density of only 2.7 g/cm³, approximately one-third as much as steel (7.83 g/cm³), copper (8.93 g/cm³), or brass (8.53 g/cm³). It can display excellent corrosion resistance in most environments.

The main properties that make aluminium a valuable material despite its low density and corrosion resistance are high strength, durability, ductility, formability, conductivity and the possibility to be 100% recycled.

Aluminium is an active metal which will oxidize whenever the necessary conditions for oxidation prevail. Nevertheless, aluminium and its alloys are relatively stable in most environments due to the rapid formation of a natural oxide film of alumina on the surface.

Aluminum is the first in order of abundance of the structural metals. In most of developed countries aluminium is used in five main areas:

- Building and construction
- Packaging and containers
- Transportation
- Electrical conductors
- Machinery and equipment

It is convenient to divide aluminum alloys into two major categories: casting and wrought compositions

Cast and wrought alloy nomenclatures have been developed by the Aluminum Association system. Their alloy identification system employs different nomenclatures for wrought and cast alloys, but divides alloys into families for simplification. There are 8 series of wrought alloys:

- 1xxx Controlled unalloyed (pure) compositions.
- 2xxx Alloys in which copper is the principal alloying element, though other elements, notably magnesium, may be specified.
- 3xxx Alloys in which manganese is the principal alloying element.
- 4xxx Alloys in which silicon is the principal alloying element.
- 5xxx Alloys in which magnesium is the principal alloying element.

- 6xxx Alloys in which magnesium and silicon are principal alloying elements.
- 7xxx Alloys in which zinc is the principal alloying element, but other elements such as copper, magnesium, chromium, and zirconium may be specified.
- 8xxx Alloys including tin and some lithium compositions characterizing miscellaneous compositions.

Wrought alloys, which are initially cast as ingots or billets and subsequently hot and/or cold worked mechanically into the desired form:

- Rolling to produce sheet, foil or plate
- Extrusion to produce profiles, tubes or rods
- Forming to produce more complex shapes from rolled or extruded stock
- Forging to produce complex shapes with superior mechanical properties

Cast alloys are directly cast into their final form by one of various methods such as sand-casting, die or pressure die casting.. These alloys contain high levels of silicon to improve their castability. Casting is used for complex product shapes.

The mechanical properties of one and the same alloy, in terms of composition, can vary drastically depending on the thermo-mechanical processing of the alloy during production or post-production. For this reason, when discussing or selecting a specific alloy, the temper should be specified.

The temper of an alloy can be varied / tuned to meet the application requirements. There are two categories of alloys in this respect:

Heat treatable alloys: Their mechanical properties can be tuned through thermal treatment on top of the work hardening processes inherent to their production or post-production. This is possible for alloys belonging to 2xxx, 6xxx and 7xxx series which can be precipitation or age hardened. There are many possible tempers because changing the heat treatment temperature and/or time results in a different microstructure and consequently a wide variety of mechanical properties may be obtained.

Non heat treatable alloys: Their mechanical properties are obtained through hot and/or cold working mechanisms during their production and in post-production work

hardening operations such as strain hardening, with intermediate and possibly final annealing. This is done for the alloys belonging to 1xxx, 3xxx, 4xxx and 5xxx series.

Many alloys respond to thermal treatment based on phase solubilities. These treatments include solution heat treatment, quenching, and precipitation, or age hardening. For either casting or wrought alloys, such alloys are described as heat treatable. A large number of other wrought compositions rely instead on work hardening through mechanical reduction, usually in combination with various annealing procedures for property development. These alloys are referred to as work hardening.

Some casting alloys are essentially not heat treatable and are used only in as-cast or in thermally modified conditions unrelated to solution or precipitation effects.



Figure 21: Aluminum alloys

The alloy used in this work, 7075-T6, belongs to 7xxx series. It is composed by Al 5.6Zn 2.5Mg 1.6Cu Cr.

In general they are very strong "heat treatable" alloys, since they can be strengthened through heat treatment(precipitation hardening) based on the combination of zinc (mostly between 4–6 wt %) and magnesium (range 1–3 wt %). Unfortunately, these alloys seem prone to stress cracking. As with some of the 2xxx series, alloys in the 7xxx series also have additions of magnesium to maximise their age-hardening potential where the precipitating phases are typically of the type MgZn₂. Such alloys give medium strength, but are relatively easily welded. Aluminium-zinc-magnesium alloys have a greater response to heat treatment than the binary aluminium-zinc alloys, resulting in

higher strengths. The additions of zinc and magnesium however decrease the corrosion resistance. Chromium amounts, generally less than 0.35 %, are added to increase the electrical resistivity and to control grain structure, by preventing re-crystallisation in aluminium-magnesium-silicon and aluminium-zinc alloys during hot-working or heat-treatment. The addition of copper to aluminium-zinc-magnesium alloys, together with small amounts of chromium and manganese, results in the highest strength aluminium alloys available. Alloys based on the quaternary Al–Zn–Mg–Cu system have the greatest potential of all aluminium alloys for age-hardening, and yield strengths approaching 600 MPa can be achieved in some alloys. Zinc and magnesium control the ageing process, while the effect of copper is the increase in ageing rate and the increase in quench sensitivity. Although copper decreases the general corrosion resistance, it improves the resistance to stress cracking.

T6 is the designation to the solution heat-treated and artificially aged alloys. It represents a group of products that are not cold-worked after solution heat-treatment and for which mechanical properties or dimensional stability, or both, have been substantially improved by precipitation heat-treatment ^[55].

Some specific properties of this allow are pointed in table 5

Ultimate Tensile Strength,	572 MPa
Tensile Yield Strength,	503 MPa
Elongation at Break	11 %
Modulus of Elasticity	71,7 GPa
Poisson Ratio	0,33
Fracture Toughness	25 MPa-m ^{1/2}
Shear Modulus	26,9 GPa

Table 5: Al-7075-T6 mechanical properties

Important critical applications of the 7075-T6 alloy are based on its superior strength, for example, aircraft and military highly stressed structural components.

Other possible applications are rolling stock for machine parts and tools (for rubber and plastics). Ski poles, tennis rackets, screws and bolts, nuts, rivets and even nuclear applications.

INTRODUCTION

3.1. AZ31 (M11311)

Magnesium is the eighth metal element in abundance (2,33% in weight). It's extremely low density (1.74 g/cm³), even lower than aluminum (2.70 g/cm³), gives significant advantages in the field of light alloys. Magnesium have a hcp crystallographic structure and a melting point of 650°C.

Is generally alloyed with aluminum, manganese, copper, lithium, zinc, zirconium, and lanthanide elements. These alloys have high strength-to-weight ratios.

Cast magnesium alloys dominate 85-90% of all magnesium alloy products, with Mg-Al-Zn system being the most widely used.

There is no international code to name magnesium alloys, but ASTM system designate two capital letters followed by two or three numbers. The letters stand for the two major alloying elements and the numbers stand for the amount of the two major alloying elements

The advantages of magnesium alloys for engineering designs are:

- 1. Ability to die cast at high productivity rate.
- 2. Good creep resistance until 120°C.
- 3. High damping capacity due to ability to absorb energy elastically.
- 4. High thermal conductivity permitting rapid heat dissipation.
- 5. Good machinability.
- 6. Easily gas-shield arc-welded.

And its disadvantages for engineering designs are:

- 1. High tendency to galvanic corrosion when contact with dissimilar metals or electrolyte.
- 2. Difficult to deform by cold working.
- 3. High cost.

The magnesium alloy used in this work is the AZ31. Its main alloying elements, as the name suggests, are aluminum and zinc with wt% between 2,50 and 3,50% for aluminum and between 0,60 and 1,40 % for zinc.

AZ31 is one of the most used magnesium alloy for applications at room or medium temperatures. It is strengthened by strain hardening and is weldable.

Mg–Al–Zn alloy system was found to have a large age hardening response, resulting from the precipitation of a transition phase β -(Mg₁₇Al₁₂) and consequently offering a combination of good strength and ductility. Some of its mechanical properties are shown in table 6:

Ultimate Tensile Strength,	260 MPa
Tensile Yield Strength,	200 MPa
Elongation at Break	15 %
Modulus of Elasticity	45 GPa
Compressive Yield Strength	97 MPa
Poisson Ratio	0,35
Shear Modulus	17 GPa

Table 6: AZ31 mechanical properties

Magnesium and its alloys are used in a wide variety of structural and non-structural applications. Structural applications include automotive, industrial, materials-handling, commercial, and aerospace equipment. The relative position of magnesium in the electromotive series allows it to be used for cathodic protection of other metals from corrosion and in construction of dry-cell, seawater, and reserve-cell batteries

As non-structural applications, is used as an alloying element in aluminum, zinc, lead, and other nonferrous metals alloys. It is also used as an oxygen scavenger and desulfurizer in the manufacture of nickel and copper alloys; as a desulfurizer in the iron and steel industry; and as a reducing agent in the production of beryllium, titanium, zirconium, hafnium, and uranium. Another important non-structural use of magnesium is in the Grignard reaction in organic chemistry. In finely divided form, magnesium finds some use in pyrotechnics.

Gray iron foundries use magnesium and magnesium-containing alloys as ladle addition agents introduced just before the casting is poured. The magnesium makes the graphite particles nodular and greatly improves the toughness and ductility of the cast iron. Because of its rapid but controllable response to etching and its light weight, magnesium is also used in photoengraving.

CHAPTER 2: EXPERIMENTALPROCEDURE

1. RAW MATERIALS

Selected feedstock powders were Ti6Al4V and Stainless steel 316L, with two different morphologies (spherical or regular and irregular). These powders were cold sprayed onto rectangular ($50x20x5 \text{ mm}^3$) and cylindrical (d=25,4mm ; h=35mm) Ti6Al4V, Al-7075-T6 and AZ31 substrates.

TLS Technik GmbH & Co. Spezialpulver KG in Germany supplied spherical Ti6Al4V powder and it was obtained by gas atomization with a crucible free melting process. Phelly Materials from USA supplied irregular Ti6Al4V powder and it was obtained by Hydride-dehydride process.

ELEMENT	COMPOSITION (%)
Aluminum, Al	5,50-6,75
Carbon, C	<=0,08%
Hydrogen, H	<=0,015
Iron , Fe	<=0,4
Nitrogen	<=0,03
Others	<=0,3
Oxygen	<=0,2
Titanium, Ti	87,725-91
Vanadium, V	3,5-4,5

Table 7: Nominal composition of Ti6Al4V

Spherical SS316L was supplied by Sandvik Materials Technology in Germany and obtained by gas atomization. Irregular powder was supplied by Ames in Spain.

ELEMENT	Composition (%)
Carbon, C	0,03
Chromium, Cr	17
Iron , Fe	65
Manganese, Mn	2
Molybdenum, Mo	2,5
Nickel, Ni	12
Phosphorous, P	0,045
Silicon, Si	1
Sulfur, S	0,03

Table 8: Nominal composition of SS 316L

Robert ZappWerkstofftechnik GmbH in Germany supplied Ti6Al4V substrates. Lumetal Plastic in Spain supplied Al-7075-T6 substrate. Air Craft Materials UK in United Kingdom supplied AZ31 substrate.

ELEMENT	COMPOSITION (%)
Aluminum, Al	87,1-91,4
Chromium, Cr	0,18-0,28
Copper, Cu	1,2-2
Iron , Fe	<=0,5
Magnesium, Mg	2,1-2,9
Manganese, Mn	<=0,3
Other	<=0,15
Silicon, Si	<=0,4
Titanium, Ti	<=0,2
Zinc, Zn	5,1-6,1

ELEMENT	COMPOSITION (%)
Aluminum, Al	2,5-3,5
Calcium, Ca	<=0,04
Copper, Cu	<=0,05
Iron , Fe	<=0,005
Magnesium, Mg	97
Manganese, Mn	>=0,2
Nickel, Ni	0,005
Silicon, Si	<=0,10
Zinc, Zn	0,6-1,4

Table 9: Nominal composition of Al-7075-T6 and AZ31 respectively

2. STRUCTURAL CHARACTERIZATION

The most important powder parameters are: morphology, particle size and particle size distribution, cross-section, chemical and phase composition, density and flowability. All these variables have been evaluated as following:

Morphology. in order to get complete information about the powder it is necessary to observe the grains from the outside as well as the inside. For this purpose, Scanning Electron Microscopy has been used. It serves to recognize the manufacturing technique as well as to complete the information of the particle size analysis by the examination of the different scale particles. A JEOL 5510 microscope equipped with a secondary electrons detector, a ROBINSON backscattered electron detector and x-ray detector has been employed, as well as a Quanta 650 from FEI Company, equipped with high and low vacuum mode, secondary and back-scattered electrons and EDS detector.

Particle size distribution: Laser Diffraction Particle Size Analyser Beckman Coulter LS 13320 was used. This analysis allows to obtain particle size distribution of the initial powder. The particle size range is comprised between 200nm and 2 mm.



Figure 22: LS detector scheme

<u>Density:</u> The density expresses the relationship between mass and volume of a body (g/cm3). In the case of powders, there are 3 types of spraying densities:

Bulk density. Calculated by ASTM B-212-89. A funnel Hall with a capacity of 25cm3 is filled. Powder is allowed to flow and flush volume is weighed. Using the equation of the mass density / volume is obtained directly from the value.

Vibrated Density. Calculated by ASTM B-527-85. In a graduated cylinder introduces a known amount of projection of powder. The probe is vibrated in an ultrasonic bath for 5 minutes. After this time you measure the volume of dust and direct the desired value is obtained.

Aparent density. Calculated by the ASTM B-238^[56]. In a 25 ml flask a known quantity of spraying powder is introduced. The flask (previously weighed) is filled with pure and known solvent with low surface tension and its weighed. The difference in weight of the flask with and without solvent allows knowing the mass of added solvent, along with its density and its volume. Once the added volume is known, it allows to know the exact amount of spraying powder. Through mathematical relationship, the density is obtained

$$\rho = \frac{m_p}{25 - \frac{m_T - m_p}{\rho_d}}$$

Equation 6: Aparent density formula

Where mp is the mass powder introduced, m_T is the total mass (powder+solvent) and p_d is the ciclohexanone density at working temperature.

Flowability. Determined according to ASTM B-213-30 standard⁵⁷. This norm establishes the use of a Hall metal funnel for those materials having good flowability. To calculate it, 50 grams of material are placed in the funnel keeping the lower outlet orifice closed. When opened, the dust flows through it and the time that the 50 grams uses to fall is clocked.

Phase composition: phase analysis has been carried out with different techniques.

<u>X-ray diffraction (XRD)</u>: This technique has been used principally for the analysis of the various phases present in the substrates and spraying powders. The equipment used was a Siemens D500 $\theta/2\theta$ Bragg-Brentano type using Cu K α_{1+2} ($\alpha_1 = 1.54060$ and $\alpha_2 = 1.54443$) radiation at 40 kV and a current of 30 mA.. The obtained diffractogram was analysed by a software program that can identify the different

phases which are present in the material by comparison with the database of the program.

<u>Light Microscopy</u>. An inverted Leika DMI 5000 M. has been used to observe the microstructures of the spraying powder and substrates after etching. The magnification used for the characterization of materials were from 50 to 500 magnifications.

<u>SEM (Scanning electron microscopy)</u>: has been used to observe at high magnifications the microstructure of the substrates and spraying powders (like the Light microscope) as well as the obtained coatings. *EDS*: normally coupled to the SEM and it has been used to make semi-quantitative analysis.

<u>ICP analisys(Inductively coupled plasma mass spectrometry (ICP-MS)</u>) is a type of mass spectrometry which is capable of detecting metals and several non-metals at concentrations as low as one part in 10¹² (part per trillion). This is achieved by ionizing the sample with inductively coupled plasma and then using a mass spectrometer to separate and quantify those ions.



Figure 23: Inductively coupled plasma mass spectrometry system

For the obtained coatings, before metallographic preparation a first non-destructive evaluation of the as-sprayed coatings included their roughness examination and x-ray analysis of the deposited material. At the same time, these were mounted and polished until a mirror-like surface was achieved in order to observe the cross section: presence of cracks, porosity or inter particle oxidation.

After, a macroscopic control: visual observation of the sprayed samples in order to detect adhesion failure, cracks, surface homogeneity etc. After this first visual observation, a CARL ZEISS stereomicroscope Stemi 2000-C, with increases from 0,65 to 5,0 were used. This stereomicroscope is coupled to a camera OLYMPUS C-4040.

EXPERIMENTAL PROCEDURE

3. EQUIPMENTS

Cold Gas Spray technique was employed to produce dense coatings, spraying the different feedstock powder materials. In each case, a careful parameter optimisation was performed both through modification of pressure and Temperature of the gas and spraying distances. Such evaluations involved an examination of the microstructure according to porosity and oxidation levels as well as deposition efficiency.

The spraying system that has been used to obtain cold gas sprayed coatings are KINETICS 4000 from CGT Company and KINETICS 8000 from CGT Company modified by the Helmut Schmidt University in Hamburg. Both equipments consist essentially in:

- Control System or console
- Power supply
- Gas Dosing System
- Hopper for feeding powder
- Spray gun

The maximum power is 34 kW: This value can achieve maximum gas pressure of 40 bar and temperatures up to 800°C for KINETICS 4000 and 60 bar and temperatures up to 1100°C for KINETICS 8000. A minimum amount 200 cm³ of spraying powder is required to be able to spray.

Spraying devices are adapted to use helium such as nitrogen as carrier gas, which are fed into a gun, where they are heated and accelerated through a DeLaval nozzle type with the spraying powder, reaching maximum speeds of 4 Match .

This supersonic speed can produce more than 120 dB of noise, making it necessary to use a soundproof chamber in order to work properly.

The control panel allows you to ensure stability of the gas flow and the temperature to ensure reproducibility of the experiments.

Figure 24 shows a scheme of the KINETICS 4000 system as well as the used spraying gun, and figure 25 shows an image of the modified KINETICS 8000 system.



Figure 24: Kinetics 4000 Cold Gas Spray equipment



Figure 25: modified Kinetics 8000 Cold Gas Spray facilities at HSU

4. MECHANICAL PROPERTIES

The mechanical properties such as hardness, microhardness, tensile strength, fracture strength, elastic modulus, toughness have been checked.

<u>Hardness</u> has been evaluated for substrates by means of a CENTAUR indenter with variable loads. Rockwell hardness measurements have been made with 100 kg. load and with a spherical tip of 1/16". The device provides a direct measurement of the Rockwell hardness, transforming to Vickers hardness through conversion tables.

5 measurements were made randomly along the substrate.



Figure 26: Hardness indenter

<u>*Microhardness*</u> has been carried out following the UNE 7-423/2 norm (ASTM E384-99 standard ⁵⁸:). A Matsuzawa MXT- α microdurometer has been used. It uses varying loads from 10 to 1000 grams.

100 gf.during 15 seconds for the substrates.

50 gf. during 15 seconds for the coatings.

The microindentations are randomly applied over the entire substrate, and the cross section of the coatings. The system contains a micrometer with an accuracy of \pm 0.25 microns to measure the pyramid-shaped footprint that the tip leaves on the surface (d₁ and d₂) in order to calculate the Vickers hardness number (HVN).

20 measurements were made in both cases.



Figure 27: Vickers microindentation scheme and hardness calculation

<u>Nanohardness</u>. A Nano Indenter XP from Agilent Technologies with loads of 500 mN and indentation depths of 2000 nm were used.

Measurements were done under the following conditions on the mirror-like sample for comparison:

2000 and 150 nanometers for the substrate

50 nanometers for spraying powders

150 nm for coatings

The nanoindenter provides in a direct way, the values of Young's modulus and hardness of the material using the algorithm of Oliver and Pharr.

$$E_{eff} = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}$$

$$\frac{1}{E_{eff}} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}$$

Equation 7: Oliver and Pharr equations ^[59].

Where A is the projected area at the selected load, S the elastic constant stiffness calculated from the load/unload curve, E_{eff} is the effective elastic modulus, E, E_i are specimen and indenter moduli, and v, v_i are Poisson's ratio of specimen and indenter, respectively.



Figure 28: Nano Indenter XP system

<u>Tensile strength</u>. coating adhesion has been evaluated following the ASTM C-633 standard^[60]. The test consists of gluing a cylindrical coated specimen with a resin to an uncoated sand-blasted specimen (Figure 29).



Figure 29: Coating adhesion test

Once the test is finished, there are 3 different rupture possibilities. It can fail in the resin, between coating layers or at the interface coating/substrate. Figure 30 shows these possibilities.


Figure 30: a. Failure in the glue (poor test); b. failure in the coating (Cohesive); c. failure at the coating/substrate interface (Adhesive)

<u>Tubular Coating Tensile strength test</u>. This test has been developed at the Institute of materials technology of the Helmut Schmidt university of Hamburg, Germany (Figure 31). The obtained results can be transformed in tensile strength multiplying them by a factor of 1,5-1,7 depending on the material ^[61].



Figure 31: Tubular Coating Tensile Test Specimen^[62]

Sliding wear:

<u>Ball-on disc test</u>. Under ASTM G99-03 standard^[63] has allowed the examination of the friction coefficient of the polished coating materials and the wear rates were calculated from the Δ volume in the wear track by means of White Light Interpherometry. The examination of the damaged surfaces determines the wear mechanism.



Figure 32:. Set-up for the Ball-on disc test

<u>Abrasive wear</u>: It was evaluated according to the ASTM G65-00 standard^[64] with a rubber-wheel test equipment. Abrasion occurs when one of the surfaces is considerably harder than the other or when hard particles are introduced between the contact surfaces. In the present work, the abrasion resistance was studied as the second case, often known as third-body abrasion.

The test (Figure 33) consists in a rotating chlorbutyl rubber wheel (C) at a constant speed of 139 rpm onto the piece to test (B). A normal force is applied on the wheel to press it against the sample and an abrasive agent (SiO₂, A) is introduced by gravity between the two bodies. The sand is collected for storage (A) and posterior discard.



Figure 33: Rubber-Wheel test equipment

<u>Cavitation test:</u> It was carried out under ASTM G32-10 standard^[65]. This test method is used to estimate the relative resistance of materials to cavitation erosion. The term cavitation erosion describes the physical phenomenon of cavitation-induced erosive wear in liquid media Cavitation is caused by the repeated nucleation, growth, and violent collapse of clouds of bubbles within the liquid. Erosion is the result of the formed vapour bubbles rapidly collapsing which produces a shock wave that can remove small amounts of metal from cylinder walls (high pressures from several hundred up to 1000 MPa and are characterized by high speeds up to 500 m/s). As this process repeats, pitting of the metal will occur and over time holes will form. Irregularities in the metal surfaces from casting or machining and the cavities from the erosion process itself encourage the formation of these vapour bubbles (figure 34).

As a consequence, it is only a question of time that important structural materials are severely damaged owing to cavitation erosion. Hence, it is of great interest to explore materials with high erosion resistance and to find the principle for selecting materials with long incubation time and low erosion rate^[66].



Figure 34: Ultrasonic equipment for cavitation erosion tests^[67]

4.1. Corrosion performance

Electrochemical tests

The corrosion resistance of the samples was evaluated by means of electrochemical measurements in 80 mL of an aerated and unstirred 3,4% NaCl solution according to ASTM D-1411 standard^[68]. A three-electrode cell was used, with a Ag/AgCl/KCl saturated as the reference electrode, a Pt-filament as counter electrode and the sample as the working electrode. The coating surface was pressed against a teflon gasket leaving around 1cm² exposed surface; the real exposed surface vary depending on the characteristic of every sample because electrolyte penetration depends on the roughness of the surface, the existence of pores, cracks, etc... .A PC-programmed EG&G 263A potentiostat/galvanostat (Princeton Applied Research, UK) was employed.



Figure 35: schematic diagram of an electrochemistry cell

This technique determines the following parameters:

Corrosion potential, E_{corr}: Is the stable open circuit potential that it is reached when the sample is immersed in the working solution. It is considered that the steady state is reached when the potential variation in one hour is less than 10 mV. The corrosion potential measured in this way is used in the following experiments as reference potential.

Polarization resistance, R_p : Determined by potentiodynamic sweep, 0.05 mVs⁻¹, varying the potential between E_{corr} ± 15 mV. The graphic E vs j gives a straight line whose slope gives the value of R_p.

Measures of Tafel slopes. The polarization curves obtained by potentiodynamic sweep pseudo-steady 0.1667 mVs-1, allows the obtention of Tafel slopes. graphically by extrapolation of Tafel lines in the polarization curves.

CHAPTER 3.RAW MATERIALS CHARACTERIZATION

1. SUBSTRATES

The main objective of the study is the improvement of light alloys wear properties, and in the case of Ti6Al4V substrate, structural reparation. All the structural and compositional characterization of the substrates has been done according to ASTM standards.

Substrates were grinded with decreasing grain size SiC papers (until 1200) and then polished with 9, 6,3 and 1µm diamond suspension. Depending on the analysis, colloidal silica has been used to obtain nano-rough surface. This metallographic preparation has been done to eliminate surface oxidation and roughness, avoiding deviations on the data obtention and to observe the microstructure after etching.

1.1. Ti-6Al-4V

Ti6Al4V substrates (50 \times 20 mm) used in all the experiments were cut out from a 500 \times 500 mm plate.

Figure 36 shows the X-ray diffractogram (XRD) of the Ti6Al4V substrate between $2\theta = 0-100^{\circ}$. X-ray analysis confirmed the existence of a biphasic structure [α -phase (HCP) + β -phase (BCC)].



Figure 36: Ti6Al4V X-Ray diffraction spectrum

The microstructure consists in ~70% α -phase and 30% of β -phase as it can be seen in figure 37. To reveal the microstructure, Ti6Al4V substrate was etched with Kroll's reagent (1% HF, 2%HNO₃, 97% distillate water) after polishing.



Figure 37: Ti6Al4V substrate microstructure by optical microscopy (A). and Backscattered SEM microscopy

On the SEM micrograph, the dark regions are the α -phase and the lighter regions are the β -phase^[69].

For hardness obtention a Vickers indenter has been used with a Force of 150Kg. The result, obtained in Rockwell C scale is $53,2 \pm 0,3$, that in Vickers scale, to be able to compare it after with the microhardness value, corresponds to 562 ± 3 HVN.

Microhardness value has been obtained according to the ASTM E384-99 standard, and the obtained hardness in Vickers is 358 ± 8 .



Figure 38: Microindentation matrix scheme onto Ti6Al4V substrate

Concerning to nanohardness, 100 indentations matrix of has been done under depth control fixed on a maximum depth of 2000 nm. Indentations must be separated at least 3 times the maximum indentation depth to avoid the influence of the deformation generated by the previous indentation. The obtained result after data treatment is 482 ± 8 Vickers. Figure 39 shows the obtained matrix.



Figure 39: Optical microscope image of Nanoindentation matrix onto Ti6Al4V substrate

50mg of milled substrate was subjected to an ICP analysis. To analyse this quantity, 5 ml H_2O , 2 ml HNO3 and 1 ml HF is added and flushed to 100ml. The mixture is leave in a Millestone reactor at 210°C. The obtained results shown in table 11 confirm the theoretical composition of the alloy.

Results in %						
Average Sd						
Ti	89,3	0,67				
Al	5,86	0,04				
V	3,98	0,04				

Table 10: Ti6Al4V substrate composition

Traces of Cu and Fe have been also detected with 0,10 \pm 0,01% and 0,195±0,006 % respectively

CHAPTER 3

1.2. Al-7075-T6

Figure 40 shows the X-ray diffractogram (XRD) of Al-7075-T6 substrate between $2\theta = 0-100^{\circ}$. It has confirmed the existence of a single phase consisted in FCC phase. It can also be observed the existence of a small pick around 44 in 2 θ that is due to the existing precipitates of MgZn₂.



Figure 40: Al-7075-T6 X-ray diffractogram

To reveal the microstructure, Keller's reagent was used (2ml HF, 3ml HCl, 5 ml HNO₃ and 190mldestilate water) It can be observed in figure 41 the elongated grains due the cold rolled. The reagent has allowed to disclose existing $MgZn_2$ precipitates in the grain boundaries.



Figure 41: Optical micrograph of Al-7075-T6 substrate microstructure

EDS analysis (figure 42) shown that, the main components are Zinc and Copper in addition to aluminum.



Figure 42: Al-7075-T6 EDS analysis

Although the 7075 aluminum alloy has a certain percentage of magnesium, due to its low concentration, it does not appear in the analysis.

To measure the hardness, a 1/8'' spherical indenter has been used with an applied force of 100Kg. The result, obtained in Rockwell B scale is $93,5\pm0,5$ HR_B (210±1 Vickers).

Microhardness was obtained indenting with a load of 100gf on the polished surface of the substrate. The obtained hardness value, in Vickers was 178 ± 8 .

For nanoindentation measures, two different penetration depths have been used, 2000nm and 150nm depth.

In the first case, the obtained results are shown in the following table:

Test	Modulus (GPa)	Modulus (GPa) Hardness (GPa)		Depth (nm)	
Mean	83,6	2,2	220	2045,6	
Std. Dev.	2,7	0,1	8	19,7	

Table 11: Modulus and hardness at 2000nm depth indentations

It can be seen that the existing deviation is very low and this is mainly because at such high penetration depths, there is no appreciable influence of the existing precipitates at grain boundaries or impurities that may exist in the sample.

In the second case, as it is shown on table 12 and figure 43, variation is higher. Penetration depth is 150nm, which implies that each nanoindentation is highly influenced by its environment.

Test	Modulus (GPa)	Modulus (GPa) Hardness (GPa)		Depth (nm)	
Mean	101,1	3,4	337	151,2	
Std. Dev.	23,1	1,1	106	9,3	

Table 12: Modulus and hardness at 150nm depth nanoindentations

Figure 43 shows graphically this hardness variation.



Figure 43:Al-7075-T6 substrate Hardness map

The ICP analysis has been done to 20mg of milled substrate. To analyse this quantity, 10 ml H_2O , 0,25 ml HNO3 and 2 ml HCl is added and flushed to 100ml. The mixture is left in a Teflon reactor at 60°C all night long. The obtained results, shown in table 13, confirm the theoretical composition of the alloy. Si, Fe and Cr with concentrations lower than 0.3% and Mn and Ti with concentrations lower than 0,05% have been detected besides those shown on the table

Results in %							
Average Sd							
Mg	2,6	0,1					
Al	92,5	0,9					
Zn	6,2	0,1					
Cu	1,7	0,1					

Table 13: Al-7075-T6 substrate composition

1.3. AZ-31

Figure 44 shows the X-ray diffractogram (XRD) of AZ31 substrate between $2\theta = 0-100^{\circ}$. X-ray analysis, confirms a single phase FCC phase.



Figure 44: AZ31 X-ray diffractogram

Optical microscopy image of the substrate microstructure is shown in figure 45. The sample for optical was etched with Keller's reagent (20ml Acetic acid, 80ml distillate water and 5g NaNO₃). The reagent has allowed to disclose existing precipitates of $Mg_{17}Al_{12}$ (Also referred as Mg_4Al_3) into the grains.



Figure 45: Optical micrograph of Al-7075-T6 substrate microstructure

A first approach to the chemical composition of the substrate has been done through an EDS analysis as it is shown in figure 46, the main components are magnesium, aluminum and zinc.



Figure 46: AZ31 EDS analysis

Hardness has been obtained using a 1/8'' spherical indenter with a Force of 100Kg. The result, obtained in Rockwell B scale is 80 ± 3 HR_B that is 120 ± 7 Vickers Hardness.

The used load for microhardness was 200gf. The obtained value, in Vickers hardness is 56 ± 2 HVN.

The quantitative composition of the substrate has been obtained, as with the previous substrates, through an ICP analysis, which has been done to 20mg of milled substrate. To analyse this quantity, 10 ml H₂O, 0,25 ml HNO3 and 2 ml HCl is added and flushed to 100ml. The mixture is left in a Teflon reactor at 60°C all night long. The obtained results shown in table 14, confirming the theoretical composition of the alloy.

Results in %							
Average Sd							
Mg	99,1	1,27					
Al	3,4	0,05					
Zn	0,94	0,02					
Mn	0,27	0,03					

Table 14: AZ31 substrate composition

CHAPTER 3

2. SPRAYING POWDERS

As it has been described before, four different spraying powders have been used during the implementation of the thesis, two of Ti6Al4V alloy and other two of 316L stainless steel, with two different morphologies (spherical and irregular) have been used to be able to later compare its viability for coatings obtention.

2.1. Ti-6Al-4V

2.1.1. Spherical Ti6Al4V

Spherical Ti6Al4V from TLS (Germany) has been obtained by gas atomization^[70].



The standard composition of this powder compared with the composition provided by the supplier is shown in the following table

element	Ti (%)	AI (%)	V (%)	O (%)	Fe (%)	C (%)	H (%)	N (%)
Testing Results	Balance	5.9	3.9	0.12	0.19	0.01	0.004	0.01
ASTM 348- 08a Gr.5	Balance	5.5- 6.75	3.5-4.5	0.2	0.4	0.08	0.015	0.05

Table 15: Ti6Al4V composition

XRD analysis shown in figure 48, has been done in order to ascertain the crystallinity and the phase composition of the powder, showing the representative peaks of α and β -phase of this material.



Figure 48: X-Ray diffractogram of Spherical Ti6Al4V powder

Figure 49 shows an homogenous and dense spherical particles. Particle size distribution of figure 50 has a mean size of 35,6 μ m and a d₁₀=24,3 μ m and d₉₀= 49,3 μ m.



Figure 49: Powder free surface and cross section SEM micrographies of spherical Ti6Al4V



Figure 50: Spherical Ti6Al4V powder size distribution

Powder microstructure of figure 51 obtained after etching the polished cross section with Kroll's reagent (1% HF, 2%HNO₃, 97% distillate water) was observed with optical microscope.



Figure 51: Spherical Ti6Al4V powder microstructure

Powder's microstructure can be mainly described as Widmanstätten type based on martensitic α phase ^[71], by solid state transformation from the high temperature β phase. This structure shows a higher hardness and lower tensile strength and ductility than the α + β structures.^[72].

Standard hardness of Ti6Al4V α + β alloy is around 350 Vickers.. Powder hardness, obtained by Nanoindentation with a maximum penetration depth of 300nm, is 490±80 Vickers.

When spraying techniques are used, it must be taking into account the spraying powder apparent density. As it has been explained in chapter 2, the apparent density is calculated under ASTM B-238 norm and for spherical Ti6Al4V powder the obtained value is 2,55 g/cc.

2.1.2. Irregular Ti6Al4V

As irregular shape powder, Ti6Al4V powder from PhellyMaterial USA, Inc. has been used. The powder has been obtained by hydride-dehydride process following ASTM F-1580-12 standard.

The *Hydride/Dehydride (HDH)* process has been known for many years in the manufacturing of transition metal powders such as tantalum, niobium, vanadium, and titanium. These particular metals undergo a reversible reaction during hydriding.

$$M + \frac{X}{2}H_2 \rightleftharpoons MH_x + Heat$$

Where M is the metal and MH_x is the metal hydride.

Absorbed hydrogen leads to an expanded metal lattice which promotes cracking and embrittlement.. Once the material is embrittled, returns to be crushed for further processing.



Figure 52: a) Hydrogen molecules adsorb onto the metal lattice. b) Absorption and chemisorption lead to an expanded metal lattice.

The dehydriding step of the process is runned in vacuum to convert the powdered metal hydride into pure metal powder. Heating in vacuum helps remove the absorbed hydrogen quickly and efficiently without contamination from oxygen and nitrogen^[73].

$$Heat + MH_x \to MH_y \to M + \frac{X}{2}H_2$$

The chemical composition of the powder provided by the supplier and compared with the standard one is as follows:

ELEMENT	Ti (%)	AI (%)	V (%)	O (%)	Fe (%)	C (%)	H (%)	N (%)
Testing Results	Balance	5.9	3.9	0.35	0.03	0.03	0.019	0.03
ASTM 348- 08a Gr.5	Balance	5.5- 6.75	3.5-4.5	0.2	0.4	0.08	0.015	0.05

Table 16: Irregular shape Ti6Al4V composition

Oxygen and Hydrogen contents are a little bit higher that the limits described by ASTM 348-08 norm but they are due to the powder obtention process. This will lately affect deposition process.

X-Ray diffractogram (Figure 53) reveal a small peak of the β phase of the Ti6Al4V around 40 degrees. In comparison with the previous spherical powder, peaks are more intense and the microstructure seems to be more crystalline due to the cleanliness of the spectrum and peaks intensity.



Figure 53: X-Ray diffractogram of irregular shape Ti6Al4V powder

As it can be observed on the free and cross section surface of figure 54, particles have an angular shape, with no internal pores.



Figure 54: SEM micrographies of irregular Ti6Al4V free surface and cross section

As received powder has been sieved in order to achieve a more adequate particle distribution for CGS because it has a d_{10} = 22,2 µm and a d_{90} =66,3 µm with a mean size of 43,2 µm. As it can be seen in figure 55, particle size distribution has a relative percentage of particles under 20 µm (<10% cumulative volume) and there is also an important percentage over 40 µm size.

When an irregular shape powder is sieved, and more when it tends to be elongated, it can pass through the sieve mesh, impeding the removal of unwanted particles. It can also happen that optimal size particles, are eliminated due to the same reason.

When particle size distribution is measured, due to the liquid medium, particles orientate its longer side parallel to the flow, causing that the showed particle size distribution in the analysis seems to be broader than in reality.

Powder mean size after sieving was 35,02 μ m with a d₁₀= 23,2 μ m and a d₉₀=53,6 μ m. Bigger particles were eliminated but not the finer ones. Figure 55 shows the obtained result



Figure 55: Irregular Ti6Al4V powder size distribution

Microstructure revealed with Kroll's reagent (1% HF, 2%HNO₃, 97% distillate water) as in the previous case, and investigated with optical microscopy, consists in α - β microstructure. The dark parts are the β -phase and the lighter and more regular zones are α -phase.



Figure 56: Irregular Ti6Al4V powder microstructure

Nanohardness is similar to the previous case 490 ± 140 Vickers, although microstructure is a little bit different than before. In this case, there is a higher content in β -phase, which is softer and more ductile than the α -phase. But it also has to be taken into

account that irregular powder obtention method has introduced a percentage of dislocations and stresses which increase the hardness.

The high standard deviation is due to the softness of β -phase and the higher hardness of α -phase. Nanoindenter is small enough to allow an indentation in each phase separately resulting in this hardness variability. α -phase surface is much higher than β -phase surface, that's why hardness is similar to the previous powder which is mostly α .

The apparent density of the feedstock powder was 2,55 g/cm³ (obtained under ASTM B-212-89 standard).

2.2. 316L Stainless steel

2.2.1. Spherical 316L Stainless Steel

Spherical 316L Stainless Steel supplier is Sandvik Materials Technology (Germany) and it has been obtained by gas atomization.

The chemical composition of the powder provided by the supplier is shown in table 17.

ELEMENT	Fe(%)	C (%)	Cr (%)	Ni (%)	Mo (%)	Si (%)	Mn (%)	S (%)	P (%)
Provider Results	Balance	0,03	16-18	10-14	2-3	1	2	0.03	0,045

Table 17: 316L Stainless Steel composition provided by the supplier

Figure 57 shows the X-Ray diffractogram of the 316L spherical powder. The powder had an FCC structure consistent with austenitic stainless steel (gamma phase iron: γ -Fe).



Figure 57: X-Ray diffractogram of spherical 316L powder

Free surface observed in figure 58 shows a spherical morphology with small satellites on the surface due to the obtention process. Cross section shows no internal pores or defects.



Figure 58: SEM micrographies of spherical 316LStainless Steel free surface and cross section

As received powder had a broad particle size distribution ($d_{10}=11$, $7\mu m - d_{90}=33.8 \mu m$) with high proportion of fines and a mean size of 20,1 μm . This distribution generates different particle velocities during spraying due to the different radios and mass of the particles.

To reduce this effect, original powder was wet sieved obtaining a narrower size distribution with a mean size of 31,5 μ m and a d₁₀=24,5 μ m and a d₉₀=40,2 μ m as it is shown in figure 59.



Figure 59: Spherical Stainless Steel 316L powder size distribution

Figure 60 shows an optical microscope micrograph of the powder microstructure after etching the polished cross-section surface with 10% w/w oxalic acid. The powder has a dendritic microstructure, which is the natural cooling microstructure of stainless steels.

Grains grow in the most energetically favourable and predominant crystallographic direction.



Figure 60: Optical micrograph of Spherical 316L Stainless Steel powder microstructure

Powder hardness was measured by nanoindentation technique. 180 ± 45 HV hardness was obtained. In figure 61 the graphic *Displacement into surface (nm)/Load on sample (mN)* of a Nanoindentation can be observed.

When the nanoindenter load ceases, the material recovers the elastic part of the deformation, maintaining the plastic one. In the case of 316L stainless steel, it has been found that the elastic deformation is relatively high and the material recovers elastically this deformation once the load ceases.

When the material has a big elastic component, and nanoindentations are observed in SEM, their size will not match exactly with the obtained hardness due to this elastic recovery. As lower the load is, higher will be this gap.



Figure 61: Displacement into surface vs. load on sample graphic of a Nanoindentation onto spherical 316L stainless steel powder

The apparent density of the feedstock powder was 3.91 g/cm^3 (obtained under ASTM B-212-89 standard) and the vibrated one is $4,55 \text{ g/cm}^3$ (obtained under ASTM B-527-85).

2.2.2. Irregular 316L Stainless Steel

Irregular 316L Stainless Steel powder from Ames (Spain) has been obtained by water atomization. This powder obtention method creates a high concentration of dislocations, hardening the material.

Chemical composition has been verified by EDX analysis (figure 62), obtaining the same composition and percentages than the standard 316L stainless steel.



Figure 62:EDX analysis Irregular 316L Stainless Steel

As in the previous case with spherical 316L stainless steel, X-ray diffractogram of figure 63 shows an FCC structure consistent with austenitic stainless steel (gamma phase iron: γ -Fe), with no oxidation traces.



Figure 63: Irregular 316L Stainless steel X-ray diffraction

Free surface of figure 64 shows an irregular morphology due to the obtention process and the cross section of the same figure shows no internal pores, cracks or defects.



Figure 64: SEM micrographies of irregular316L Stainless Steel free surface and cross section

As received, irregular powder has a mean size of 50,1 μ m with d₁₀=32,2 μ m and d₉₀= 81,4 μ m. After sieving mean size has been reduced to 29,4 μ m with d₁₀=15,6 μ m and d₉₀= 50,6 μ m with a fine powder tail as it can be seen in figure 65.



Figure 65: Irregular Stainless Steel 316L powder size distribution

As in the case of Ti6Al4V irregular powder, unwanted particles are very difficult to remove completely. Nevertheless, particle size distribution has been narrowed significantly to later compare the obtained coatings with the spherical powder coatings. Microstructure shown in figure 66 is also dendritic but with a smaller grain size.



Figure 66: Optical micrograph of Spherical 316L Stainless Steel powder microstructure

Both powders, spherical and irregular 316L stainless steel, have dendritic microstructure. As it can be observed, spherical powder dendrites (figure 60) are bigger than the irregular powder ones (figure 66). That means that the spherical powder has been obtained with a slower cooling rate, where the grain growth mechanism is favoured over nucleation, than the irregular powder, which has been obtained by water
atomization, where the cooling rate is faster and nucleation is favoured over grain growth.

Powder hardness has been obtained with a Nanoindenter XP. Used load was 3gf (30mN) with maximum displacement into surface of 2000 nm. The obtained result in Vickers was 161±29. Figure 67 shows the performed nanoindentations onto the polished and parallel-plane cross section of the powder.



Figure 67: Nanoindentation matrix onto powder cross section

Nanoindentation sizes are an indicator of the hardness; the larger is the size of the nanoindentation, lower is the hardness. The same load generates different nanoindentation sizes as a function of hardness.

CHAPTER 4:Ti6Al4V COATINGS

The optimization of spraying parameters for each coating will depend on the final application. A general goal in Cold Gas Spray technology is to ensure that all particles impacting onto the substrate are in solid state and have a velocity equal or above critical velocity in order to trigger CGS bonding mechanism and adhere to the surface. In the present case, to settle on the spraying parameters, in addition to the studied bibliography, previous experience of the Thermal Spray Center (CPT) with similar nature spraying powders was taking into account.

Initially, a 3² experiments design was used in order to obtain the maximum number of response variables and information with a minimum number of experiments (Figure 68) Low porosity, good adherence and high thickness are desirable if good oxidation resistance and wear resistance is pursued. Since no molten or semi-molten material is involved, oxidation levels will be the same in the coating than in the spraying powder.



Three different pressures with 4 bars difference between them, and three different temperatures with 50°C difference among them were used.

Under the spraying conditions determined by the experimental design, Ti6Al4V powders were sprayed onto the three substrates.

Nine different experiments were carried out under the parameters shown in the experimental design (figure 68). The substrates were grinded before spraying to eliminate impurities and surface oxide layer which will reduce the efficiency of the process, but also to increase the surface roughness. Grinding process before spraying,

help with substrate's surface activation, which improves deposition efficiency of the first coating layer.

The range of spraying conditions was the same for the three substrates.

Temperature (°C)	680	730	780
Pressure (bar)	30	34	38
Spraying distance (mm)	40		
Spraying angle (°)	90		
Nozzle speed (mm/s)	500		
Powder feeding rate (rpm)	3		
Pre-chamber (°C)	450		

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Table	18.	(oatings	spraving	conditions
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In cold gas spray, first coating layer does not behave as the following ones. The goal was obtain a fully dense coating with a medium-high thickness in one quick and effective step, without the necessity of changing spraying conditions from one layer to other.

With KINETICS 8000 from the HSU, a reduced 3^2 design of experiments has been used to define the spraying conditions. Four different spraying conditions were established:

	Temperature (°C)	Pressure (bar)
Condition A	780	38
Condition B	900	38
Condition C	1000	38
Condition D	1000	50

Table 19: HSU Temperature and pressure spraying conditions

The other spraying variables were kept as follows:

Spraying distance (mm)	60
Spraying angle (°)	90
Nozzle speed (mm/s)	235
Powder feeding rate (rpm)	3
Number of layers	4

Table 20: Spraying variables with Kinetics 8000

Figure 69, shows in a graphic a theoretical approximation, obtained thanks to the program provided by Kinetic spray solutions (<u>http://kinetic-spray-solutions.com/</u>) of particle's velocity and temperature at the impact moment with the used spraying conditions. The obtained values are independent of particle's morphology because it is not taking into account on this approximation.



Figure 69: Ti6Al4V window of deposition at lowest and highest spraying conditions

The black line represents the critical velocity for Ti6Al4V spraying powder, and the blue line (upper one) represents the erosion velocity, both determined by equation 3.

As it can be seen, particle's temperature and velocity at impact are higher as the spraying conditions increase, independently of particle's diameter

The simulation program also provides specific velocity and temperature data, allowing to compare numerically both spraying conditions.

The usefulness of this simulation program lies in the ability to determine the spraying conditions that will result in a coating obtention even before performing any spraying, reducing manufacturing costs.

It must be taken into account that powder morphology is a parameter which influences bonding mechanism and the properties of the obtained coating.

Particle's velocity and temperature, as well as its behaviour during flight and impact moment, are properties highly dependent of particle's morphology.

Angular shape particles have larger drag coefficient than spherical ones acquiring higher velocities in flight^[74]. This fact is positive because particles will reach faster its critical velocity fulfilling one of the necessary principles to produce the adhesion with the substrate.

One of the main problems is that surface area of the irregular particle does not acquire homogenous temperature, as what is happening with spherical particles. Some areas of the irregular particle will acquire certain temperature quicker than others, and if in flight time is also taken into account, a particle will have different levels of deformability, influencing the deposition efficiency.

Figure 70 shows a schematic representation on how the temperature reaches the particle surface, showing the heterogeneity of the process.



Figure 70: comparative of surface temperature between irregular and spherical spraying particles

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4.1. Ti6Al4V substrate

Figure 71 shows the SEM micrographies of the obtained spherical Ti6Al4V coatings onto Ti6Al4V substrate after metallographic preparation.



Figure 71: Ti6Al4V coatings with spherical Ti6Al4V spraying powder

The SEM micrographies of figure 66 correspond to the following parameters:

Pressure/Temperature	780°C	730°C	680°C
30 bar	А	D	No deposited coating
34 bar	В	E	No deposited coating
38 bar	С	F	No deposited coating

Table 21: Coatings parameters

As it is shown in table 22, those coatings obtained at the highest temperature present lower porosity and higher deposition efficiencies than the ones obtained at medium temperatures. Also, at the same temperature, porosity decreases with pressure increase. As it has been said before, an increment in pressure generates a higher particles velocity, which means, higher impact energy and more deformation and compaction. After the first particles impact onto the substrate, the following ones will deform more the already deposited ones, closing the existing pores and reducing the coating porosity. Intrinsically related with the porosity is the coating thickness or viceversa, for the same temperature, as the pressure increases thickness reduces.

Particles are more ductile at higher temperature, they deform more and thickness reduces, as well as porosity. With similar deposition efficiencies, thicker coatings have higher porosities

Spraying Conditions	Deposition Efficiency (%)	Thickness	Porosity (%)
780°C, 30 bar	86 ± 3	500 ± 25	2,1 ± 0,3
780°C, 34 bar	89 ± 3	492 ± 32	$1,1 \pm 0,2$
780°C, 38 bar	91 ± 2	405 ± 36	$0,9 \pm 0,1$
730°C, 30 bar	62 ± 2	691 ± 39	2,2 ± 0,4
730°C, 34 bar	75 ± 5	700 ± 17	$1,9 \pm 0,8$
730°C, 38 bar	87 ± 4	613 ± 18	$1,6 \pm 0,6$

Table 22: Coatings deposition efficiency, thickness and porosity



Figure 72: Variation of tensile ductility with temperature for Ti–6Al–4V at a nominal strain rate of $10^{-2} \text{ s}^{-1[75]}$

The increase in ductility due to the temperature, and the plastic deformation increase due to pressure, makes of the coating obtained at 780°C and 38 bar the optimum one at the range of studied spraying conditions. Although the thickness, in this case, is the thinnest, it has the lowest porosity and highest efficiency being most compact and dense.

As it has been explained before, first impinging particles or first coating layer behaves differently than the following ones. This difference in behaviour is due to the nature of spraying powder and substrate material. Hardness, thermal conductivity, hardening due impact, ductility or thermal softening are some of the properties which influence the behaviour of this first layer.

In the case of irregular Ti6Al4V the obtained efficiencies onto Ti6Al4V substrate under table 18 spraying conditions are:

Spraying Conditions	Deposition efficiency (%)
780°C, 30 bar	50 ± 4
780°C, 34 bar	47 ± 3
780°C, 38 bar	51 ± 2
730°C, 30 bar	49 ± 7
730°C, 34 bar	47 ± 7
730°C, 38 bar	50 ± 5
680°C, 30 bar	49 ± 9
680°C, 34 bar	47 ± 7
680°C, 38 bar	49 ± 8

Table 23: irregular Ti6Al4V deposition efficiencies onto Ti6Al4V substrate

In this occasion, all spraying conditions are in the same range of deposition efficiency being the highest the one obtained at 780 °C and 38 bars.

Trying to illustrate the difference between layers, a new experiment apart from the ones included in the experimental design, was developed. At the optimum conditions (780°C, 38bar) the number of deposited layers have been varied.

The experiment consists in four substrates sprayed with one, two, three and four layers respectively as figure 73 shown.



Figure 73: Simulation of multiple layer experiment

The four substrates were sprayed at the same time, programing the ABB robot which holds the spraying gun to spray one layer on all substrates, a second layer on three of them, a third layer on two of them and the fourth layer on just one of them, all consecutively to avoid changes in the spraying and ambient conditions. The obtained coatings after metallographic preparation are shown in figure 74



Figure 74: Optical microscope multilayer micrographies

Table 24 shows the efficiency, thickness and porosity of every coating

Coating onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
1 layer(A)	93 ± 2	215 ± 18	5,5 ± 0,6
2 layers (B)	92 ± 3	343 ± 28	6,2 ± 0,5
3 layers (C)	90 ± 5	481 ± 22	3,2 ± 0,7
4 layers (D)	89 ±2	585 ± 23	2,8 ± 0,5

Table 24: Multiple layer coatings properties of spherical Ti6Al4V

In all cases deposition efficiency is around 90%. Thickness gain between layers is about 160 microns and the porosity reduces as the thickness increases.

If only the lower layers are taking into account and not the last sprayed one (for the 2, 3 and 4 layers coating) the porosity reduces to a 2%, showing the pores elimination due

to the compression caused by the impinging particles. Porosity of the upper layer is very similar in all cases.

In this case, due to the same nature of substrate and spraying material, first coating layer behaves like the following ones.

For irregular Ti6Al4V based on the obtained results, the highest conditions were tested to carry out the same multilayer experiment as with the spherical Ti6Al4V

Coating onto Ti6Al4V	Efficiency (%)
1 layer	45 ± 4
2 layers	48 ± 5
3 layers	48 ± 3
4 layers	50 ± 2

Table 25 shows the obtained efficiency for each sample

Gained weight per layer is between 0,23 and 0,26 grams. Substrate and powder's nature is the same, so the main reason to not have obtained higher deposition efficiencies is that a high percentage of the particles are not reaching their critical velocity and therefore not bonding to the substrate. KSS simulation situates particles impact velocity under critical velocity line as it can be seen in figure 69.

Figure 75 shows graphically deposition efficiency evolution as the number of layers increase.

Table 25: Multiple layers coatings deposition efficiency for irregular Ti6Al4V



Figure 75: deposition efficiency as a function of number of layers

After the obtained results, the study and understanding of bonding mechanisms became more important to try to explain the impact behaviour of irregular particles.

Wipe-Test and Cavitation experiments

As consequence of the obtained results and the doubts that arises when bonding mechanism between particle/substrate in CGS is explained, wipe-test and cavitation experiments have been performed.

These experiments were done at Material Science department of Helmut-Schmidt-Universität (HSU) in Hamburg (Germany). After the obtained results from the experiments performed at the Thermal Spray Center, higher temperatures and pressures were tested at the CGS system of the HSU during the Phd stay.

HSU is equipped with a Kinetiks 8000 spraying gun (figure 76), has been modified by the research group to enlarge the types of materials that can be sprayed by CGS and reach higher temperatures and pressures.



Figure 76: Modified CGS gun Kinetics 8000

The highest temperature that the Kinetics 4000 can reach is 800°C and the highest pressure is 40 bars. With the kinetics 8000, 1100°C and 60 bars can be reached.

To obtain wipe tested samples, the substrate is fixed on a guillotine system, which frees the sample by remote control to fall under its own weight and in its trail, cross the gas+particle's beam. Figure 77 shows a scheme of this system.



Figure 77: Wipe test obtention system

Due to the previous experience of the HSU research group, and the previous experiments done at CPT two different conditions (table 26) were tested for wipe tests experiments, in order to analyse not only particle's impact morphology but also bond strength through cavitation test. In the case of irregular Ti6Al4V it must be taken into account that due to the irregular shape of the powder, the impact morphologies are not going to be as clear as with spherical powder since it is not possible to determine the previous real morphology.

Parameters	Test A	Test B
Temperature	780 °C	38 bar
Pressure	1000 °C	50 bar

Table 26: Wipe test spraying conditions with modified Kinetics 8000

For spherical Ti6Al4V three substrates were polished, titanium grade II, Al-7075-T6, AZ31 and lately Ti6Al4V substrate was grinded to have certain surface roughness and simulate real spraying conditions. In the case of irregular Ti6Al4V, with the exception of grinded Ti6Al4V substrate, the same substrates, with the same metallographic preparation were used.

Figure 78 shows free surface micrograph of the obtained spherical Ti6Al4V wipe test at 780 °C and 38 bar onto Titanium grade II. All particles are bonded to the surface; there are no imprints on the polished substrate surface which may indicate rebound, showing

that all particles had reach its critical velocity. In this case, particles are the ones which had experiment deformation due to the impact and not the substrate.



Figure 78: SEM micrographies of wipe test free surface

Figure 79 shows the obtained wipe test with irregular powder at 780 °C and 38 bar onto Titanium grade II. As before, all particles are bonded to the surface; no imprints on the polished substrate surface and no jets can be appreciated onto the substrate. In this case, as before, probably are the particles the ones which had experiment the deformation due to the impact but due to the irregular shape, it is not possible to determine with absolute certainty.



Figure 79: SEM micrographies of wipe test free surface

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Figure 80 shows spherical Ti6Al4V wipe test 75° tilted. Tilting allows to observe more clearly the interface substrate/particle, material displacement, particle's flattening and compression level or imprints depth if any particle has not adhere or jets formation.



Figure 80: SEM micrographies of wipe test tilted free surface

It can be seen with greater clarity the deformation that particles have undergone due to impact. Independently of particle size, jets have been formed.

Figure 81 shows two micrographies of the 75° tilted irregular Ti6Al4V wipe test sample



Figure 81: SEM micrographies of wipe test tilted free surface

Particles are lightly elevated on their limits from the substrate surface due to the deformation of the particle. It also can be appreciated how the substrate is also a little bit deformed due to impact.

When the highest temperature and pressure conditions are used (1000 °C and 50 bar) particles experiment higher deformation than before, but the mechanism seems to be similar as it can be observed in figures 82 and 83.



Figure 82: SEM micrographies of wipe test free surface at 1000°C and 50 bar



Figure 83: SEM micrographies of 1000°C and 50 bar wipe test tilted free surface

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Figures 84 and 85 shows the obtained wipetest at 1000 °C and 50 bar with irregular Ti6Al4V spraying powder. As it had happened with spherical powder, particles are more deformed and jets zones are bigger than before.



Figure 84: SEM micrographies of wipe test free surface at 1000°C and 50 bar



Figure 85: tilted SEM micrographies of 1000°C and 50 bar wipe test free surface

Due to the combined effect of higher temperature and pressure particles have higher ductility so they can deform more and also, its impact velocity is higher and particles are much more flattened than before (Figures 80 and 81).

At 1000 °C and 50 bar, particle impact velocity is 10% higher and particle temperature is 25% higher than at 780 °C and 38 bar for the studied powder (mean size of 35,6 μ m with a d₁₀=24,3 μ m and d₉₀= 49,3 μ m).

After the wipe test was analysed, cavitation test were performed under ASTM 32/10 standard.

To carry out the experiment, ultrasounds frequency must be set to 20 kHz. Wipe tested substrate is separated from the horn head 0,5 mm and the distilled water bath, must be between 20 and 25°C. It is important to take into account that the deposit must be completely clean to avoid impurities and make simpler the recovery of detached particles due to the process.

Figure 86 shows the SEM images of the 780°C and 38bar spherical Ti6Al4V sample obtained after 1,3,5,10,15,20 and 30 minutes cavitation. Starting from a reference point marked on the sample, always the same x and y point is analysed.



Figure 86: Cavitation test at different times onto 780°C and 38 bar wipe test

As it can be seen, after 30 minutes cavitation no particles remain bonded to the surface.

For the irregular Ti6Al4V sample at the same spraying conditions and cavitation times, micrographies showed in figure 87 were obtained.



Figure 87: Cavitation test at different times onto 780°C and 38 bar wipe test

As in previous case after 30 minutes cavitation no particles remain bonded to the surface.

For the most energetic conditions (1000°C, 50 bar), like in the previous case, the wipe test sample has been subjected to 1,3,5,10,15,20 and 30 minutes cavitation and the surface has been lately analysed. Figure 88 shows the SEM micrographies at different cavitation times for the spherical Ti6Al4V powder.



Figure 88: Cavitation test at different times onto 1000°C and 50 bar wipe test

When figures 86 and 88 are compared, the first thing that is noticed is that at 1000°C and 50 bar more particles remain bonded to the substrate during every cavitation period, and on the contrary to the experiment at 780°C and 38 bars, particles break before detach.

Figure 89 shows this phenomenon magnified. Rupture produces firstly at the particle's edges where there is no bond between particles and substrate (jets zone), and lately the rupture is produced by fatigue due to cavitation mechanism itself.



Figure 89: Adhered particles before testing (A) and cavitation test at 5 (B),15 (C) and 30 (D) minutes onto 1000°C and 50 bar wipe test

For the irregular Ti6Al4V sample at the same spraying conditions and cavitation times, micrographies showed in figure 90 are obtained.



Figure 90: Cavitation test at different times onto 1000°C and 50 bar wipe test

After 30 minutes cavitation, there are still particles bonded to the substrate surface.

If figure 87 and figure 90 are compared, the first thing that it is notice is that at 1000°C and 50 bar more particles remain bonded to the substrate during every cavitation period and in both cases, particles break down before detaching.

If both Ti6Al4V systems are compared and Cavitation test time is plotted against % of bonded particles, the graphics shown in figures 91 and 92 are obtained



Figure 91: % of Bonded particles during cavitation for spherical Ti6AL4V



Figure 92: % of Bonded particles during cavitation for irregularTi6AL4V

Due to the interest that involves bonding mechanism in Cold Gas Spray, modifications were made in cavitation's beaker system to recover the particles that were detached from the substrate. This idea came after having observed the existing footprints with

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ring shape form, left by the particles onto the substrate surface after cavitation. Figure 93 shows a random sample of these footprints left by spherical particles.



Figure 93: Substrate footprints left by spherical particles after cavitation test

As it can be observed, in all micrographies showing in figure 83, footprints follow the same pattern, an outside ring which seems to be the bond-zone particle/substrate.

This morphology is related with shear instabilities mechanism and particle deformation mechanism, which are extensively explained by T. Schmidt et al. in their article "From particle acceleration to impact and bonding in cold spray".

To corroborate this theory, detached particles were recovered, confirming the existence of a ring shape bonding zone (Figure 94).



Figure 94: detached particles after cavitation

For irregular Ti6Al4V, modified cavitation test was also used, but in this occasion, no particle was found. Nevertheless, substrate was analysed searching for the footprints left by the particles, and surprisingly, the same results were found.

It seems that particles behave similar at the impact moment independently of its shape. Areas with higher temperatures and deformations, allow the formation of the footprints on the substrate. Some examples of the footprints left by the irregular powder onto Titanium substrate are shown in figure 95.



Figure 95: footprints on substrate left by particles after cavitation

Particles deform upon impact, as it simulated by T. Schmidt et al in figure 96. The energy of the impact is transformed in deformation (in this case particle's deformation) and thermal energy, which is concentrated around impact point, increasing material's temperature and triggering bonding mechanism.



Figure 96: Single sequences of an impact^[76]

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The morphology of the recovered particles and its footprints for spherical Ti6Al4V (Figure 97) perfectly fits with the simulation showed in previous figure.



Figure 97: Detached particle and its footprint on substrate surface

Due to the substrate footprints and recovered particles morphology (spherical Ti6Al4V), EDS analysis of both structures were done (Figure 98 and 99).

The outside ring of the particles contains almost no traces of aluminium and vanadium, major alloying elements in Ti6Al4V. The main element is pure titanium.

When the central zone of the particle is analysed, the same elements composition than in the spraying powder appears.

On substrate's footprints opposite results were obtained. The ring is composed by Ti6Al4V and the central zone is pure titanium.



Figure 98: Detached particle DRS analysis



Figure 99: Substrate footprint EDS analysis

The hypothesis under consideration is that, due to the high energy with which particles impact onto the substrate, there is an increase in temperature that may cause microfusions at the adiabatic shear instabilities zone.

These microfusions create a high strength bonding between particle and substrate, causing the rupture in weaker zones and allowing material transfer between substrate/particle under cavitation processes.

Since one of the objectives of wipe test and later cavitation test is to find the optimal conditions for obtaining a well bonded coating, Ti6Al4V substrate have been also used since is one of the substrates under study.

The substrate has been prepared under the same conditions than it is prepared for coating spraying, grinded with 220 SiC paper.

Wipe test was performed at 1000°C and 50 bar pressure spraying conditions since bonding between particle and substrate is stronger at this conditions. Figure 100 shows the spherical Ti6Al4V wipe test free surface at these conditions. As in the previous case onto titanium grade II at 1000°C and 50 bar, particles are greatly deformed and no imprints could be observed onto the roughened substrate's surface.



Figure 100: wipe test free surface micrographies of at 1000°C and 50 bar onto Ti6Al4V

Figure 101 shows the cavitation test at different times. Comparing these micrographies with the ones shown in figure 88, particle loss is higher on the Ti6Al4V substrate. As with

grade II Titanium substrate, particles break before detaching, but it seems that particle bonding with Ti6Al4V substrate is not as strong as with titanium substrate.

Figure 102 shows the relationship between % of bonded particles and cavitation time.



Figure 101: Cavitation test at different times onto 1000°C and 50 bar wipe test

Ti6Al4V substrate is much harder than Titanium substrate, it deforms less due to impact which becomes on a weaker bonding.



Figure 102: % of Bonded particles during cavitation

At higher magnifications, it is possible to observe the fatigue failure surface distinguishing beachmark ridges (figures 103 and 104).



Figure 103: Beachmark ridges on Ti6Al4V particles after cavitation test



Figure 104: Cavitation test at higher magnifications

As in previous case, when no particle is remaining (Figure 104 H), a footprint with a ring shape form can be distinguished. In this case carry out an EDS analysis was not useful because substrate and spraying powder are both Ti6Al4V and it would be impossible to distinguish if corresponds to particle or substrate material.

After the obtained results with wipe-test and cavitation, the reduced 3² design of experiments defined for KINETICS 8000 gun for coatings obtention was performed (Tables 20 and 21).

Figure 105 shows the obtained spherical Ti6Al4V coatings onto Ti6Al4V substrate under the HSU spraying conditions.



Figure 105: Optical microscopy micrographies of Ti6Al4V coatings onto Ti6Al4V

DE, thickness and porosity of the obtained coatings are shown in table 27.

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	55 ± 2	250 ± 21	14
B - 900°C, 38 bar	65 ± 2	283 ± 18	11
C - 1000°C, 38 bar	64 ± 0	258 ± 13	6
D - 1000°C, 50 bar	57 ± 3	231 ± 14	3

Table 27:	Ti6Al4V	' coatings	properties
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As it can be observed in table 27, porosity is reduced as temperature and pressure increases. An increment in 220°C with the same pressure (A vs. C), reduces porosity in 58%. If the pressure is increased from 38 to 50 bar, porosity is reduced to half.
Figure 106 shows the obtained irregular Ti6Al4V coatings onto Ti6Al4V substrate with the same conditions than for spherical Ti6Al4V.



Figure 106: Optical micrographies of Ti6Al4V coatings onto Ti6Al4V

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	35 ± 2	149 ± 10	11 ± 5
B - 900°C, 38 bar	38 ± 2	174 ± 9	6 ± 4
C - 1000°C, 38 bar	38 ± 4	196 ± 11	3 ± 2
D - 1000°C, 50 bar	37 ± 2	157 ± 10	3 ± 2

Table 28: Ti6Al4V coatings properties

As it can be observed in table 28, as the temperature increases, porosity reduces. From A to B (780°C to 900°C) porosity is reduced to almost the half, and from B to C where

the temperature increase is 100°C, porosity is reduced to half. In return, an increment in pressure (C vs. D), does not have any significant influence in porosity.

Thickness increases with temperature increase, but it seems that this fact is not having any remarkable influence in deposition efficiency. As the pressure increases, thickness reduces because particles impact with higher energy, compacting the previous layers.

A the results of the coatings process obtention at different spraying parameters did not provide the expected results, an hypothesis that arose to explain these results was that spraying powder was oxidized due to over time and storage, creating an oxide layer which covered the particles. This oxide layer has mainly two drawbacks:

- Since the oxide layer is a ceramic, it protects the metallic core of heating during flight. This means lower temperature at the impact moment (less ductility).
- One of the main properties of the ceramics is its hardness. Ceramics are hard but also brittle, so at impact moment, part of the energy will be lost in breaking the oxide layer, so there is less energy for bonding mechanisms.

In order to test this hypothesis, other spherical Ti6Al4V spraying powder batch was ordered to the same supplier with the same composition, particle distribution (-45+25µm), microstructure and oxygen content. Unfortunately, for irregular Ti6Al4V powder it was not possible to acquire a new batch to test.

The same parameters as in the previous case were used (Table 19 and 20), obtaining the coatings showed in figure 107.



Figure 107: Optical micrographies of new Ti6Al4V coatings onto Ti6Al4V

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	83 ± 4	775 ± 38	16 ± 4
B - 900°C, 38 bar	82 ± 2	637 ± 38	13 ± 4
C - 1000°C, 38 bar	79 ± 4	718 ± 30	9 ± 3
D - 1000°C, 50 bar	83 ± 5	636 ± 27	4 ± 2

Table 29: Non-oxidized Ti6Al4V coatings properties

In terms of thickness, from A to B, as the temperature increase, the thickness do it also, which indicates that more particles adhere (porosity is in the same range). From B to C, the thickness has been reduced while efficiency remains and porosity reduced to almost half. This thickness reduction responds to a higher compaction of the coating due to a higher deformation of the particles (ductility is higher at higher temperatures).

From C to D where only the pressure has change, porosity was again reduced to half which means, as in the previous case, a higher compaction of the coating. The only

variable which does not respond as it should, is the efficiency. Several substrates have been coated to ascertain these results, but in all cases the same results have been obtained.

Despite a higher compaction of the coating due to a higher deformation of the particles, it is possible that some of them have reached its erosion velocity and they are not bonding to the substrate/coating.

In general, deposition efficiency has increased considerably up to 80% (it means between 25 and 50% increase depending on the spraying conditions) and thickness has increase between 125 and 200% depending on the parameters.



Porosity followed the same trend as with the former spraying powder.

Graphic 1: Deposition Efficiency comparison between former and new Ti6Al4V spraying powder



Graphic 2: Thickness comparison between former and new Ti6Al4V spraying powder

So far, despite having sprayed at the highest equipment potency in terms of pressure and temperature, no satisfactory results have been achieved. Deposition efficiencies were still low and porosity was remaining excessively high. Higher particle velocities or higher particle temperature before impacting is required (or both). There are two methods to achieve these aims:

- Changing the nozzle.
- Using He instead of N₂

Firstly, a D50 nozzle has been used in order to replace the standard one (D24 nozzle). This nozzle is longer than the standard one (D50 Divergent section length is almost 40% longer than the one of D24) and the radius of the thought is also bigger (22% bigger), allowing that particles reach higher temperatures and velocities.

In both previous cases, better results were obtained at the highest temperature and pressure, so only the most energetic spraying conditions were used.

Temperature (°C)	950
Pressure (bar)	50
Spraying distance (mm)	60
Spraying angle (°)	90
Nozzle speed (mm/s)	235
Powder feeding rate (rpm)	3
Number of layers	4

Table 30: TI6Al4V spraying parameters with D50 Nozzle

Figure 108 shows the obtained window of deposition with Kinetics solution simulation program under these spraying conditions:



Figure 108: Window of deposition for 950°C, 50 bar pressure and D50 Nozzle

As it can be seen, particles are more separated depending on its diameter and their impact velocities are between 250 and 500 m/s over the simulated critical velocity.

when this graphic is compared with the previous simulation with D24 nozzle (Figure 69), where particles impact velocity were slightly over critical velocity, and the difference between particle's size was not as pronounced as in this case, iIt must be noticed that with D50 nozzle, particles are colder than before, but faster. Particle's temperature is already considered when the critical velocity is calculated.

Optical microscopy micrograph of the cross section of the coating is presented on figure 109.



Figure 109: Ti6Al4V coating onto Ti6Al4V substrate sprayed with D50 nozzle

As it is shown in table 31 efficiency almost reached 90% and porosity was reduced below 2%

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
D50,950°C, 50 bar	88 ± 2	611 ± 21	<2

Table 31: Ti6Al4V coating properties

The second test to achieve the desired results (higher DE and lower porosities than with D"\$) was to use Helium instead of Nitrogen as propellant gas. Cold spraying with helium gives better performance than with nitrogen even without gas heating mainly because its sonic velocity is three times the nitrogen one.

Theoretically, particles behave differently depending on their mass and the velocity of the steaming gas in which they are immersed. As higher the velocity of the streaming gas is, higher is the difference between particles (Figure 110).

In Cold Gas Spray when helium is used as streaming gas and particle size distribution of the powder is not extremely narrow, clogging phenomena can appear.



Figure 110: Simulation of particle velocity and temperature before impact

Several temperatures and pressures were tested, but in all cases nozzle clogging appeared due to size distribution.

To improve the process, powder was sieved to obtain a narrower particle size distribution. This would make that particles behave similar into the gas flow, avoiding collisions between them, which can produce trajectory deviations and develope clogging effects.

Once the powder was sieved, it was possible to spray at 900°C and 30 bar without clogging. The used nozzle was the standard one (D24) and the other parameters were kept constant. Figure 111 shows the obtained coating.



Figure 111: Ti6Al4V coating sprayed with Helium

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
D24,900°C, 30 bar	99 ± 1	813 ± 24	< 0,1

Table 32: Ti6Al4V coating properties

The maximum deposition efficiency was reached and the porosity was highly reduced (below 0,1%)

<u>Nanoindentation</u>

Nanoindetation test has been done in order to analyze the evolution of the hardness from the substrate until the coating surface for irregular Ti6Al4V coatings.

Applied load was 5gf and the separation betwwen nanoindentations is 25 $\mu m.$

Ti-6Al-4V substrate has a hardness of 358 ± 8 HV while after spraying on it, in the closest zone to the interface with the coating, it has a hardness of 445 ± 15 HV. On coating, the hardness depends on where the nanoindentation is done. Closer to interparticle zone, where the deformation is higher, hardness increases due to the

impact deformation hardening. But when the indentation is done closer to pores or to not binded zones, hardness reduces.

Figure 112 shows a matrix of 7×15 nanoindentations done onto the coating obtained at 38 bar and 780°C.

The obtained hardness result of the irregular sprayed coating was 494 ± 70 HVN, which could mean two things when it is compared with the hardness of the irregular powder before spraying (490 ± 70 HVN).

No hardening due to deformation has been produced

The reduced hardness values of some indentations due to porosity, low adherence or being in an interparticle zone, is high enough to reduce the global value of the coating's hardness



Figure 112: Nanoindentations onto irregular Ti6Al4V coating onto Ti6Al4V substrate

4.2. Al-7075 Substrate

The same spraying conditions as for Ti6Al4V substrate were used (table 18). Figure 113 shows the obtained spherical Ti6Al4V coatings onto Al-7075-T6 substrate after metallographic preparation.



Figure 113: Ti6Al4V coatings onto Al-7075-T6 substrate

As it can be observed in figure 113, no homogeneous (or very erode) coating has been formed. At the highest temperatures and pressures, more particles were adhered, and some clusters were formed, but not in the enough amount to form a coating and cover the hole substrate surface.

Al-7075 substrate hardness is 50% lower than Ti6Al4V substrate hardness and 38% of Ti6Al4V spraying powder hardness.

To obtain a coating, not only the hardness must be taking into account. Substrates with high thermal conductivity dissipates the heat produced by the particle impact as well as particle's temperature at impact moment and the absorbed heat due to the streaming gas easily than low thermal conductivity substrates. The formation of adiabatic shear instabilities to form a coating is hindered because impact zone does not reach the

required temperature. This effect leads either to lower deposition efficiency or the no obtention of a coating.

Al-7075-T6 thermal conductivity is almost 20 times higher that Ti6Al4V thermal conductivity (130 W/mK vs. 6,7 W/mK).

Since no coating has been formed, only the deposition efficiency can be measure.

Spraying Conditions	Deposition efficiency
780°C, 30 bar	0
780°C, 34 bar	11,3
780°C, 38 bar	0
730°C, 30 bar	1,2
730°C, 34 bar	0
730°C, 38 bar	7,7
680°C, 30 bar	0
680°C, 34 bar	0,13
680°C, 38 bar	0

Table 33: Ti6Al4V deposition efficiency onto Al-7075-T6 substrate

Figure 114 shows the micrographies of the obtained irregular Ti6Al4V coatings onto Al-7075-T6 substrate after metallographic preparation.



Figure 114: Ti6Al4V coatings onto Al-7075-T6 substrate

For all spraying conditions an homogeneous coating was produced.

It can be appreciated that the last layer is much more porous than the previous ones. This effect is because onto this layer no subsequent compaction has been occurred. To measure the porosity of the coatings, it must be taken into account which is the final application of the piece. If it is going to be mechanized, the last layer will disappear and it should not be take into account when porosity is measured. In this case, although the theoretical final application of these coatings needs mechanization, the entire coating's porosity was measured.

Table 34 shows the efficiency, thickness and porosity of the obtained coatings.

Spraying Conditions	Efficiency %	Thickness µm	Porosity %	Porosity without last layer %
780°C, 30 bar	36 ± 7	321 ± 22	7 ± 1	4 ± 1
780°C, 34 bar	36 ± 5	307 ± 21	6 ± 2	1,5 ± 0,5
780°C, 38 bar	37 ± 6	333 ± 17	6 ± 1	1 ± 0,3
730°C, 30 bar	34 ± 8	322 ± 24	8 ± 4	4 ± 1
730°C, 34 bar	35 ± 4	321 ± 24	5 ± 3	2 ± 1
730°C, 38 bar	36 ± 2	345 ± 24	5 ± 4	1 ± 2
680°C, 30 bar	30 ± 7	306 ± 26	10 ± 5	5 ± 2
680°C, 34 bar	33 ± 6	308 ± 28	9 ± 2	4 ± 1
680°C, 38 bar	33 ± 8	365 ± 30	6 ± 3	2 ± 1

Table 34: Irregular Ti6Al4V coatings onto Al-7075-T6 properties

By representing graphically deposition efficiency and porosity with respect to spraying conditions, clear trendlines are observed as it can be seen in figure 115.

At the same temperature when pressure increases, porosity was reduced and deposition efficiency is lightly increased.



Figure 115: D.E. and porosity at different spraying conditions for irregular Ti6Al4V coatings onto Al-7075-T6

Taking into account the properties of the obtained coatings, the best one in terms of efficiency and porosity is the one obtained at 780°C, 38 bar.

As it has been observed, substrate has a high influence on the first layer, making coating growth onto AI-7075-T6 difficult.

In previous case (onto Ti6Al4V substrate) the best conditions were 780°C and 38 bar. These spaying conditions allow Ti6Al4V to acquire higher temperature (more ductile) and higher velocities.

Due to this reason, as with Ti6Al4V substrate, four Al-7075-T6 substrates per powder were sprayed with one, two, three and four layers respectively to see the influence that substrate creates. Table 35 shows the obtained deposition efficiencies for spherical and irregular Ti6Al4V coatings

Coating onto Al-7075-T6	Efficiency sph. (%)	Efficiency irr. (%)
1 layer (A)	15 ± 3	9 ± 4
2 layers (B)	33 ± 4	23 ± 5
3 layers (C)	44 ± 4	30 ± 4
4 layers (D)	52 ± 3	34 ± 6

Table 35: Multiple layers coating efficiencies

Although efficiency has increased as the number of layers increase, coatings were highly porous and irregular due to the erosion in both cases. Tests were repeated but the same results were achieved.

Figure 116 shows graphically the evolution of the coatings for both spraying powders



Figure 116: Deposition efficiency per layer for spherical Ti6Al4V (black line) and irregular Ti6Al4V (red line)

If the gained weight per layer is represented graphically as it can be seen in graphic 3, it can be observed a substantial difference as the coating grows, between layers and between spraying powders.



Graphic 3: gained weight per layer

Spherical Ti6Al4V deposited mass on the second layer was 200% over the first one. For the third and the fourth layer, the deposited mass in comparison with the previous one is stabilizing around 130% and 120% more.

For irregular Ti6Al4V, the weight gain was 165% from the first to the second layer and then it was reduced to 32% and 13% for the third and fourth layer respectively.

The optimal coating obtained with irregular Ti6Al4V powder has been subjected to several tests.

<u>Abrasive wear - Rubber-wheel</u>

The abrasive wear was evaluated according to the ASTM G65-00 standard The obtained results with a load of 50 N are shown in table 37

Time (min)	Abrasive wear rate (mm ³ /Nm) Al-7075-T6	Abrasive wear rate (mm³/Nm) Ti6Al4V
1		3,16E-04
2	3,32E-04	3,41E-04
3		3,58E-04
4	3,53E-04	3,65E-04
5		3,66E-04
6	3,68E-04	3,82E-04
7		3,68E-04
8	3,62E-04	3,67E-04
9		3,71E-04
10	3,58E-04	3,69E-04
15	3,62E-04	3,67E-04
20		3,52E-04
25		3,40E-04
30		3,29E-04

Table 36: example of abrasive wear rates for AI-7075-T6 substrate and Ti6AI4V coating

The abrasive wear rate of Ti6Al4V coating is similar to the one of Al-7075-T6 substrate, which means high decohesion of the coating. Particles are not well bonded and the material loss is extremely high. SiO₂ particles are tearing off Ti6Al4V particles of the coating and producing a high mass loss. Figure 117 shows graphically a comparative between both abrasive wear rates.



Figure 117: Al7075-T6 substrate and Ti6Al4V coating abrasive wear rates

On rubber-wheel test, the cohesion between particles plays a very important role and has a big influence. Anyway, looking at the last layer, which is very porous, it should have been considered the mechanization of the coating and thus probably the abrasive wear rate would have been lower.

<u>Sliding wear. Ball on disc</u>

Sliding wear rate has been tested onto the optimum coating through ASTM G99-03 standard. The assay was performed in a closed chamber at controlled temperature and humidity (T = 25°C and RH \leq 20%). The used ball as frictional torque is made of stainless steel, the load at the arm is 5 N and the diameter of the path that the ball describes is 14 mm. The sample under study has a rotation speed of 131 rpm (linear velocity 0.11 m / s). The covered distance during the test is set at 1000 m.

The obtained results for the friction coefficient and volume loss are as follows:

Material	Friction coefficient (µ)	Volume loss (mm ³)
AI-7075-T6 substrate	0,409	3,23 ± 0,4
Ti6Al4V coating	0,487	5,6 ± 0,5,

Table 37: Friction wear coefficient and volume loss

Coating friction coefficient is higher than substrate coefficient, as well as volume loss, which means that the friction wear protection that Ti6Al4V coating obtained at 780°C and 38 bar offers to the substrate, is low, and it does not serve as wear protection. The obtained value for the coating is due to the low cohesion that particles have. As the stainless steel ball runs on the sample, is ripping out particles which act also as friction body increasing friction wear coefficient.

Figure 118 shows the obtained path left by the stainless steel ball onto Ti6Al4V coating.



Figure 118: ball on disc path on Ti6Al4V coating onto Al-7075-T6 substrate.

A confocal image of the coating and the substrate were done, obtaining the figures shown in figure 119.



Figure 119: Ball on disc path onto AI-7075-T6 substrate and Ti6Al4V coating

Nanoindentation

A matrix of 7×15 nanoindentations has been done onto the optimal substrate under the same load conditions as in previous case with Ti6Al4V substrate (Figure 120). On Al-7075-T6 substrate, the hardness increases from 178 ± 8 HV to 225 ± 10 HV due to cold working. In the case of the coating, there are differences in the nanohardness depending on where in the coating the nanoindenter is indenting. Closer to interparticle zone, where the deformation is higher ,and where a strong bonding has been produced, the hardness increases due to the impact deformation hardening. A higher hardness is also been observed when the nanoindentation is on the middle of a particle. Nanoindentations closer to pores or to not binded zones show a lower hardness.

The obtained result for the coating was 429 ± 158 HVN. A lower value and a much higher variability than before

Coating is much more porous than before and adherence between particles is lower.



Figure 120: Nanoindentation matrix onto 780° and 38 bar Ti6Al4V coating

Wipe-Test and Cavitation experiments

As in the previous case, two different conditions were tested for the wipe tests, in order to analyse not only particle's impact morphology but also bond strength through cavitation test.

	Test A	Test B
Temperature	780 °C	38 bar
Pressure	1000 °C	50 bar

Table 38: Wipe test spraying conditions with modified Kinetics 8000

AI-7075-T6 substrate was polished to have a clear vision of the impact morphology.

Figure 121 shows the free surface of the obtained wipe test at 780 °C and 38 bar, while figure 122 shows the tilted surface.



Figure 121: SEM micrographies of wipe test free surface



Figure 122: SEM micrographies of wipe test tilted free surface

Figure 122 shows SEM micrographies of tilted sample, where jets have been formed on the substrate and not on the particle as in previous case. On the higher magnification micrograph of the same figure, jets of substrate material can be clearly observed.

With irregular Ti6Al4V powder, figure 123 shows the free surface of the obtained wipe test at 780 °C and 38 bar, while figure 124 shows the tilted surface to be able to observe how deep the particles have penetrate onto the substrate besides interface substrate/particle and formed jets.



Figure 123: SEM micrographies of wipe test free surface



Figure 124: SEM micrographies of wipe test tilted free surface

As it can be seen in the lower magnification micrograph of figure 123, some particles are missing so already from the first moment, it is possible to determine that deposition efficiency is going to be affected. On the high magnification micrograph, jets on substrate surface can be observed.

Figure 124 shows SEM micrographies of tilted sample. Substrate has been deformed by the impact, forming jets and mass displacement.

When 1000 °C temperature and 50 bar pressure are used, wipe test surface morphologies with spherical Ti6Al4V, shown in figures 125 and 126, are obtained.



Figure 125: SEM micrographies of wipe test free surface



Figure 126: SEM micrographies of wipe test tilted free surface

Substrate's surface suffers higher deformation than before. Particles have a higher velocity going deeper into the substrate and suffering themselves higher deformation due to ductility increase. A greater amount of material is moved, hence the larger size of the jets.

For irregular Ti6Al4V powder, at 1000 °C and 50 bar pressure spraying conditions, the morphologies showed in figures 127 and 128 were obtained.



Figure 127: SEM micrographies of wipe test free surface



Figure 128: SEM micrographies of wipe test tilted free surface

As it happened with the spherical powder, particles deform the substrate and remain embedded in it with a weaker bond compared to Ti6Al4V substrate.

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After the wipe test samples were analysed, cavitation test were performed under ASTM 32/10 standard. Figure 129 shows the obtained cavitation test micrographies at 1,3,5,10,15,20 and 30 minutes onto 780°C and 38 bar wipe test.



Figure 129: Cavitation test at different times onto 780°C and 38 bar wipe test

After 30 minutes of cavitation test no particles remained bonded to the surface. Surface was too damaged to be able to find the exact coordinates of the zone under study.

For irregular Ti6Al4V spraying powder wipe test sample at 780°C and 38 bar pressure, the same cavitation test conditions have been employed (Figure 130).



Figure 130: Cavitation test at different times onto 780°C and 38 bar wipe test

After 20 minutes cavitation, no particles remained bonded to the surface. Surface zone under study was too impaired due to cavitation that it was not possible to recognize the exact zone of study.

For the most energetic conditions (1000°C, 50 bar), like in the previous case, wipe test sample was subjected to 1,3,5,10,15,20 and 30 minutes cavitation and the surface has been lately analysed. Figure 131 shows the SEM micrographies of the spherical Ti6Al4V powder wipe test sample.



Figure 131: Cavitation test at different times onto 1000°C and 50 bar wipe test

Between 20 and 30 minutes cavitation, all particles detached from substrate surface,

The cavitation evolution for spherical Ti6Al4V wipe test at 780°C and 38 bar and 1000°C and 50 bar is very similar. Although at 1000°C and 50 bar particles are deeper anchored into the substrate, it seems that they were not strongly bonded than the ones sprayed at 780°C and 38 bar.

Figure 132 shows graphically the comparison between cavitation time and % of bonded particles.



Figure 132: % of bonded particles during cavitation for spherical Ti6Al4V both spraying conditions

For both cases, on contrary to what happened with Ti or Ti6Al4V substrate, particles do not break before detaching.

In this occasion no particles were recovered during cavitation experiment, and since substrate is strongly affected due to cavitation, no footprints were remained on substrate's surface.

At 1000 °C temperature and 50 bar pressure, the surface morphologies for irregular Ti6Al4V after cavitation are shown in figure 133.

Like in the previous case, wipe test sample has been subjected to 1,3,5,10,15 and 20 minutes cavitation and the surface has been lately analysed.



Figure 133: Cavitation test at different times onto 1000°C and 50 bar wipe test

After 20 min cavitation, no particles remained bonded to the surfaces.

Cavitation behaviour of irregular Ti6Al4V wipe test sample is very similar at 780°C and 38 bar and at 1000°C and 50 bar. Although at 1000°C and 50 bar particles are deeper anchored into the substrate, they do not appear to be strongly bonded than the ones at 780°C and 38 bar, as it had happened with the spherical Ti6Al4V onto the same substrate.

Figure 134 shows graphically a comparison between cavitation time and % of bonded particles.



Figure 134: % of bonded particles during cavitation for both spraying conditions

Due to irregular morphology, particles do not contact with substrate's surface in only one point at impact moment as it happened with spherical morphology; they do it in several points at the same time, so the impact energy is distributed and particles are not so deep introduce into the substrate as the spherical ones. It must be also taken into account surface oxidation layer of the powder and substrate.

This fact makes that they detach from the substrate surface easily than the spherical ones.

After the obtained results with wipe-test and cavitation, the experiment design for coating obtention defined for the KINETICS 8000 (Table 20 and 21) was carried out.

Figure 135 shows the obtained spherical Ti6Al4V coatings onto AI-7075-T6 substrate.



Figure 135: Optical micrographies of Ti6Al4V coatings onto Al-7075-T6

Table 39 shows the efficiency, thickness and porosity of the obtained coatings

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	29 ± 4	194 ± 18	19 ± 7
B - 900°C, 38 bar	41 ± 2	243 ± 10	13 ± 5
C - 1000°C, 38 bar	49 ± 2	219 ± 13	9 ± 3
D - 1000°C, 50 bar	33 ± 2	167 ± 14	4 ± 1

Table 39: Ti6Al4V coatings properties onto Al-7075-T6

As it can be observed, as the temperature and the pressure increases, porosity reduces. An increment in 220°C with the same pressure (A vs. C), reduces porosity in 32%. If the pressure is increased from 38 to 50 bar, porosity is reduced less than a half. In terms of thickness, from A to B, as the temperature increase, thickness does it also, which indicates that more particles adhere. From B to C, thickness has been reduced while efficiency increases a little bit and porosity is reduced in a 31%. This thickness reduction, as in the previous case, responds to a higher compaction of the particles, and therefore the coating.

From C to D where only the pressure has change, porosity is reduced more than half which means, as in the previous case, a higher compaction of the coating. Like with Ti6Al4V substrate, efficiency reduces as the pressure increases. As temperature and pressure increases, particles acquire higher velocities, so they can exceed its erosion velocity and although they compact the coating, it may not come to adhere to the surface, reducing the efficiency regarding to the previous coating.

With Al-7075-T6 it must be also taking into account the passivation layer, which is all over the substrate surface and protects it from further oxidation in most environments. It is a tough resistant oxide, (Al_2O_3) and even though substrates are grinded before spraying, this layer is formed almost immediately.

Figure 136 shows the obtained irregular Ti6Al4V powder coatings onto Al-7075-T6 substrate at the same spraying conditions



Figure 136: Optical micrographies of Ti6Al4V coatings onto Al-7075-T6

Table 40 shows the efficiency, thickness and porosity of the obtained coatings

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	31 ± 2	123 ± 9	29 ± 5
B - 900°C, 38 bar	32 ± 2	148 ± 11	18 ± 4
C - 1000°C, 38 bar	29 ± 3	172 ± 11	12 ± 4
D - 1000°C, 50 bar	31 ± 2	144 ± 7	7 ± 2

Table 40: Ti6Al4V coatings properties onto Al-7075-T6

An increment in temperature produces porosity reduction. From A to B there is a 37% reduction and from B to C there is a 33% porosity reduction. There is also a 42% porosity reduction as pressure increases (C to D),

Although between the lowest spraying conditions and the highest ones, the porosity has been reduced in a 76%, 7% porosity is still really high for the theoretical final application. Deposition efficiency could not be increased more than 32%.

In the multiple layers previous experiment, the first coating layer had a very low efficiency. This oxide layer, in addition to the reasons before explained, contributes to this phenomenon.

The second spherical Ti6Al4V powder was also tested with Al-7075-T6 substrate, to see if the coating obtention behaves as before. The same parameters as in the previous case were used (Table 19 and 20), obtaining the coatings shown in figure 137.



Figure 137: Optical micrographies of new Ti6Al4V coatings onto Al-7075-T6

With the non-oxidized powder, properties have improved markedly as it can be notice in table 41.
Ti6Al4V onto Al-7075-T6	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	40 ± 4	496 ± 41	22 ± 3
B - 900°C, 38 bar	54 ± 1	476 ± 32	16 ± 3
C - 1000°C, 38 bar	56 ± 1	610 ± 21	7 ± 2
D - 1000°C, 50 bar	70 ± 1	546 ± 17	3 ± 2

Table 41: Non-oxidized Ti6Al4V coatings properties

Efficiency has increased considerably up to 70% at the highest temperature and pressure (it means between 37 and 112% increase depending on the spraying conditions) and thickness has also increase between 155 and 230% depending on the parameters.

Porosity has followed the same trend as with the former spraying powder.



Graphic 4: Deposition Efficiency comparison between former and non-oxidized Ti6Al4V spraying powder



Graphic 5: Thickness comparison between former and new Ti6Al4V spraying powder

In terms of efficiency and porosity, the best coating is the one obtained at 1000°C and 50 bar pressure. Thickness due to deformation and compaction is around 10% lower than the one obtained at 1000°C and 38 bar, but efficiency is 25% higher and porosity is reduced to more than half.

With D24 nozzle, the maximum obtained deposition efficiency was obtained at 1000°C and 50 bar, and it was 70% with 3% porosity. As in previous case, D50 nozzle has been used in order to obtain better deposition efficiencies and lower porosities. Spraying conditions are already showed on table 30.

The obtained coating is shown in figure 138. Deposition efficiency has increased up to 82% and porosity is reduced to 2%. Table 42 shows the characteristics of the obtained coating.



Figure 138: Ti6Al4V coating onto Ti6Al4V substrate sprayed with D50 nozzle

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
D50,950°C, 50 bar	82 ± 3	568 ± 26	<2

Table 42: Ti6Al4V coating onto Al-7075-T6 properties

The properties of the obtained coating are in the same range than the ones of the Ti6Al4V coating onto Ti6Al4V substrate with the same spraying conditions. The kinetic energy that particles contain at impact moment, due to the influence of D50 nozzle, is high enough to break the oxide layer, which protects the substrate and bond to the surface.

Despite the great improvement of the coating properties, Helium was also used as propellant gas in an attempt to further improve these properties. The obtained coating is shown in figure 139.



Figure 139: He sprayed Ti6Al4V onto Al-7075-T6

As a result of the experiment, the maximum deposition efficiency has been reached and the porosity has been reduced to the max as it can be seen in table 43.

Ti6Al4V onto Al-7075-T6	Efficiency (%)	Thickness (µm)	Porosity (%)
D24,900°C, 30 bar	98 ± 2	711 ± 24	<0,1

Table 43: Ti6Al4V coating properties

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Ti6Al4V COATINGS

4.3. AZ31 Substrate

Unfortunately, when the 3² experimental design has been performed, spraying the samples, as what happened with AI-7075-T6 substrates, no homogeneous coating have been obtained, and with the exception of the coatings obtained at the at the highest spraying conditions (780°C and 38 bar), very low efficiencies have been obtained.

AZ31 hardness is close to 1/3 of Al-7075-T6 hardness, and it has 2/3 of its thermal conductivity. (Ti6Al4V Thermal conductivity is almost 15 times smaller than Al-7075-T6). It should also be noted that AZ31 does not create a passivity layer as fast as Aluminum and although it is oxidized very quickly, the formed oxide is not as continuous as Al_2O_3 layer.

Magnesium alloys, particularly AZ31, presents a highly plastic behaviour due to the sliding mechanisms and microstructural characteristics^[77,78].

As particles impact onto substrate surface, it becomes more resistant to plastic deformation, due to strain hardening. This characteristic in combination with thermal conductivity makes AZ31 an intermediate material between the Ti6Al4V and Al-7075-T6 for Cold Spray.

The combination of these effects make that theoretically, the first layers should have a higher deposition efficiency than in the case of Al-7075-T6 substrate.

Figure 140 shows the obtained micrographies of the coatings obtained under the spraying conditions of table 18 with irregular Ti6Al4V powder after metallographic preparation.



Figure 140: Ti6Al4V coatings onto Al-7075-T6 substrate

For all spraying conditions a homogeneous coating has been formed.

As with Ti6Al4V / Al-7075-T6 system, the last layer of the obtained coatings is much more porous than the previous ones.

Table 44 shows the efficiency, thickness and porosity of the obtained coatings.

Spraying Conditions	Efficiency %	Thickness µm	Porosity %
780°C, 30 bar	42 ± 5	494 ± 33	9 ± 3
780°C, 34 bar	40 ±6	471 ± 23	7 ± 4
780°C, 38 bar	41 ± 4	476 ± 15	4 ± 2
730°C, 30 bar	43 ± 7	582 ± 26	5 ± 2
730°C, 34 bar	40 ± 5	539 ± 19	5 ± 2
730°C, 38 bar	41 ± 4	515 ± 16	4 ± 1
680°C, 30 bar	42 ± 4	529 ± 23	10 ± 3
680°C, 34 bar	38 ± 6	521 ± 18	8 ± 3
680°C, 38 bar	40 ± 4	497 ± 31	7 ± 2

Table 44: Irregular Ti6Al4V coatings onto Al-7075-T6 properties

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When deposition efficiency and porosity are represented against spraying conditions, clear trendlines are observed for porosity but not for efficiency as figure 141 shows. At the same temperature, porosity reduces and DE it was maintained in the same range.



Figure 141: D.E. and porosity at different spraying conditions for AZ31

Seeing that in terms of D.E. and porosity the coatings obtained at conditions 780°C-38 bar, 730°C-30 bar, 730°C-34 bar and 730°C-38 bar are comparable (Figure 42), the best one seems to be the one obtained at 780°C and 38 bar pressure. It must be also taking into account that at higher temperatures, spraying material is more ductile, and the compaction will be better with higher pressures.



Figure 142 : optimum coatings at higher magnifications

With the optimum spraying parameters, the influence of the substrate in the coating growth has been studied layer per layer.

Figure 143 shows the polished cross section micrographies of the obtained coatings with spherical Ti6Al4V powder.



Figure 143: Multiple layers spherical Ti6Al4V coatings onto AZ31

Table 45 shows the properties of the obtained coatings

Coating onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
1 layer(A)	67 ± 9	174 ± 28	18 ± 6
2 layers (B)	77 ± 9	496 ± 40	7 ± 4
3 layers (C)	79 ± 6	564 ± 39	11 ± 5
4 layers (D)	76 ± 5	774 ± 39	7 ± 3

Table 45: Multiple layers coating properties

Deposition efficiency, increases from the first to the second layer in a 10% and it is maintained for the following layers. Porosity is in all cases high. Although a high percentage of particles are adhering, they do not have enough energy to compact the previous layer besides bonding.

Table 46 shows the obtained deposition efficiencies when irregular Ti6Al4V powder is used.

Coating onto AZ31	Efficiency (%)
1 layer	35 ± 8
2 layers	39 ± 6
3 layers	41 ± 6
4 layers	42 ± 5

Table 46: Multiple layers coating efficiencies at 780° and 38 bar

For all layers, the gained weight is practically the same, it increases lightly as the substrate reduces its influence, but it keeps constant layer per layer as it can be observed in figure 144.



Figure 144: D.E. variation depending on the number of layers for irregular Ti6Al4V

Wipe-Test and Cavitation experiments

The spraying parameters for wipe-test obtention were the same ones than with Ti6Al4V and Al7075-T6 substrate (Table 34). AZ31 substrate was mirror polished to be able to observe if dislocation mechanisms takes place, in addition too, of course, impact morphologies.

Figure 145 shows the free surface of the obtained wipe test at 780 °C and 38 bar, while figure 146 shows a backscattered SEM micrograph, also from the free surface, to clearly observe the produced twinnings due to particles impacts.



Figure 145: SEM micrographies of wipe test free surface



Figure 146: Slip planes and twinnings onto AX31 surface due to impact

Immediately after impact, deformation mechanism onto AZ31 substrate takes place. Firstly the substrate is deforming through slipping planes, but if the deformation energy is too high and fast as it happens in Cold Gas spray impacts, the material is not able to absorb it through slipping planes and twinning deformation mechanisms takes places

Figure 147 shows SEM micrographies of 70° tilted wipe test.



Figure 147: Wipe test tilted micrographies

Figure 147 shows clearly the slipping planes and twinnings that surrounds the impacted particles as well as the formed jets of substrate material. As it has been explained before, AZ31 is hardened by deformation. It seems that as higher the deformation is, less could the particles penetrate independently of its size.

When 1000 °C temperature and 50 bar pressure were used, the surface morphologies shown in figures 148 and 149 are obtained.



Figure 148: SEM micrographies of wipe test free surface

SEM micrographies of figure 148 are a combination of secondary and backscattered electrons to be able to observe the deformation mechanism which surround the particles.

Figure 149 shows tilted sample micrographies. In this case, particles are deeper embedded into substrate surface, displacing a greater amount of material, something logic due to spraying conditions.



Figure 149: SEM micrographies of wipe test free surface

Cavitation test is a good method to test particle/substrate bond strength It was performed as before, at the lowest and the highest spraying conditions.

On 780°C and 38 bar wipe test, after the first cavitation minutes, no particles remained bonded to the substrate's surface, which means a weak bond between particles and substrate, or inclusive that no bonding has been formed and the mechanical anchoring was also very poor. Particle's energy at impact moment is mainly used in deforming the substrate, suffering itself very low deformation and making that CGS bonding mechanisms do not take place.

When cavitation was performed onto 1000°C and 50 bar wipe test, better results were achieved. On contrary as in previous cases with these spraying parameters in between 5 and 10 minutes cavitation, all particles were detached, so even at these energetic conditions, bond is relatively weak (Figure 150).

Figure 151 shows the same experiment but at higher magnification to be able to observe not only the particles and its morphology but also the substrate degradation over cavitation time.



Figure 150: Cavitation test at different times onto 1000°C and 50bar wipe test



Figure 151: Cavitation test at different times onto 1000°C and 50 bar wipe test

After the unsatisfactory results with wipe-test and cavitation, four different spraying conditions (Table 19 and 20) have been tested in order to check if a higher amount of particles impinging onto the substrate creates a different bonding behaviour due to compaction.

Figure 152 shows the polished cross section of the obtained spherical Ti6Al4V coating onto AZ31 substrate. Porosity reduces as the temperature and pressure increases and thickness does it also.



Figure 152: Optical micrographies of Ti6Al4V coating onto AZ31

Table 47 shows the efficiency, thickness and porosity of the obtained coatings.

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	49 ± 7	256 ± 21	30 ± 6
B - 900°C, 38 bar	35 ± 4	229 ± 21	20 ± 7
C - 1000°C, 38 bar	48 ± 8	215 ± 12	12 ± 5
D - 1000°C, 50 bar	33 ± 5	181 ± 16	9 ± 4

As it can be observed, as the temperature and the pressure increases, porosity reduces. From A to B it reduces a 33%, from B to C a 40%, and from C to D where only the pressure increases, a 25% reduction has achieved. Porosity is the only variable which behaves according to what is expected. Figure 153 shows the obtained irregular Ti6Al4V coatings onto AZ31 substrate under the same spraying conditions.



Figure 153: Optical micrographies of irregular Ti6Al4V coatings onto AZ31

Ti6Al4V onto Ti6Al4V	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	28 ± 3	165 ± 13	18 ± 5
B - 900°C, 38 bar	29 ± 3	145 ± 10	13 ± 5
C - 1000°C, 38 bar	38 ± 6	121 ± 15	9 ± 4
D - 1000°C, 50 bar	31 ± 3	143 ± 8	5 ± 2

Table 48 shows the efficiency, thickness and porosity of the obtained coatings

Table 48: Ti6Al4V coatings properties onto AZ31

As it can be observed in table 51 an increment in temperature leads to a porosity reduction. From spraying condition A to B, porosity is reduced in a 28%, and if temperature is increased 100°C more, porosity is further reduced by 30% more.

As the pressure increases, porosity decreases in a 45%.

Like with AI-7075-T6, pressure has a higher influence in porosity decrease than the temperature.

To compare the obtained results with the second high purity and low oxygen content spherical Ti6Al4V powder, the same spraying conditions have been tested. (Figure 154).



Figure 154: Optical micrographies of non-oxidized Ti6Al4V coatings onto AZ31

With the non-oxidized powder, properties have improved markedly.

Ti6Al4V onto AZ31	Efficiency (%)	Thickness (µm)	Porosity (%)
A - 780°C, 38 bar	67 ± 3	704 ± 28	20 ± 5
B - 900°C, 38 bar	61 ± 8	627 ± 39	20 ± 5
C - 1000°C, 38 bar	63 ± 3	652 ± 41	15 ± 4
D - 1000°C, 50 bar	65 ± 3	656 ± 21	10 ± 3

Table 49: New Ti6Al4V coatings properties

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Efficiency has increased between 20 and 30% depending on the parameters and thickness has also increased between 2 and 3 times. Porosity has followed the same trend as with the former spraying powder, reducing, but not as much as before



Graphic 6: Deposition Efficiency comparison between former and new Ti6Al4V spraying powder



Graphic 7: Thickness comparison between former and new Ti6Al4V spraying powder

As in previous cases, the best coating is the one obtained at 1000°C and 50 bar. Since these are the maximum spraying conditions that the system can achieve, D50 nozzle was used in order to achieve higher particle velocities.

Spraying conditions were the same ones as in previous cases. Figure 155 shows the obtained coating with non-oxidized spherical Ti6Al4V powder.



Figure 155: Ti6Al4V coating onto AZ31 substrate sprayed with D50 nozzle

The improved coating properties are shown in table 50

Ti6Al4V onto AZ31	Efficiency (%)	Thickness (µm)	Porosity (%)
D50,950°C, 50 bar	70 ± 5	592 ± 21	<2

Table 50: Ti6Al4V coating properties onto AZ31

Thickness and porosity is comparable to the ones obtained onto Ti6Al4V and Al-7075-T6 substrates, but the efficiency is around 10% lower.

The better way to obtain a dense and high efficiency coating is using Helium as propellant gas. The obtained coating sprayed under the same parameters than in previous cases is shown in figure 156.



Figure 156: He sprayed spherical Ti6Al4V onto AZ31

Table 51 shows the main response variables that were analysed

Ti6Al4V onto AZ31	Efficiency (%)	Thickness (µm)	Porosity (%)
D24,900°C, 30 bar	98 ± 2	795 ± 38	<0,2

Table 51: Ti6Al4V coating properties

Deposition efficiency and porosity have been highly improved

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4.4. Adhesion test

In order to determine the bond strength of the coatings, two different adhesion test have been carried out

- ASTM C-633 standard
- TCT-Test

ASTM C-633 standard was done onto 780°C and 38 bar coating Figure 157 shows a scheme of the process



The obtained results depend not only of the coating material but also of the substrate. If the bonding between the first layer and the substrate surface is weaker than the bonding between particles, the structure will fail at the interface producing an adhesive failure. If the failure is produced within the coating, is a cohesive rupture

For AI-7075-T6 and AZ31 an adhesive failure occurred and for Ti6AI4V substrate the failure was cohesive

The obtained results for the three substrates are shown in table 52 and figure 158

Substrate	Ti6Al4V	Al-7075-T6	AZ31
Adherence (MPa)	76 ± 7	45 ± 2	39 ± 5

Table 52: Ti6Al4V adherence onto the 3 substrates



Figure 158: Adherence test values of different substrates

The obtained value for Ti6Al4V substrate is a 68% higher than the adherence value for Al-7075-T6 substrate and 95% higher than for AZ31 substrate.

In order to determine the bond strength of the coating itself, Tubular Coating Tensile strength test developed by the Institute of materials technology of the Helmut Schmidt University of Hamburg was used.



Figure 159: TCT test^[79]

As the coating, the spraying conditions were as follows:

Conditions	Temperature (°C)	Pressure (bar)
Condition A	780	38
Condition B	900	38
Condition C	1000	38
Condition D	1000	50

Table 53: TCT Test spraying conditions

Spraying distance (mm)	60
Spraying angle (°)	90
Nozzle speed (mm/s)	4
Powder feeding rate (g/min)	39
Sample rotation speed (mm/s)	250
Sample material	Aluminum

Table 54: Spraying conditions

Figure 160 shows schematically how TCT samples were sprayed



Figure 160: TCT test spraying scheme

Figure 161 for spherical Ti6Al4V powder, figure 162 for non-oxidized spherical Ti6Al4V powder and figure 163 for irregular Ti6Al4V powder, show two micrographies per spraying condition (Table 53) at different magnifications of the rupture zone.



Figure 161: TCT test micrographies at different spraying parameters of spherical Ti6Al4V powder

As it can be observed in figure 161, the right column micrographies (A.1, B.1, C.1 and D.1), show rupture zones highly magnified. Fusion areas can be appreciated and give evidence of the high temperatures reached after (during) impact of the particles onto the substrate.

Table 55 shows the TCT test obtained results. For every spraying condition, five samples have been coated and tested.

Conditions	Condition A	Condition B	Condition C	Condition D
TCT test (MPa)	77 ± 6	79 ± 5	69 ± 3	90 ± 10

Table 55: TCT results

It should be mentioned that the geometrical design of the TCT samples, leads to a stress concentration in the pulled coating. This stress concentration increases the Mises stress at the gap between the substrates to a factor of 1.5 to 1.7. The measured coating strength has to be multiplied with this factor to get a tensile strength value ^[59].

Under these conditions, TCT-test results have been multiplied by a factor of 1,6 in order to obtain tensile strength values shown in table 56.

Conditions	Condition A	Condition B	Condition C	Condition D	
TS value (MPa)	123 ± 10	127 ± 7	111 ± 4	143 ± 16	

Table 56: tensile strength values

Like with previous coatings, the results obtained with the low oxygen content Ti6Al4V spraying powder of TLS are better as is shown in table 57.

Conditions	Condition A	Condition B Condition C		Condition D
TCT test (MPa)	86 ± 9	109 ± 6	113 ± 4	133 ± 8
TS value (MPa)	137 ± 14	175 ± 9	180 ± 6	213 ± 13

Table 57: Tensile strength values with new TLS powder



Figure 162: SEM micrographies TCT rupture zone



Figure 163: TCT test micrographies at different spraying parameters for irregular Ti6Al4V powder

Micrograph B.1 shows the top particles of the last layer. It can be observed how the particles, due to the impact and the produced tensions, have elevated on the sides producing jets.

With irregular powder is more difficult to observe if microfusion phenomena has occurred, but is still observable.

Table 58 shows the TCT test obtained results. For every spraying condition, five samples have been coated.

Conditions	Condition A	Condition B	Condition C	Condition D
TCT test (MPa)	123 ± 6	129 ± 8	137 ± 6	155 ± 8



As previously, the measured coating strength has to be multiplied with a factor of 1,6 to get a tensile strength value 59 which are shown in table 59

Conditions	Condition A	Condition B	Condition C	Condition D
Tensile strength	107 ± 10	206 ± 13	210 ± 0	2/18 ± 13
value (MPa)	197 1 10	200 ± 15	21919	240 ± 13

Table 59: tensile strength values

Figure 164 shows graphically the evolution of the adherence when spraying conditions change.

As the temperature and pressure increase, TCT obtained values are increasing. Temperature influence is lower than pressure effect as it can be observed on the obtained values. Temperature increase ($780^{\circ}C \rightarrow 900^{\circ}C \rightarrow 1000^{\circ}C$) leads to increments on TCT values of around 5%, while pressure increase (from 38 to 50 bar) leads to an increase on the TCT value of 13%.



Figure 164: TCT adherence values at different spraying conditions for irregular Ti6Al4V powder

The optimal results obtained with low oxygen content spherical Ti6Al4V sprayed with D50 nozzle and at the highest spraying conditions are shown in table 60.

Spraying Parameters	TCT test (MPa)	Tensile strength value (MPa)
950°C, 50bar, D50	181 ± 8	290 ± 14

Table 60: Tensile strength values with D50

The following figure shows a comparison between the obtained results on the TCT test depending on the spraying powder and conditions.



Figure 165: Tensile strength values with different powders

As the velocity increase, particles are more deformed and interphase and / or intersplat bonding is higher making tensile strength values higher.

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4.5. Corrosion test

The corrosion resistance of the samples was evaluated by means of electrochemical measurements in 80 mL of an aerated and unstirred 3,4% NaCl solution according to ASTM D-1411 standard. Open-circuit potential-time curves for three substrates and assrayed coatings in aerated and unstirred chloride solution are shown in figure 166.

The electrochemical tests were conducted with polished samples (below 1μ m roughness) because corrosion properties are also assumed to be considerably affected by the surface roughness since the roughness of the coatings promotes a better solution contact in certain areas. The three coatings were firstly evaluated in the assprayed form but the obtained result showed high oscillations on the E_{OC} curves due to the variation of the contact area (roughness).



Figure 166: E_{OC} potential for substrates and coatings of open circuit test

As it can be observed, after 24 hours test, no electrolyte has arrived to the substrate surface. E_{OC} potential provides information about the evolution and degradation of the

coatings and substrates For all samples, the E_{OC} has been stabilized after 2 hours without significant oscillations.

As more positive the potential is, more resistant is the material to corrosion (is less active, less anodic). The obtained curves show clearly that AZ31 has the lowest potential, being also the most susceptible to corrosion, followed by AI-7075-T6 substrate and then Ti6AI4V substrate. In all cases, the coated substrates are over the substrates potentials.

In order to estimate the corrosion current density, potentiodynamic curves have been done and anodic and cathodic curves were recorded around the corrosion potential (E_{corr}). From the intercept between the anodic and cathodic linear plots and, by extrapolating to the y and x axis, both E_{corr} and i_{corr} are respectively estimated. According to these Tafel-plots, the observed corrosion potentials are fairly similar to those obtained from the E vs. time curves.



Figure 167: Potentiodynamic curves of Ti6Al4V coatings onto the three substrates.

This means that the cathodic polarization did not cause appreciable change to the electrode surface.

	Substrates			Ti6Al4V coatings onto		
	Ti6Al4V	AI-7075-T6	AZ31	Ti6Al4V	AI-7075-T6	AZ31
E _{OC} (V)	-0,128	-0,774	-1,519	-0,075	-0,136	-0,005
E _{corr} (V)	-0,013	-0,78	-1,51	-0,013	0,15	0,011
i _{CORR} (mA/cm²)	1,78·10 ⁻⁷	10 ⁻⁶	5·10 ⁻⁶	1,78·10 ⁻⁷	1,78·10 ⁻⁷	1,78·10 ⁻⁷
R _p (ohm cm ²)	768,3	35,23	0,27	768,3	525,3	732,5

Table 61 shows a comparative of the different obtained data of the curves

Table 61: Corrosion parameters for the analysed substrates/coatings

As it can be observed in table 61, E_{OC} and E_{CORR} are very similar and the slight differences between Eoc (2 h) and Ecorr values might be associated to the established corrosion velocity. For all the coated samples i_{corr} was the same.

4.6. Results and partial discussion

Comparing the 3 different systems that have been studied, independently of the used powder and conditions, the best efficiencies and lower porosities have been achieved onto Ti6Al4V substrate.

For spherical powder. figure 168 shows a comparison of the efficiency onto the three substrates based on the number of deposited layers.



Figure 168: DE based on number of layers for 3 substrates

Al-7075-T6 substrate had the lowest deposition efficiency in all layers. The influence of the substrate is much higher in Al-7075-T6 than in AZ31 followed by TI6Al4V where the substrate has almost no influence at all.

When bonding strength onto the different substrates is compared through % of bonded particles in function of cavitation test time (figure 169), Titanium grade II and Ti6AIV have the strongest bonding due to a higher deformation of particles and the existence

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of microfusions which increase adherence. On contrary, on AI-7075-T6 and AZ31 substrate, particle's adherence is low for both cases.

Particles are not deformed as much as before, and substrate's thermal conductivity hinders cold gas spray bonding mechanism.



Figure 169: Cavitation test onto the four substrates at 1000°C and 50bar substrates

Comparing the cross section of spherical Ti6Al4V powder wipe tests onto Ti6Al4V and Al-7075-T6 substrate, figure 170 was obtained.


Figure 170: Sph. Ti6Al4V wipe test cross sections onto Ti6Al4V (A) and Al-7075-T6 (B)

It can be clearly observed the difference on bonding mechanism between Ti6Al4V and Al-7075-T6 substrate. While in the first ones, the mechanism described by T. Schmidt simulation is met (Figure 96) and the particle's impact point is not adhere to the substrate surface corroborating founded substrate imprints and detached particles, on the second ones (B) no fusion zones are observed and is more a mechanical bonding instead of metallurgical bonding.

With AI-7075-T6 and AZ31 substrates, the high kinetic energy that particles contain at impact moment, is distributed as deformation of the substrate (mainly) and particle and the other part is dispersed as heat preferentially through the substrate due to their much higher thermal conductivity (AI-7075-T6TC= 130 W/mK, AZ31TC= 98 W/mK and Ti6AI4VTC= 6,7 W/mK).

Ti6Al4V coatings from spherical spraying powder improve their properties with temperature and pressure increase, independently of the sprayed substrate.

Table 62 shows a deposition efficiency comparison between the different spraying conditions and the oxidized and non-oxidized spherical Ti6Al4V powders onto the 3 substrates.

Deposition Efficiencies						
SUBSTRATE	Ti6Al4V		Al-7075-T6		AZ31	
Spraying Powder Spraying conditions	Oxidized	Non-oxidized	Oxidized	Non-oxidized	Oxidized	Non-oxidized
780°C, 38 bar	55	83	29	40	49	67
900°C, 38 bar	65	83	41	54	35	61
1000°C, 38 bar	64	79	49	56	49	63
1000°C, 50 bar	57	83	33	70	32	65
950°C, 50 bar, D50		87		82		70
900°C, 30 bar, He		99		98		99

 Table 62: Deposition efficiencies onto the three substrates at different spraying conditions

For the three substrates, the highest deposition efficiencies are obtained when helium is used as propellant gas.

Porosity in all cases, as the temperature and the pressure increases, reduces, arriving to the minimum when Helium is used as propellant gas.

In the case of irregular Ti6Al4V powder, sprayed with Kinetic 4000 system, deposition efficiencies are shown in graphic 8.



Graphic 8: deposition efficiencies carried out with KINETICS 4000 system

It can be seen in graphic 8 that Deposition efficiencies onto Ti6Al4V substrate are the higher ones, followed by AZ31 substrate and then Al-7075-T6 substrate.

Despite temperature and pressure increase, DE were almost not varying for all substrates. Is believed that irregular spraying powder has a high oxidation level due to obtention process and aging, and this oxidation layer reduces in fligh velocity of the particles and also avoids an intimate contact at impact moment reducing the efficiency of the process.

Particles that do not adhere, compact the coatings, hence that porosity reduces when temperature and pressure increase.

Combined with spraying powder oxidation is substrate oxidation layer and substrate's own properties which influence in deposition efficiency.

Figure 171 shows an efficiency comparison between the three substrates based on the number of deposited layers.



Figure 171: 3 substrates DE based on number of layers

For all spraying conditions, from 680°C and 30 bar to 1000°C and 50 bars, the best coatings in terms of deposition efficiency, porosity and adherence have been obtained always onto Ti6Al4V substrate.

When Al-7075-T6 and AZ31 are compared, deposition efficiency is higher onto AZ31 as well as coating thicknesses, independently of the spraying conditions. As it has been said before, the first impinging particles hardens strongly AZ31 substrate, allowing greater deformation on the following particles triggering bonding mechanisms.

When coatings adherence is taking into account, the obtained values for AI-7075-T6 are better. Despite of the aluminum tendency to oxidize, bonding is stronger than with magnesium. As it has been explained on spherical Ti6Al4V coatings onto AZ31 substrate chapter , AZ31 deforms mainly through two mechanism , slipping and twinning. These mechanisms besides hardens the substrate and reduce the plasticity, increase the

tension on the structure avoiding material recovery, difficulting intimate contact between particle and substrate and avoiding CGS bonding mechanisms.

With the experiments carried out with modified KINETICS 8000 from HSU, better results in deposition efficiencies were expected. Graphic 9 shows de obtained deposition efficiencies.



Graphic 9: deposition efficiencies carried out with modified KINETICS 8000 system

As before deposition efficiencies are higher onto Ti6Al4V substrates and as temperature and pressure increase, Al7075-T6 and AZ31 change their position. At 780°, 38 bar and 900°, 38 bar Al-7075-T6 substrate has higher DE than AZ31 but at 1000°C are the coatings onto AZ31 substrate the ones with higher DE.

Comparing Deposition efficiencies of both powders onto the three substrates, graphic 10 is obtained.



Graphic 10: DE comparative onto the three different substrates

To see the influence of pressure and temperature on the deposition efficiency of the coating formation with irregular Ti6Al4V, interaction diagrams have been done as it is shown in figure 172. The results are shown in table 63, were for the case of Ti6Al4V substrate and AZ31 substrate the parameter which have more influence is the pressure, and for Al7075-T6 substrate is the temperature the parameter with a highest influence, and with a bigger difference than in the other cases.

	Sum of squares		
Term/Substrate	Ti6Al4V Al-7075-T6 AZ31		AZ31
Temperature	0,65	34,01	1,26
Pressure	11,76	4,73	14

Table 63:interaction diagrams results



Figure 172: Deposition efficiency, temperature and pressure interaction diagrams for Ti6Al4V (A,A.1), Al-7075-T6 (B,B.1) and AZ31 (C,C.1) substrates

4.7. Publications derived from this section

From the obtained results in this section, the following articles have been proposed:

"Ti6Al4V cold gas sprayed coatings: Impact morphologies, splat adhesion and correlations to coating microstructures"

M.Villa¹, S. Dosta¹, F. Gärtner², A. List², T. Klassen², JM.Guilemany¹* ¹*Thermal Spray Center (Spain), ² Helmut Schmidt University (Germany)* International Thermal Spray Conference 2013 (ITSC 2013): Innovative Coating Solutions for the Global Economy JTST-13-05-1756 May 13–15, 2013, Busan, Republic of Korea "Special issue" Journal of Thermal Spray Technology

"Experimental study of Ti-6Al-4V coatings on light alloys obtained by cold gas dynamic spray"

M.Villa, S.Dosta, J. Fernández, J.M.Guilemany Journal of Thermal Spray Technology, International Thermal Spray Association (USA). Under revision

"Deposition of Ti6Al4V onto different substrates using cold gas spray with nitrogen and helium as propellants"

M.Villa¹, S. Dosta¹, F. Gärtner², A. List², T. Klassert², JM.Guilemany¹* ¹*Thermal Spray Center (Spain), ² Helmut Schmidt University (Germany)* To be submitted to Material Science and engineering A

"Experimental study of Cold Gas Spray bonding mechanism based on spraying powders and substrate nature"

M.Villa, S.Dosta, J.M.Guilemany Thermal Spray Center (Spain) Abstract ITSC 2014

Ti6Al4V cold gas sprayed coatings: Impact morphologies, splat adhesion and correlations to coating microstructures

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Abstract

The $\alpha+\beta$ structure of Ti-6Al-4V gives excellent mechanical properties and medium resistance to high temperatures. The combination of a light alloy core with a Ti6Al4V coating opens a new window for industrial applications.

Cold spraying of Ti-6Al-4V was performed with nitrogen as process gas onto Ti-, Aland Mg-alloy substrates to study influences of the interaction with different hardness base materials. Impact morphologies and particle removal in cavitation testing were subsequently studied bv SEM. The investigations demonstrate that Ti-6Al-4V particles are well bonded to the substrate or within the coating due to shear instabilities. Areas of shear instabilities increase with process gas temperature or pressure and coating quality can be successfully optimized.

Introduction

Cold gas spray (CGS) is a solid-state coating technique, exposing the substrate to a high-pressure gas stream (nitrogen or helium) that contains powder particles with a certain size distribution. These particles acquire high kinetic energy, thus allowing them to reach speeds between 300 and 1200 m/s, depending on several parameters: pressure and temperature of the process gas, the powder material, particle size and morphology, and the geometry of the nozzle.

The mechanism behind this process is based in plastic deformation rate of the particles and the substrate and in consequence, the formation of adiabatic shear instabilities. The study and control of the parameters involved in CGS, allows to identify the most suitable conditions for the production of a coating from particles in solid state. Given that high temperature is not involved in CGS, this technique is appropriate for the deposition of temperature-sensitive materials, such as nanophased and amorphous substances. Furthermore, many deleterious phenomena caused by high temperatures, such as grain growth, which happens during thermal spraying, or oxide formation, are minimized or even prevented by CGS. Therefore the potential to produce nanostructures by Cold Spray technology using nanostructured powders is much higher than when using other methods. Other typical advantages of coatings obtained by this technique include compressive rather than tensile stresses, wrought-like microstructure, near theoretical density, oxides, and other inclusion-free coatings [Ref 1]

advantages of coatings Other typical obtained by this technique include compressive rather than tensile stresses, highly deformed, means work hardened microstructures, near theoretical densities and the lack of oxides and other impurities in the coatings Even for oxygen sensitive materials like titanium and aluminium, practically no increase of impurities as compared to the feedstock powder is observed by CGS, as shown by N. Cinca et al. for titanium grade 2 coatings on aluminium alloy [Ref.2].

Upon impact of these particles onto the substrate surface, plastic deformation occurs. Depending on the substrate and the powder characteristics, this deformation can

take place in the powder, in the substrate, or in both. Only when the impact velocity of the particles exceeds a critical value, coating formation is obtained [Ref.3].

The most widely accepted hypothesis concerning bonding mechanisms in cold gas spraying is based on conditions that cause extensive plastic deformation under ultra-high strain rates and associated phenomena at the interface (adiabatic shear instabilities).[Ref. 4] The extensive local plastic deformation in areas of shear instability is due to the fact that thermal softening over-compensates strain rate hardening effects. Thus high temperatures close to the melting point are reached locally. Under the high strain, surface oxides are ruptured, allowing for intimate contact between the particles and the substrate or previously deposited materials.

As T. Schmidt et al. described, material deposition takes places only if the impact velocity of the particles exceeds the so-called critical velocity. The critical particle velocity depends on various factors, mainly the properties of the sprayed material. [Ref.5]

In the current study, the impact and bonding behaviour of Ti6Al4V onto four different substrates was examined. Titanium grade II, Titanium grade V, Aluminum alloy Al-7075-T6, and Magnesium alloy AZ31 were selected to investigate the impact morphologies and splat adhesion of the Ti6Al4V particles and related to the coating microstructure. Single impacts were produced by so called wipe tests, and single splat adhesion was investigated by applying a modified cavitation test. Impact morphologies and particle removal in cavitation testing were subsequently studied.

Experimental Procedure

Materials

Commercially available spherical Ti6Al4V powder from TLS with low oxygen content was used as feedstock material in the process.

Figure 1 shows the morphology and the cross-section of the powder as observed by scanning electron microscopy (SEM).



Figure 1: Powder morphology (left) and powder cross section (right) of Ti6Al4V powder by scanning electron microscopy

The as received powder had a particle size distribution $d10=24 \ \mu m - d90=49,3 \ \mu m$ and a mean size of 35,5 μm . Figure 2 shows the particle size distribution of the original powder according to Laser scattering techniques.



Figure 2: Size distribution of the powder

For wipe test experiments and processing coatings, a Cold Gas Spray system Kinetics 8000 modified by the Helmut-Schmidt-University in Hamburg was used. Nitrogen was used as carrier and process gas. The process gas temperatures and pressures were varied between 800 and 1000°C, and 38 and 50 bar, respectively. The stand-off distance was set to 60mm and transversal gun velocity was 30% of the maximum gun velocity.

Wipe test experiments were performed onto polished substrates (Titanium grade II, AI-7075-T6 and AZ31) to be able to observe the surface modifications after impact without the disturbance of surface roughness. For these experiments, the lowest and the highest pressures and temperatures were used.

For processing coatings, AI-7075-T6 and AZ31 substrates were grinded with 220 grade SiC paper and Ti6AI4V substrate was grit blasted with alumina before spraying. To obtain a coating, 4 passes were done

Sample Characterization

To observe the structure of the particles of the wipe test experiments and the 219

microstructure of the coatings, surfaces were prepared. Semi-quantitative composition of the powder, as well as the thickness, porosity and semi-quantitative composition of the coatings, were measured by means of scanning electron microscopy (Quanta 650, FEI Company, The Netherlands)

Coatings cross sections have to be prepared with grinding papers ranging from P80 to P1400. After grinding, the surfaces were polished with 9 μ m, 6- μ m and 1- μ m diamond paste. Polishing was completed using a colloidal silica suspension.

Cross-sections of the coatings were also observed by Optical Microscopy (OM) (Leica DMI 5000 M,Germany)

Results and Discussion

Wipe-test and Cavitation

20-40 µm spherical Ti6Al4V powder (TLS, Germany) was used as feedstock powder on polished Titanium, Al-7075-T6, and AZ31 substrates.

Nitrogen was used as carrier gas. Temperature and Pressure of the streaming gas were between 780-1000°C and 38-50bar respectively. In all cases, standoff distance, spray angle and powder feedrate were kept constant.

The powder microstructure was investigated by optical microscopy and is shown in figure 3. The microstructure can Ti6Al4V COATINGS

be mainly described as Widmanstätten type based on martensitic α phase [Ref.6], by solid state transformation from the high temperature β phase. This structure shows a higher hardness and lower tensile strength and ductility than the α + β structures.[Ref. 7]



Figure 3: Optical microscopy micrograph of Ti6Al4V powder microstructure

Ti6Al4V powder was sprayed onto 3 different substrate types (Titanium, Al-7075-T6 and AZ31). Substrates hardness are shown in "table 1". It is expected that the substrate hardness is going to influence the deformation rate of the particles upon impact and thus and also the bonding nature between particles and substrate.

Substrate	Hardness (HVN)
AI-7075-T6	178 ± 8
AZ31	75 ± 5
Titanium	215 ± 9

Table 1: Substrates hardness

The difference in hardness of the substrates, results in different deformation of the particles. The harder the substrate is, higher is the plastic deformation of the particle [Ref.8]. Figure 4 shows examples of the experimental results of the Ti6Al4V particles onto the different substrates at low temperature and pressure (a,b,c) and at a high temperature and pressure (a.1., b.1, c.1)

Aluminum and magnesium substrates are highly deformed due to the impact of the Ti6Al4V particles, and material jets of the substrate were formed. In the case of the magnesium substrate, twinnings have been observed on the surface that surrounds the impacted particle. For titanium substrates, material jets originate from the particles



Figure 4: Single impact morphologies (wipe test experiments) at low temperature and low pressure. (a) on AI7075-T6; (b) on Titanium; (c) on AZ31. Single impact

morphologies (wipe test experiments) at high temperature and high pressure. (a.1) on Al7075-T6; (b.1) on Titanium; (c.1) on AZ31.

Particles are intensively more deformed at high temperature and pressure (Fig. 4, a.1,b.1 and c.1) than in the case of low temperature and low pressure due to the higher energy impact of the particles, but the characteristics of the impacts are similar

In both cases, either low pressure and temperature or high pressure and temperature, higher deformation takes place on the substrate for AI-7075-T6 and AZ31 substrates and on the particle for Titanium substrate.

As explained by T. Schmidt et al., particles suffer an inhomogeneous deformation and localized heating at the impact surface [Ref.9]. Since deformation takes place in a short period of time, the produced heat generates temperatures that can be close to the melting point of the materials and facilitate the bonding

Single splat adhesion was investigated applying a modified cavitation test (ASTM G32/85 standard) where impact morphologies and removed particles were studied. As it can be seen in figures 5 and 6, the generated heat due to the impact produced a temperature higher than the melting point of the materials, producing rings on the surface of the substrate as well as rings on the Ti6Al4V particles. An EDX analysis was done to confirm the composition of the removed particles.



Figure 5: Removed particle with EDX analysis.



Figure 6: Footprint on titanium substrate.

For aluminum and magnesium, no removed particles were found and the substrate surface were damaged due to cavitation test that no footprints were remain as it can be seen in figure 7.



Figure 7: Aluminum substrate (A) and Magnesium substrate after 10 min cavitation.

To be able to study the behaviour of the same material as substrate and as spraying

particle, another wipe test experiment was performed onto Ti6Al4V substrate

The surface of the substrate was not polished but roughing with a 220 SiC paper to simulate the same spraying conditions used when coatings are obtained. Temperature and pressure spraying conditions were the most energetic ones, stand-off distance, spray angle and powder feedrate were kept constant.

Before cavitation test, adhered particles have been examined by SEM, observing that some of them, besides jets, have cracks due to the impact as it is shown in figure 8.



Figure 8: Ti6Al4V particles.

As in the previous cases, cavitation test were performed. The sample is exposed to the test during consecutive periods until 30 minutes. In previous cases, after 15 minutes cavitation no particles were remaining adhered to the substrates, but with Ti6Al4V substrate, after this period of time, some particles are still adhered to the surface. Instead of detaching, particles have broken as it is shown in figure 9. The morphology

of the broken zone indicates a strong bonding between particle and substrate.



Figure 9: Ti6Al4V particles onto Ti6Al4V substrate after 15 min cavitation test.

In the same way to what happened with titanium substrate, the footprints on the substrate once the particle is removed are very similar (as it is shown in figure 7).

Cross section of wipe test onto Ti6Al4V and Aluminum has been polished to visualize the particles impact shape as it is shown in figure 10. In the case of Ti6Al4V substrate, one can observe the existence of no bonding in the middle area of the particle which has been the impact point. This confirms the formation of ring shapes formed on the substrate surface after the detaching of the particles due to cavitation test. These results illustrate that the union between particle and substrate is stronger at higher spraying conditions. Ti6Al4V particles are well bonded to the different substrate surfaces and for Titanium and Ti6Al4V substrates there are evidences of melting.

The obtained results with wipe-test and cavitation experiments show that the most energetic conditions are better for coating obtention due to a higher particle deformation and a stronger union between particle and substrate

Figure 11 shows the obtained coatings under the following spraying conditions. Steaming gas was Nitrogen, stand-off distance was set to 60mm,transversal gun velocity was 30% of the maximum gun velocity, spraying angle was kept in 90° and powder feed rate was 3rpm. The coatings have been build-up onto Ti6Al4V, AI-7075-T6 and AZ31 substrates. Ti6Al4V substrate was grit-blasted before spraying to activate the surface and eliminate the passivation oxide layer of the surface and AI-7075-T6 and AZ31 substrates were grinded with 220 SiC paper for the same reason than before.



Figure 10: Backscattered SEM micrographs of Ti6Al4V cross-section onto Ti6Al4V and aluminum



Figure 11: Optical microscope micrographies of Ti6Al4V onto a. Ti6Al4V; b. Al7075-T6; c. AZ31.

Coating thickness onto the different substrates are shown in table 2

Substrate	Ti6Al4V coating Thickness (µm)
Ti6Al4V	596 ± 16
Al-7075-T6	566 ± 24
AZ31	613 ± 19

Table 2: Coating thicknesses

For all cases, thickness is around 600 microns.

A modified bond strength test called Tubular Coating Tensile Test (TCT-Test) developed by the Helmut Schmidt University was used as method to obtain information on the mechanical coating strength complementary to deposition efficiency and coating microstructure.

TCT-Test values are 185 ± 5 MPa and to get a tensile strength value, which is comparable to conventional tensile tests (MFT-test), this value must be multiplied by 1.6, resulting in 295 \pm 9 MPa [Ref.10].

Porosity has been also measured and in all cases lower to the 3%. Table 3 shows the porosity vales for different substrates.

Substrate	Ti6Al4V coating Porosity (%)
Ti6Al4V	1,6 ± 0,2
Aluminum	2,3 ± 0,3
Magnesium	1,4 ± 0,2

Table 3: Coatings porosity

The main differences in porosity are in the interface zone. As discussed previously, Ti6Al4V particles undergo a large deformation when impacting onto Ti6Al4V suffering impact hardening and even breakage. Toughness is reduced so when new particles impact the surface, they may cause breakage in the already deposited particles, and they will not deform as much as the first impacting particles. Therefore impact hardening is not as severe, allowing greater deformation when new particles impacting on them. As it has been shown in figure 11a, porosity is higher in the interface zone but is very homogeneous all over the coating. For aluminum and magnesium substrates the porosity is higher on the upper parts of the coating. The influence of the substrate decreases with the thickness of the coating. As the thickness of the coating increases, the influence of the substrate in the deposition and on the particles deformation decreases, increasing the influence of the already deposited particles. This implies for the case of aluminum and magnesium substrates that particles are depositing onto the same material, already hardened due to impact, explaining the pores formation.

Conclusions

Hardness, plasticity, thermal conductivity and toughness of the used materials have a big influence in the coating final microstructure. A low thermal conductivity of the substrate and particles, allows higher temperature at the impact zones.

When Ti6Al4V particles impact onto substrates with similar nature (Titanium or Ti6Al4V), jets and cracks can be observed on the particles, as well as melted zones with ring shapes on the removed particles and on the substrate surface. Conversely, when Ti6Al4V impacts onto softer materials like aluminum or magnesium and its alloys, the main deformation is produced on the substrate and not on the impacting particles, until a minimum thickness coating layer has formed, and the particles experience a higher deformation. At high temperature and pressure, adhesive strength is higher than 280 MPa.

Porosity is in all cases lower than 3%, there are slight differences between the first and the last layers due to the impact morphologies and the influence of the substrate.

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References

- R. Ghelichi, M. Guagliano
 Frattura ed Integrità Strutturale, 8 (2009) 30-44
- N. Cinca, M. Barbosa, S. Dosta, J.M. Guilemany Surf. Coat. Technol. 205/ 4 (2010) 1096-1102.
- 3. V.K. Champagne, *The cold spray materials deposition process: Fundamentals and applications*, Woodhead Publishing Itd, England, 2007

- H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye Acta Mater. 51 (2003) 4379–4394.
- 5. T.Schmidt, F. Gärtner, H. Assadi, H. Kreye Acta Mater. 54 (2006) 729–742
- F.J. Gil , M.P. Ginebra, J.M. Manero, J.A. Planell
 J. Alloys Compd 329 (2001) 142–152
- 7. Ian Polmear *Light Alloys: From Traditional Alloys to Nanocrystals* Four edition (2006), Ed. Butterworth-Heinemann
- 8. S. Yina,X-f. Wanga, W.Y. Li, Hong-en Jiea Appl. Surf. Sci.
 Volume 257, Issue 17, 15 June 2011, Pages 7560–7565
- T. Schmidt, H. Assadi, F. Gärtner, H. Richter, T.Stoltenhoff, H. Kreye, and T. Klassen
 J. Therm. Spray Technol. Dec. 2009, Vol. 18/ 5-6, pp 794-808.
- 10., T. Schmidt, F. Gärtner, H.Kreye, J.Therm. Spray Technol. 15(4), 2006, S. 488-494.

Experimental study of Ti-6Al-4V coatings on light alloys obtained by cold gas dynamic spray

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Abstract

The use of light alloys in industries such as aerospace, transport and biomedical devices has increased strongly in the last years. The α + β (hcp+bcc) structure of Ti-6AI-4V gives excellent mechanical properties and medium resistance to high temperatures. Ti-6AI-4V forms a stable oxide film upon the exposure to oxygen, making it an excellent corrosion resistance material in a variety of media.

The combination of Ti-6Al-4V properties with its medium density (4,43 g/cm³) make possible to use it in several applications like aircraft turbines, engine components, automotive parts, medical devices or aerospace components^[1]

1. INTRODUCTION

Cold gas spray is a solid-state spraying technique for coatings obtention by exposing a substrate to a high-pressure gas stream that contains powder particles with a certain size distribution. These particles are accelerated to speeds between 300 and 1200 m/s depending on the pressure and the temperature of the streaming gas (N_2 or He), the feedstock material, size and morphology of the particles, and the geometry of the nozzle². When the particles impact onto the substrate surface, a plastic deformation takes place. Only if the impact velocity of the particles reaches a critical value, a coating can be obtained³

The mechanism of this process is based on a high kinetic energy, localized plastic deformation of the particles and the substrate (depending on its properties) and adiabatic shear instabilities.

The study and control of the different parameters of the process, allows the obtention of a coating from particles in solid state⁴.

Since high temperature is not involved, it is ideally suitable for depositing temperature-sensitive materials such as nanophased and amorphous materials as well as for substrates with sensitivity to medium and high temperatures⁵.

Light metals are those which density is lower than 4,5 g/cm³.

Lightness property translates directly to material property since by far, the greatest weight reduction is achieved by density decrease. This is a reason why light metals

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and its alloys have been associated with strong industries as transport or aerospace.

Weight saving aspect should not opaque the fact that light metals possess other "technological importance" properties like the high corrosion resistance and high electrical and thermal conductivity of aluminium, the machinability of magnesium and the extreme corrosion resistance of titanium.

It must be taken into account that despite these technological importance properties, due to their density, among some other physical properties, aluminium and magnesium have a low hardness and low wear resistance, which provokes the need of improving its surface properties.

The main objective is the obtention and optimization of thick and dense Cold gas sprayed Ti6Al4V coatings, to improve light alloys wear resistance especifically aluminium alloy 7075-T6 and magnesium alloy AZ31, and also to repair industrial pieces fabricated with Ti6Al4V, reducing the cost of producing a complete new one. The influence of pressure and temperature has been studied for the deposition of irregular shape Ti-6Al-4V powder

2. EXPERIMENTAL PROCEDURE

Commercially available irregular Ti-6Al-4V powder with 15-45 μ m size distribution was used as feedstock material. As

substrate, three different light alloys have been used: Ti6Al4V, AI-7075-T6 and AZ31.

Free surface and cross section of the spraying powder were observed by Scanning Electron Microscopy (JEOL 5310). Spraying powder and substrates microstructure were studied through X-Ray diffraction with a Bragg-Brentano $\theta/2\theta$ Siemens D-500 diffractometer and also after chemical surface attack, in an optical microscope (DMI 5000M from Leica Optical Microscope).

Hardness measurements were done with a NANO INDENTER XP of Agilent Technologies

To optimize the process and obtain coatings as dense as possible, a 3^2 experiment design has been used in order to obtain the maximum information with the minimum number of experiments.

The studied parameters were temperature and pressure of the propellant gas. Powder feeding rate, transversal gun speed, spraying distance and spraying angle were kept constant. The influence of parameters was studied through deposition efficiency, coating thickness and hardness.

Deposition efficiency was obtained weighing every substrate (2,5cm x 5cm) before and after cold spray deposition, and the Ti-6Al-4V obtained coating area was measured. Deposition efficiency was calculated comparing the actual deposited

weight with the theoretical weight that should be deposited with 100% efficiency.

Single impacts were produced by so called wipe tests, and single splat adhesion was investigated by applying a modified cavitation test. Impact morphologies and particle removal in cavitation testing were subsequently studied.

Wipe test experiments were performed onto polished substrates (Titanium grade II, Al-7075-T6 and AZ31) to be able to observe the surface modifications after impact without the disturbance of surface roughness. For these experiments, the highest pressures and temperatures were used.

Coating thickness and semiquantitative composition of the coatings were measured, as well as the microstructure after polishing to determine the existence of oxides and to compare it with the powder microstructure confirming the maintenance of the initial microstructure.

Coatings and substrates microhardness was measured using a MATSUZAWA MXT- α machine, under the UNE 7-423/2 standard.

The tensile strength has been evaluated according to the ASTM C-633.

3. RESULTS AND DISCUSSION

3.1. Substrates

Figure 1 shows the microstructure of each substrate after etching observed with a light microscope.

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Figure 1: A.Ti6Al4V, B. Al-7075-T6, C. AZ31 microstructure

Figure 1A shows the typical $\alpha+\beta$ structure of the Titanium alloys⁶ where the Widmanstätten alpha is in a beta structure matrix.

AI-7075-T6 Figure 1B shows microstructure with elongated grains in the direction which the substrate plates were rolled. There are also MgZn₂ and Al₂Mg₃Zn₃ precipitates, due to the nature of the aluminum alloy and the heat treatment. For magnesium alloy AZ31 (Figure 1C) equiaxed grains with manganese-aluminum precipitates are observed.

3.2. Feedstock powder

Irregular Ti-6AI-4V powder (Phelly INC., USA) was used Materials as feedstock. Particle size distribution of the as received powder was too broad for cold spraying. Theoretically with a narrower particle size distribution, better results can be obtained⁷. Particles with similar size and morphology, have a similar behaviour during flight, similar flight times, and they reach its critical speed at similar time. These characteristics allows a better optimization of the spraying parameters⁸

Figure 2 shows the particle size distribution of the powder after its sieving. It agrees with a Gaussian curve, with a mean size of 19 μ m and d₁₀=10 μ m - d₉₀=31 μ m.



Figure 2: Powder size distribution after sieving

Particle morphology is a main parameter in cold gas spray as it has been mentioned before. Depending on it, particle behaviour in means of critical velocity or impact behaviour among others, are different. Figure 3 shows a SEM image of powder free surface (3A) and a light microscope micrograph of the etched cross section (3B)



Figure 3: Spraying powder free surface SEM micrography (3A) Light microscopy micrograph of etched cross section (3B)

As it can be observed in figure 3A, particles have a multiple faces shape. This so irregular shape, is going to influence strongly on the deposition efficiency. As well as in the case of the substrate, figure 3B shows the typical α + β structure of the Titanium alloys where the Widmanstätten alpha structure is in a beta structure matrix.

The hardness of the feedstock powders has been obtained by Nanoindentation technique. The result shows that the feedstock powder has a hardness of 450 ± 45 HV.

Typical hardness value for Titanium grade V is around 350 Vickers ^[10]. That means that the investigated spraying powder has

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25% higher hardness than the standard one

3.3. Coatings

Figure 4 shows a simulation of the window of deposition for Ti6Al4V, the zone between lines is the area where particles are between its critical velocity and its maximum velocity (where erosion can occur²) and theoretically coating can be formed. The dotted line represents the critical velocity and the above line is the maximum velocity.

To obtain the graphic the simulation of T. Schmidt et al. has been used^[3]



Figure 4: Ti6Al4V window of deposition

Deposition efficiency in the present case, is around 50% maximum (only for Ti6Al4V substrate). This not so high deposition efficiency corresponds to a low plastic deformation, low heat transfer and high hardness properties of the spraying material.

Lately it is seen how this deposition efficiency increases from the low energetic parameters to the highest one because Ti6Al4V ductility starts to increase because the yield strength reduces significantly at temperatures well above 200°C ⁹. As the impinging particle increases its temperature, the mechanisms of deformation and bonding in CGS are more efficient.

The used 3² design of experiments consists in three levels of temperature (680°C,730°C,780°C) and pressure (30,34,38 bar) of the carrier gas are studied, keeping constant the spraying distance, gun speed and powder feeding rate.

Figure 5 represents on the X axis the temperature and pressure at which the coatings were sprayed, and Yaxis represents deposition efficiency. In general, higher temperature and pressure means higher thickness because particles reach its critical velocity easier, plasticity is higher due to temperature increase and deformation due to the impact is also higher due to the pressure increase.



Figure 5: Coating deposition efficiency evolution onto different substrates.

As it can be observed in figure 5, DE is very similar in every condition for each substrate. The interval of studied temperature may not be high enough to produce the required increase in ductility to obtain higher deposition efficiencies. It must be also taking into account that spraying powder hardness is relatively high, so despite the temperature and pressure increase, these are not high enough to obtain high deposition efficiencies.

Nevertheless, for all cases, better results in DE are obtained at the maximum temperature. Table 1 shows the maximum deposition efficiency at the highest pressure and temperature (38bar, 780°C)

Substrate	Ti6Al4V	Al7075-T6	AZ31
Deposition Efficiency	49,7 %	36,50 %	40,6 %

Table 1: Ti6Al4V deposition efficiency at 780°C/38 bar onto diferent substrates

In order to explain more deeply the reasons for the low deposition efficiency, several parameters must be taking into account.

Considering just substrate's hardness (Table 2) as well as spraying powder's, DE of the coating obtained onto aluminum alloy substrate should be higher than onto magnesium alloy substrate, because after Ti6Al4V, AI-7075-T6 has the highest hardness, and deposition should be easier, but experimental data doesn't show this. To explain it, not only hardness must be taking into account but also Thermal conductivity.

Substrate	Ti6Al4V	Al7075-T6	AZ31
Hardness (HVN)	358 ± 8	178 ± 15	50 Brinell

Table 2: Substrate hardness

The thermal conductivity of the different substrates is as follows,

Substrate	Ti6Al4V	Al7075-T6	AZ31
Thermal Conductivity (W/mK)	6,7	130	96

Table 3: Substrate's thermal conductivity

Substrates with higher thermal conductivity dissipates the heat produced by the particle impact and the actual temperature of the particle itself as well as the streaming gas easily than the low thermal conductivity substrates, so the formation of adiabatic shear instabilities it is hindered because impact point doesn't reach the required temperature. This effect leads in a lower deposition efficiency of the process. Taking these effects into account, AI-7075-T6 substrate will have theoretically, and experimentally, the lowest deposition efficiency followed by AZ31 and Ti6Al4V respectively.

As it has been explained before, first impinging particles or first coating layer behaves differently than the following ones. This difference in behaviour is due to the nature of spraying powder and substrate material. Hardness, thermal conductivity, hardening due impact, ductility or thermal softening are some of

the properties which influence the behaviour of this first layer.

Trying to illustrate the difference between layers, a new experiment apart from the ones included in the experimental design, was developed. At the optimum conditions (780°C, 38bar) the number of deposited layers have been varied.

Figure 6 shows an efficiency comparison between the three substrates based on the number of deposited layers.



Figure 6: substrates DE based on number of layers

As the figure 6 shows,onto Ti6Al4V and AZ31 substrates deposition efficiency increases lightly as the number of layers increase, but in the case of Al-7075-T6, the substrate has a big influence on deposition efficiency, going from less than 10% on the first layer to over 30% on the fourth

Hardness of Ti6Al4V coating is in all cases similar to the powder hardness. This confirms the low deformation of Ti6Al4V particles. As it is explained before, Ti6Al4V has a low thermal conductivity coefficient, particles acquire certain temperature during flight, but due thermal coefficient and also morphology, ductility does not increase homogenously. Deformation will be higher in the external part of the particle than in inner zone, so hardness increase due cold work is produced at the interface zones and not in the whole volume.

For all substrates the optimum coatings, under the terms of porosity, adherence and taking into account that DE, are the ones obtained at highest pressure and temperature. Figure 6 shows the etched interface of the optimum Ti-6Al-4V coating onto Ti-6Al-4V substrate, showing the powder microstructure maintenance after spraying and the deformation of the particles at the impact area with the with themselves. substrate or The roughness of the substrate remains unchanged after deposition.



Figure 7: Optical microscope image of the etched interface coating/substrate

Figure 7A shows the interface of the optimum Ti-6AI-4V coating onto AI-7075-T6 substrate. Contrary to the previous case, deformation has taken place on the substrate surface and not on the first impacting particles. The microstructure of the coating, that can be seen on figure 7B, the remains equal to powder microstructure, and deformation due impact can only be observed at the particles interfaces. Substrate surface deformation as a result of impact is higher as in the previous case. Ti6Al4V hardness is double than AI-7075-T6 hardness and its ductility is lower, so the first impinging particles will produce a big deformation on the substrate and not on themselves resulting on a hardening of the substrate surface due to cold work.



Figure 8: A.SEM micrograph of the interface of the optimum Ti-6AI-4V coating onto AI-7075-T6 substrate. B. Optical microscope image of the etched coating

Figure 8 shows the optimum Ti-6Al-4V coating on AZ31 substrate. The interface coating/substrate presents a high irregular profile, due to the powder impact. High porosity can be also be observed on the last coating layer. In this layer, particles are impacting onto the previous ones so the hardness, ductility and thermal conductivity is different than before. Particles are now impacting onto a harder material due to the previous cold work, with a lower thermal conductivity than the substrate, and also with a lower ductility, that's why porosity has increase in the last layer and also because there are not following particles impinging and compacting the coating. In total 3 layers have been deposited



Figure 9: SEM micrograph of the optimum Ti-6AI-4V coating onto AZ31 substrate

3.4. Wipe-test

Ti6Al4V powder was sprayed Titanium and Al-7075-T6. Nitrogen was used as carrier gas. Temperature and Pressure of the streaming gas were 780°C and 38bar, because under these spraying conditions, powder acquire higher velocity and temperature Standoff distance, spray angle and powder feedrate were kept constant.

Substrates hardness are shown in "table 2". It is expected that the substrate hardness is going to influence the deformation rate of the particles upon impact and also the bonding nature between particles and substrate.

The difference in hardness of the substrates, results in different deformation of the particles. The harder the substrate is, higher is the plastic deformation of the particle [Ref.10]. Figure 9 shows examples of the experimental results of the Ti6Al4V particles onto the different substrates



Figure 10: Wipe-test free an tilted surface onto titanium (A, A.1) and AI-7075-T6 (B, B.1)

Aluminum substrate is highly deformed due to the impact of the Ti6Al4V particles, and material jets of the substrate were formed. For titanium substrate, material jets are originated on particles

3.4. Mechanical characterization

Tensile strength test were performed for all the coating/substrate system, resulting on the data collected in table 4.

SUBSTRATE/COATING ADHERENCE				
Ti-6Al-4V Al-7075-T6 AZ31				
75,7 ± 6,6 MPa	45,7 ± 1,6 MPa	38,5 ± 5,3 MPa		

Table 4: Substrate/Coating Adhesion test

Ti-6Al-4V hardness values are normally between 350 and 400 HV^{11} , which depends on the α and β phase proportion. A higher α phase implies a higher hardness. α Phase is hcp which allows lower dislocation movements than β phase which is bcc.

Nanoindentation technique has been used to obtain the hardness of the spraying powder, this value is 450 ± 90 HVN, whereas the final cold gas sprayed coatings microhardness were similar for the three substrates and is between 490 and 510 HVN To be able to compare the evolution of the coating hardness due to impact of the particles onto the substrate, Nanoindentation technique in addition to microindentation has been also used.

There are differences in the nanohardness of the coating depending on where the nanoindentation has been done. Closer to interparticle zone, where there is high deformation due to impact, hardness increases because of cold work. Nanoindentations closer to pores or to not binded zones show a lower hardness.

Ti-6Al-4V substrate hardness is increased by 24% after spraying on it, in the closest zone to the interface with the coating. In the case of Al-7075-T6, the hardness increase was 26%.

4. CONCLUSIONS

The main conclusions of the present work can be summarised as follows:

- Ti-6AI-4V irregular powder has been deposited successfully onto light alloys and onto Ti-6AI-4V bulk material as recharging material.
- At higher pressures, the thickness and the efficiency of the deposition process is better and its effect is higher than temperature's effect.
- Deposition efficiency depends not only on the critical velocity of the particle or the hardness of the materials, but also on the thermal conductivity and the material structure.

- Substrate's influence on DE has been demonstrated with multiple-layer experiment.
- CGS is a good and economic affordable technique for the obtention of free oxide coatings versus other thermal spray techniques onto light alloys.

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REFERENCES

1 ASM HANDBOOK. Vol. 2. Properties and selection :non-ferrous alloys and special purpose materials p.1770-1886

2 The cold spray materials deposition process. Fundamentals and applications. Vicor K. Champagne, woodhead publishing limited, Cambridge

3 Development of a generalized parameter window for cold spray deposition Tobias Schmidt, Frank Gärtner, Hamid Assadi, Heinrich Kreye,. Acta Materialia 54 (2006) 729–742

4 Bonding mechanism in cold gas spraying. Hamid Assadi, Frank Gärtner, Thorsten Stoltenhoff b, Heinrich Kreye, Acta

Materialia 51 (2003) 4379-4394

5 Parameter Selection in Cold Spraying H. Assadi, T. Schmidt, H. Richter, J.-O. Kliemann, K. Binder, F. Gärtner, T. Klassen, and H. Kreye, On JTTEE5 20:1161–1176_ ASM International

6 ASM HANDBOOK. Vol. 9. Metallography and Microstructures 2004. P.2157-2207

7 Relationship between particle size and deformation in the cold spray process Peter C. King, Mahnaz Jahedi Applied Surface Science 256 (2010) 1735– 1738

8 Cold spray deposition: Significance of particle impact phenomena Sergei Vladimirovich Klinkov, Vladimir Fedorovich Kosarev, Martin Rein Aerospace Science and Technology 9 (2005) 582–591

9 The high-strain-rate response of alphatitanium: experiments, deformation mechanisms and modeling D.R. Chichilia, K.T. Ramesha, , K.J. Hemkera Acta Materialia Volume 46, Issue 3, 23 January 1998, Pages 1025–1043

 S. Yina,X-f. Wanga, W.Y. Li, Hong-en Jiea Applied Surface Science Volume 257, Issue 17, 15 June 2011, Pages 7560–7565

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Deposition of Ti6Al4V onto different substrates using cold gas spray with nitrogen and helium as propellants

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Abstract

This study addressed the interaction of Ti-6AI-4V powder with base materials of distinct hardness. For this purpose, Ti-6AI-4V powder was deposited onto Ti-, AI- and Mg-alloy substrates by cold spraying using nitrogen and helium as process gas. The impact morphology and microstructure of the coatings obtained were then examined. Ti-6AI-4V microstructure consisted mainly of a 95% α -phase, which conferred great strength and low ductility and formability, with some retained β -phase.

Ti-6Al-4V particles bonded well to the substrate, and the coatings obtained with helium as propellant gas showed a lower porosity and a higher resistance to corrosion than those achieved with nitrogen.

1.Introduction

The use of light alloys in aerospace, transport and biomedical industries has

increased exponentially in recent years, as has surface engineering technologies to enhance the properties of these alloys for a specific end use.

Cold gas spray (CGS) is a solid-state spraying technique that produces coatings by exposing a substrate to a high-pressure gas stream (nitrogen or helium) that contains powder particles with a certain size distribution. These particles acquire high kinetic energy, thus allowing them to reach speeds between 300 and 1200 m/s.

The mechanism behind this process is based on high kinetic energy, localized plastic deformation of the particles and the substrate, and adiabatic shear instabilities. The study and control of the parameters involved in CGS, namely pressure, temperature, particle speed, standoff distance, powder morphology, feedstock rate, gun angle, and substrate roughness, allows the production of a coating from particles in solid state.

Plastic deformation occurs upon the impact of these particles with the substrate surface. Depending on the characteristics of the substrate and the powder, this deformation can take place in the powder, in the substrate, or in both. Only when the impact velocity of the particles reaches a critical value is a coating obtained [1].

Given that CGS does not involve high temperature, this technique is appropriate for the deposition of temperature-sensitive materials, such as nanophased and amorphous substances. Furthermore, many deleterious phenomena caused by high temperatures, such as grain growth, which happens during thermal spraying, or oxide formation, are minimized or even prevented by CGS.

Other typical advantages of CGS include compressive rather than tensile stresses, wrought-like microstructure, near theoretical density, absence of oxides, and other inclusion-free coatings [2].

The oxygen content of coatings is dramatically reduced or even absent when high oxygen-reactive materials like titanium, aluminium or copper are deposited by CGS, as shown by N. Cinca et al. for titanium grade 2 coatings on aluminium alloy [3].

CGS allows material cost reduction, the minimization of surface treatments, the possibility to increase machinery lifetime, and the reduction of problems associated with material melting. These features make it an efficient, more ecological, and economically more affordable technique than conventional thermal spray and deposition methods. The main objective of the present study was to apply CGS technology to obtain high density Ti6Al4V coatings on Ti6Al4V substrates as a way to repair industrial equipment, and onto aluminum and magnesium alloys to enhance wear and corrosion resistance.

Ti6Al4V requires a high impact velocity to produce a coating. An increase in the temperature and the pressure of the propellant gas leads to an increase in particle velocity. However, there are some technical limitations when increasing the inlet temperature, namely the particles are more reactive with the propellant gas, and there are technical limitations of the system itself. Helium is lighter than nitrogen and therefore cold spraying with helium as propellant gas shows better performance. The use of this gas allows particles to reach a higher speed with a lower temperature, thereby avoiding the detrimental effects of high temperature [4]. However, helium is costly and therefore not viable for most applications, particularly at industrial level.

First CGS was performed with nitrogen as propellant gas, using high temperature and pressure, as well as distinct nozzles. Once the process had been optimized with nitrogen, it was done using helium. The Ti6Al4V coatings achieved with helium were denser, had a greater thickness and showed better adherence than the optimum coating obtained with nitrogen.

2.Experimental procedure

In this study, commercially pure Ti6Al4V powder grade 5 with a size distribution of - $45 + 25 \mu$ m and low oxygen content was used as feedstock material. A CGT Kinetics 8000 modified by the Helmut Schmidt University was used first with nitrogen and then with helium. Two nozzles were used, D24 and D50, the latter longer than the former and allowing a higher gas speed at nozzle exit.

Ti6Al4V grade 5, Al-7075-T6, and AZ31 were used as substrates.

То study the morphology and microstructures of the Ti6Al4V powder, free surface and cross sections were observed by scanning electron microscopy and optical Hardness microscopy. measurements done with were а Nanoindenter with a Berkovich indenter on the polished cross surface, and X-Ray diffraction tests were done to check the absence of oxides in the powder.

Although there are previous reports of Ti6Al4V coatings by cold spray, in the present study a theoretical approach was followed using the numerical technique developed by T. Schmidt et al. [5], where the critical velocity was calculated as:

$$v_{crit}^{th,mech} = \sqrt{\frac{F_1 \cdot 4 \cdot UTS \cdot \left(1 - \frac{T_i - T_R}{T_m - T_R}\right)}{\rho}} + F_2 \cdot c_p \cdot (T_m - T_i)$$

Nomenclature for calculations:

F ₁	Constant
F ₂	Constant
UTS	Ultimate Tensile Strength
Ti	Impact temperature
T _R	Room temperature
T_{m}	Melting temperature
ρ	Density
Cp	Specific heat

Table 1: Nomenclature for equation 1.

The application of specific values for Ti6Al4V in equation 1 gave graph 1, which shows the window of deposition based on critical particle velocity and impact temperature.



Graph 1: Ti6Al4V window of deposition.

Graph 1 shows the critical velocity (blue line) above that particles should reach to obtain a coating and the erosion velocity (red line) below which particles should reach in order not to result in erosion on the substrate surface.

Once the windows of deposition had been established and on the basis of previous experience, four parameter values were

tested with nitrogen and the D24 nozzle and other one with D50 nozzle. Once the optimum spraying parameters were found, three more tests with helium were done with the D24 nozzle.

At the same time, with the lowest and the highest parameter values, wipe tests were done to study single impact morphologies on polished substrates by SEM. Particle impacts were observed with the sample perpendicular to the electron beam and also tilted 65-75 degrees.

Deposition efficiency was calculated by weighing the substrates before and after spraying, and comparing the gain with the theoretical weight gain.

Light microscopy was used to study the porosity of the polished cross section of the coatings.

To determined the tensile strength of the coatings, the Tubular Coating Tensile Test (TCT Test) was done [6]. For each parameter value, three samples were tested. As K. Binder et al. explain, the values measured should be multiplied by a factor between 1.5 and 1.7 to obtain the true ultimate tensile strength of the coatings [7].

3.Results and discussion

3.1 Materials

Figure 1 shows a micrograph of powderfree surface and polished cross section. Particles were spherical and showed no internal porosity.



Figure 1: Ti6Al4V-free surface and cross section.

Ti6Al4V grade 5, aluminum alloy Al-7075-T6 and magnesium alloy AZ31 were used as substrates.

Table 2 shows the hardness of thesubstrates and feedstock powder.

Substrate	Hardness (Vickers)	Microhardness
Ti6Al4V	560	358 ± 8
AI-7075-T6	210	178 ± 8
AZ31	176	56 ± 2

Table 2: Substrate hardness.

3.2. Influence of increased temperatures and nitrogen pressure on coating deposition

The wipe test morphologies shown in Figure 2 were obtained under the lowest and the highest parameter values for all substrates using a D24 Nozzle and nitrogen as propellant.



Figure 2: Wipe test morphology of coatings onto AI-7075-T6 (A), Ti6Al4V (B) and AZ31 (C) using the lowest and highest parameter values.

Higher energy conditions produced greater impact velocities, and particle penetration of the substrate was higher. For Ti6Al4V substrate, particles were more flattened, not only because of a higher impact velocity but also because of the greater ductility of the spray material at higher temperature. Figure 2 shows jets surrounding the impacted particles on Al-7075-T6 and AZ31 TI6AI4V COATINGS OBTENTION

substrates; in contrast, for Ti6Al4V, jets formed in the particles. Aluminium and magnesium substrates are softer and more ductile than Ti6Al4V particles; however, titanium substrate is harder than the spraying powder, thus the highest deformation took place on the particles and not on the substrate.

Figure 3 shows the coatings obtained using the lowest (A,B,C) and the highest (A_1 , B_1 , C_1) parameter values for all the substrates; the same conditions as for the wipe test.



Figure 3: Coatings obtained using the lowest (A,B,C) and the highest (A_{1} , B_{1} , C_{1}) parameter values for Ti6Al4V (A, A_{1}), Al-7075-T6 (B, B_{1}) and AZ31 (C, C_{1}) substrates.

For the Ti6Al4V substrate, the deposition efficiency in both cases, lower and highest parameters, was over 80%, but porosity
decreased from 12.6% to 3.6%. For AI-7075-T6, porosity decreased from 14.6% to 1.4% while deposition efficiency increased from 40% to 70%. Finally, for AZ31, porosity fell from 14.1% to 7.3% and, like the Ti6Al4V substrate, deposition efficiency did not change, and was around 65% for both parameters.

Table 3 Variations in coating thickness for the three substrates

Low Conditions High condition				
Ti6Al4V	785 µm	623 µm		
Al-7075-T6	496 µm	546 µm		
AZ31	707 µm	656 µm		

Low conditions are for the lowest parameters and high conditions for the highest parameters.

Porosity reduction with no increase in deposition efficiency produced thinner coatings, as found for Ti6Al4V and AZ31 substrates. In contrast, for Al-7075, deposition efficiency increased by 30%.

At higher parameter values, particles reached their critical velocity earlier and the deformation during impact was higher as a result of greater ductility caused by higher spraying temperature and more energetic impact produced by pressure.

The greater deformation of the particles led to lower porosity, and particles showed improved bonding to the substrate, thereby resulting in a higher tensile strength. Figure 4 shows the TCT strength evolution for different spraying parameters.



Figure 4: TCT strengths of cold-sprayed Ti6Al4V coatings for several temperatures of nitrogen process gas.

Higher tensile strength implies that particles are better bonded. Modified cavitation tests were performed on wipe test probes to study impact morphologies and removed particles. Titanium grade 2 was used as a substrate for the same spraying powder. The results were consistent with those observed for cold-sprayed copper particles [⁸], and for cold-sprayed aluminium particles onto aluminium substrate [⁹] by numerical modelling.

Ring-shape morphologies were observed on the substrates after the modified cavitation test (Figure 5).



Figure 5: Substrate imprints after particle removal.

These imprints, in combination with the obtained particles (Figure 6), provide an experimental example of the numerical model developed.



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Figure 6: Particles removed after modified cavitation test.

Figure 7 shows an EDX analysis of a particle removed and of a substrate ring after the modified cavitation test. In both cases, signs of material transference between particle and substrate were detected



Figure 7: Particle EDX analysis.

The material melting had generated strong bond and had caused higher tensile strength.

3.3. Nozzle influence

Coating can also be improved by using different nozzles. Depending on the nozzle shape, particles can reach higher velocity, and therefore attain greater impact energy.

After the first approach with the D24 nozzle, porosity was still too high to be considered optimum. Moreover, since it was not possible to keep increasing the temperature and the pressure of the streaming gas because of system limitations, the D50

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nozzle was used. This nozzle is longer and narrower than the D24 one, thus allowing higher acceleration of the streaming gas. On the basis of previous experience with the D24 nozzle, only the most energetic conditions were used.

Figure 8 shows the coatings obtained for the three substrates. The following table shows the results for porosity and thickness of the coatings.

Substrate	Porosity	Thickness	
Ti6Al4V	1.9 %	596 µm	
AI-7075-T6	2.0 %	566 µm	
AZ31	1.8 %	613 µm	

Porosity was dramatically reduced for Ti6Al4V and AZ31 substrate and for Al-7075-T6, it was maintained.

The thicknesses reached with the D50 nozzle were similar to those achieved with D24.

A decrease in porosity is caused by an increase in impact velocity of the particles. Particles deform more and were able to fill the gaps in the structure. The efficiency for Ti6Al4V and Al-7075-T6 substrates was above 80% while for AZ31 it exceeded 70%.

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Figure 8: Coatings obtained with the D50 nozzle.

TCT strength was above 180 MPa for all samples, with an increase of almost 30% with respect to the coatings obtained with the most energetic conditions with the D24 nozzle.

3.4. Helium as streaming gas

When the temperature of the streaming gas is too high, the risk of particle oxidation or nitridation increases. Elevated qas temperature may also increase the substrate temperature, which may be detrimental for the coating properties. In helium overcomes this regard, these

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problems because it is inert and allows higher particle velocity at a lower temperature.

Figure 9 shows the coatings obtained using helium as propellant. In all cases the porosity was around 0.1%. Thicknesses of 830 μ m, 720 μ m and 880 μ m were achieved for Ti6Al4V, Al-7075-T6 and AZ31 respectively. Deposition efficiency was around 99% in all cases, implying that almost all the particles hitting the substrate adhered to it.



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Figure 9: Cold gas-sprayed Ti6Al4V onto Ti6Al4v, Al-7075-T6 and AZ31substrates using helium as propellant.

Coatings were dense, thick and with no traces of oxidation or nitridation.

4. Conclusions

- -When nitrogen was used as carrier gas, cold gas-sprayed Ti6Al4V coatings were denser and better bonded as the temperature and the pressure of the carrier gas increased. Such an increase caused greater particle velocity and also higher ductility due to the temperature and greater compaction due to pressure.
- -When helium was used as carrier gas, the temperature required was lower than that needed by nitrogen, and particles reached higher velocities, hitting the substrate with greater kinetic energy, thus producing denser coatings with higher deposition efficiencies.
- -Porosity was dramatically reduced, and TCT strength was increased by choosing the correct nozzle for each material/substrate pair, thus achieving an increase in impact velocity.
- -Modified cavitation tests were performed on wipe test probes to study impact morphologies and removed particles. Due to the high kinetic energy on particle impact, evidence of material transference between particle and substrate was detected for high and low parameters.

Material melting generated a strong bond and caused higher tensile strength.

Thermal Spray 2007: Global Coating Solutions (ASM International) (2007) 248-253

5. References

- 1 T.Schmidt, F. Gärtner, H. Assadi, H. Kreye Acta Mater. 54 (2006) 729–742
- 2 R. Ghelichi, M. Guagliano Frattura ed Integrità Strutturale, 8 (2009) 30-44;
- 3 N. Cinca, M. Barbosa, S. Dosta, J.M. Guilemany Surf. Coat. Technol. . Vol. 205/ 4.(2010) 1096-1102
- 4 .Wong, E.Irissou, A.N. Ryabinin, J-G.Legoux, S.Yue
 JTTEE5 20:213–226
 DOI: 10.1007/s11666-010-9568-y
- 5 T. Schmidt, F. Gärtner, H. Assadi, H. Kreye Acta Materialia 54 (2006) 729–742
- 6 Tubular-Coating-Tensile –Test
- T. Schmidt, F. Gärtner, , H. Kreye
- 7 K. Binder, J. Gottschalk, M. Kollenda, F. Gärtner, and T. Klassen Journal of Thermal Spray Technology, Vol. 20, 1-2, (2011), 234-242(9)
- 8 T.Schmidt, H.Assadi, F.Gärtner, H.Richter, T. Stoltenhoff, H.Kreye and T.Klassen JTTEE5 18:794–808 DOI: 10.1007/s11666-009-9357-7
- 9 W.-Y. Li, H. Liao, C. Coddet, C.-J. Li, H.-S. Bang

Experimental study of Cold Gas Spray bonding mechanism based on spraying powders and substrate nature

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Cold spraying of spherical Ti-6Al-4V was performed with nitrogen and helium as process gas onto titanium, steel, and aluminum alloy substrates, to study particle's bonding mechanism based on the structure and physical properties of the materials.

Single impacts were produced by so called wipe tests, and single splat adhesion was investigated by applying a modified cavitation test. Impact morphologies and particle removal in cavitation testing were subsequently studied by SEM and TEM.

The investigations demonstrate that spherical Ti-6Al-4V particles bonding mechanisms are different depending on substrate properties (hardness, thermal conductivity, crystal structure, melting point, ductility and cold work hardening). The more similar the materials are, stronger bonding is formed due to adiabatic shear instabilities and microfusion produced because of impact. With dissimilar materials, mechanical anchoring is produced, and no microfusion traces are found, having lower adhesion strength values.

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CHAPTER 5: SS316L COATINGS

Stainless steel 316L, offers higher creep resistance, stress to rupture, and tensile strength at elevated temperatures, and it can be hardened by cold working, which can also result in increased strength ^[80].

316L coatings have been previously obtained by thermal spray techniques, containing a relatively high amount of oxides. Three thermal spray techniques (HVOF, APS and SPS) to obtain 316L stainless steel coatings have been compared by Zhao et al.^[81]. The HVOF coating was the only one with an oxygen content of around 1%, with a hardness value in the range between 240 and 315 HV. Other authors also used HVOF ^[82,83,84]; for example, Totemeier even obtained a porosity lower than 1%, with high efficiency and a higher hardness than the wrought material; however, these coatings also had a high oxygen content (4 - 6,5%) and showed relatively high dislocation densities, more than two orders of magnitude greater than the starting powder. In addition, the ones performed by K. Dobler et al., also with HVOF but with a low oxygen content to achieve low particle temperature, showed to result in detrimental bonding and cohesive strength of the coating ^[64].

The use of atmospheric thermal spraying for this material leads to the formation of oxides, thus reducing corrosion resistance and mechanical properties. The ability to control the oxygen content of the coating is therefore essential to achieve maximum corrosion resistance. In that case, Cold Gas Spraying (CGS) can be actually useful since it can be employed for oxygen sensitive materials.

Using CGS, K. Spencer et al. have obtained 316L stainless steel coatings onto AZ91E magnesium alloy. Different particle size distributions have been used in order to optimize the obtained coatings, reaching corrosion resistance behaviour close to SS316L bulk material; however, they have low deposition efficiencies (25-30%)^[85].

Since no molten or semi-molten material is involved, oxidation levels will be the same in the coating than in the spraying powder. This, in combination with low porosity, high deposition efficiency and good adherence, are desirable coating properties if good oxidation resistance and wear resistance is pursued.

As in the case of Ti6Al4V coatings, a 3^2 experimental design was used (Figure 68 and table 19).

Substrates were grinded with 220 SiC paper before spraying to avoid oxides or impurities interferences with deposition, influencing efficiency and coating characteristics and to increase surface roughness.

In this system, spraying powder nature is different from the three substrates, is not like in previous case were one substrate was also Ti6Al4V.

It is necessary to take into account some properties in order to be able to analyse the incoming results.

SS316L has almost the double density than Ti6Al4V and between 3 and 5 times more than Al-7075-T6 and AZ31 respectively.

Its thermal conductivity is 14-16 W/mK, which is between 2 and 3 times higher than the Ti6Al4V one, but still much lower than the Al-7075-T6 or AZ31 one.

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5.1. Ti6Al4V substrate

Despite 316L stainless steel has not a real application onto Ti6Al4V substrate because is not going to improve its properties (wear resistance and corrosion), the idea was to obtain this coatings onto a harder substrate to study the influence on the coating obtention and compare them with the ones obtained onto aluminum and magnesium alloys.

Figure 173 shows the SEM micrographies of the obtained spherical 316L coatings onto Ti6Al4V substrate after metallographic preparation with the conditions showed in Table 18.



Figure 173: 316L coatings onto Ti6Al4V

As it can be appreciated in figure 173 micrographies, a homogeneous coating has been formed for all spraying parameters of the experiments design. Analysing the obtained results, it has been consider that the best spraying conditions of the experimental design are 780°C and 38bar.

Table 64 shows the deposition efficiency and thickness of the obtained coatings.

Spraying Conditions	Deposition Efficiency %	Thickness µm
780°C, 30 bar	94 ± 5	545 ± 15
780°C, 34 bar	94 ± 6	578 ± 17
780°C, 38 bar	96 ± 3	545 ± 15
730°C, 30 bar	85 ± 4	530 ± 22
730°C, 34 bar	89 ± 4	518 ± 26
730°C, 38 bar	85 ± 5	484 ± 22
680°C, 30 bar	78 ± 4	495 ± 24
680°C, 34 bar	46 ± 3	445 ± 20
680°C, 38 bar	50 ± 4	447 ± 23

Table 64: deposition efficiency and thickness of the obtained coatings

Figure 174 shows the obtained irregular 316L coatings onto Ti6Al4V substrate. As it can be appreciated, coatings have been obtained on the whole range of spraying conditions. As happened with spherical 316L the most homogeneous and less porous coating was obtained at 780°C and 38 bar.



Figure 174: Optical micrographies of the obtained coatings

Spraying Conditions	Deposition Efficiency %	Thickness µm
780°C, 30 bar	63 ± 5	388 ± 17
780°C, 34 bar	66 ± 4	377 ± 11
780°C, 38 bar	68 ± 3	387 ± 23
730°C, 30 bar	62 ± 4	379 ± 19
730°C, 34 bar	58 ± 4	291 ± 20
730°C, 38 bar	65 ± 3	414 ± 15
680°C, 30 bar	51 ± 6	249 ± 46
680°C, 34 bar	55 ± 4	326 ± 18
680°C, 38 bar	60 ± 4	345 ± 29

Table 65 shows the deposition efficiency and thickness of the obtained coatings

Table 65: deposition efficiency and thickness of the obtained coatings

Porosity is less than 1% for all cases, this fact does not mean that all coatings are fully dense; inner porosity can exist, and inter-particle space is too small to be measure by these kind of programs. Figure 175 shows an example of this inter-particle porosity for non-optimal parameters which can trigger corrosion complications on the substrate if there are infiltrations (either from liquids or gases).



Figure 175: inter particle porosity 780°C and 30bar sample

Figure 176 shows a SEM image of the interface of the obtained coating at 780°C and 38 bar, where no deformation on the substrate surface has occurred and an optical microscopy micrograph of the same zone but chemically etched to be able to distinguish particles microstructure.



Figure 176: SEM and etched optical micrograph of the optimal coating

In the case of irregular powder, porosity is higher compared to spherical, but still lower than 2%. Nevertheless it can be appreciated in figure 174 that with some spraying parameters, exist decohesion between layers and cracks have being appeared. As in previous case, coating microstructure has been obtained by etching the sample to reveal particle limits and internal structure as it can see in figure 177.



Figure 177: Etched coating

Particles are highly deform, much more than Ti6Al4V, despite its irregular shape make impossible the quantification is this deformation.

Interface substrate/coating does not present pores or decohesion.

Figure 178 shows a comparison between powder and coating X-ray diffraction in the case of spherical powder.



Figure 178: X-Ray diffractogram of 316L spraying powder and the obtained coating

No traces of new phases or oxide formation are visible. It can be seen how inner structure of the particles is the same than the one of the spraying powder, but at the inter-particle zone, strong deformations have taken place.

5.2. Al-7075-T6 substrate

The same spraying conditions as for Ti6Al4V substrate were used (table 19). Figure 179 shows the micrographies of the obtained spherical 316L coatings onto Al-7075-T6 substrate after metallographic preparation.



Figure 179: Spherical SS316L coatings onto AI-7075-T6 substrate SEM micrographies

Spraying Conditions	Efficiency %	Thickness µm	Hardness (HVN)
780°C, 30 bar (A)	80 ± 4	463 ± 20	338 ± 44
780°C, 34 bar (B)	88 ± 4	458 ± 17	340 ± 66
780°C, 38 bar (C)	89 ± 3	495 ± 17	358 ± 36
730°C, 30 bar (D)	75 ± 5	463 ± 32	353 ± 72
730°C, 34 bar (E)	74 ± 4	479 ± 19	314 ± 58
730°C, 38 bar (F)	84 ± 3	474 ± 18	333 ± 57
680°C, 30 bar (G)	58 ± 6	336 ± 33	310 ± 61
680°C, 34 bar (H)	19 ± 7	_	_
680°C, 38 bar (I)	22 ± 8	-	-

Table 66: coatings properties onto Al-7075-T6 substrate

Table 66 shows the deposition efficiency, thickness and hardness of the obtained coatings under the spraying parameters described by the experiments design.

One of the first things that must be taken into account when figure 177 is observed is that at 680°C and 34 and 38 bar no homogeneous coating has been formed.

Probably, as it has been described in previous chapter with irregular Ti6Al4V spraying powder and Al-7075-T6 substrate, the oxide layer of the substrate is hampering coating's growth. Additionally, particles do not have enough energy to be able to bond to the substrate because its temperature and velocity is not high enough (streaming gas temperature is 680°C) and critical velocity is not reached.

Thickness is in the same order of magnitude for high and medium temperature, in all pressure range, and it reduces around a 30 % when the lowest temperature is used.

Figure 180 shows graphically deposition efficiency evolution through all spraying parameters.



Figure 180: deposition efficiency evolution

As the temperature and pressure increases, the deposition efficiency does it also. Particles reach the surface hotter and with higher velocity, which means that its higher ductility allows a better deformation.

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Analysing the obtained results from table 65, is obtained that temperature of the streaming gas has a higher influence in coating obtention than the pressure. Figure 181 shows a Pareto chart where this influence can be seen.



Figure 181: Pareto chart of spraying conditions influence for spherical SS316L

For all response variables, temperature has higher influence than pressure. Yaxis is the tvalue of effect, and as it can be observed, despite temperature's higher influence, the difference between them is not so high.

Irregular 316L coatings obtained under the same parameters are shown in figure 182.



Figure 182: 316L coatings onto Al-7075-T6

At the lowest temperature (680°C) no homogeneous coating has been formed (G,H,I micrographies). Spraying conditions are not sufficiently energetic, and particles are not reaching their critical velocity.

Spraying Conditions	Deposition Efficiency %	Thickness µm
780°C, 30 bar	31 ± 8	198 ± 30
780°C, 34 bar	41 ± 7	196 ±35
780°C, 38 bar	51 ± 7	361 ± 19
730°C, 30 bar	19 ± 8	207 ± 47
730°C, 34 bar	26 ± 7	171 ±32
730°C, 38 bar	41 ± 9	235 ±42
680°C, 30 bar	2 ± 1	-
680°C, 34 bar	10 ± 5	-
680°C, 38 bar	19 ± 6	_

Table 67: sprayed coatings properties

Table 67 shows the properties of the obtained coatings. As in previous cases, as the pressure increases, deposition efficiency does it also, for all temperature levels As it was already observed, at 680°C, no thickness values have been given because no proper coating has been formed.

As in previous cases, as the pressure increases, deposition efficiency does it also, for all temperature levels

As it was already observed, at 680°C, no thickness values have been given because no proper coating has been formed.

As with spherical powder, the influence of spraying parameters has been studied through Pareto charts. The obtained results are shown in figure 183.



Figure 183: Pareto chart of spraying conditions influence for irregular SS316L

In this case, pressure and temperature has a much higher influence than before, but the proportion between them remains similar as before.

In order to observe the microstructure maintenance at the interface the optimal coatings for spherical and irregular powder have been etched with Kroll's reagent.

Figure 184 shows the interface of the spherical powder optimal coating after etching.



Figure 184: optical microscopy micrographies of the etched coating at the interface coating/substrate

A severe deformation of the dendrites in the outer zone of the particles can be observed. This deformation will influence on coating's hardness as it will be seen later with Nanoindentation test. Particles at interface are not highly deformed. The strong deformation is suffered in this case, by the substrate.

Figure 185 shows the irregular powder etched coating at the interface with the substrates. Particles suffered high deformation and compaction as it can be seen due to the absence of pores. No decohesion appears on the rough interface due to the high energetic impact.



Figure 185: etched cross section

Compared to Ti6Al4V substrate, Al-7075-T6 is much more deformed by SS316L powder.

This high deformation will lead to a hardening of the particles, making that the coating has a higher hardness than the spraying powder.

Cold work due to impact hardens the substrate surface and also, the powder. Although the microstructure does not change, the strengthening occurs because of dislocation movements and dislocation generation within the crystal structure of the material.

Initial powder has a hardness of 180 ± 45 HVN. To be able to compare, a matrix of 7×9 nanoindentation has been executed onto the optimal coatings under the following parameters.

Poisson ratio	0,27
Maximum load (gf)	5
Distance between indentations (µm)	50
Number of indentations	63/60

Table 68: Nanoindentation parameters

Figure 186 shows the obtained matrix of nanoindentations onto the optimal coating obtained with the spherical SS316L powder



Figure 186: Nanoindentation matrix

Once the nanoindentation matrix was obtained, the sample was chemically etched to be able to observe where the nanoindentations were done. Depending of the indentation zone, inparticle, interparticle, pore... the obtained value is different.

Figure 187 shows the matrix once it has been etched and analyzed.



Figure 187: etched and analysed nanoindentation matrix

The main difference was between those indentations which are inside the particle or those which are in particle limits. There is also a difference inside the particle itself depending on the deformation grade of the microstructure. The bigger the deformation is, higher is the hardness. Lower hardness corresponds to nanoindentations that was done on the particle limits where the cohesion were not good or in a pore, and higher hardness corresponds to inner-particle zones or where the cohesion between particles due to the impact was good. The measured hardness of the optimal coating was 310 \pm 45 HVN that is almost the double than the measured hardness of the initial powder.

In the case of irregular powder, a 10×6 nanoindentation's matrix have been done onto the substrate to be able to compare the obtained hardness with powder hardness. Figure 188 shows the obtained matrix.



Figure 188: Nanoindentation matrix onto SS316L coating

Test	Modulus	Hardness									
	GPa	GPa									
1	94,653	1,654	16	95,188	1,934	31	82,56	1,93	46	118,304	2,92
2	123,401	3,07	17	****	****	32	84,074	2,467	47	125,214	2,768
3	****	****	18	75,772	1,859	33	104,418	2,207	48	130,012	3,438
4	97,812	2,569	19	91,902	1,483	34	119,304	2,979	49	111,153	2,671
5	94,117	1,856	20	114,339	2,551	35	132,923	3,36	50	117,795	2,347
6	110,209	2,911	21	129,388	2,934	36	103,222	2,162	51	145,248	3,667
7	122,384	2,659	22	137,025	2,88	37	124,052	2,557	52	141,695	3,533
8	127,866	3,206	23	124,982	2,859	38	123,688	2,702	53	128,818	2,974
9	119,969	2,821	24	113,36	2,298	39	140,266	3,241	54	135,191	3,603
10	106,809	2,35	25	123,574	2,961	40	110,43	2,192	55	133,745	3,432
11	137,978	2,964	26	130,243	2,877	41	93,419	1,673	56	109,164	2,394
12	127,613	2,737	27	133,055	3,186	42	112,815	3,287	57	114,58	2,893
13	114,804	2,499	28	106,434	2,904	43	119,933	3,182	58	135,78	3,251
14	129,176	2,964	29	141,941	3,318	44	107,08	3,425	59	120,201	3,561
15	121,89	2,631	30	148,407	3,23	45	81,813	2,416	60	138,588	3,537

Table 69: Nanoindentation hardness and modulus values

The obtained media values are:

Test	Modulus At Max Load GPa	Hardness At Max Load GPa
Mean	122 ± 14	$2,9 \pm 0,4$

Table 70: hardness and modulus values

Spraying powder has a hardness of $1,61 \pm 0,29$ GPa which means less than half of coating's hardness.

Analysing Figure 184 and table 69, despite all indentations have been done under the same load, indentations have different sizes. As harder the coating is where the indentation is performed, smaller is the footprint that the tip left. If indentation 19 and 41 are taking as an example, its hardness is lower than powder's hardness. This is because is an inter-particle zone where there has been a bad adhesion between particles. On contrary, all the upper line of indentation, from indentation number 51 to 60, hardness values are over 2,9 with the exception of 1 indentation, which means high compaction of the particles and hardening due to cold work in addition to well bonded particles.

When Nanoindentation values are analysed, it must be taking into account that the obtained values are very influenced by the surround, which means that interparticle zones, pores, cracks or impurities will change the obtained value. As higher the load is, lower is the influence of the surroundings.

Other Nanoindentation test have been performed onto the irregular powder optimal coating. Figure 189 shows schematically the conducted experiment.



Figure 189: Nanoindentation test

The nanoindentations were made to a depth of 150 nm, starting from the substrate and ending at the last layer of the coating. The obtained results are shown in figure 190.



Figure 190: Hardness evolution

The nanoindentations were made to a depth of 150 nm peak load, starting from the substrate and ending at the last layer of the coating.

The curve on the graph show a high variability in the results and a hardness values much greater than those obtained in microindentation or on the previous Nanoindentation test. As upper on the coating, greater hardness reveals the indentations.

On nanoindentation test, pile-up phenomena may occur due to material ductility. This phenomenon will generate a decrease in the contact area, which causes that the observed hardness by the nanoindenter is much higher than real.

To determine if this effect has occurred, the ratio of residual height and the actual height of the indentation should be above 0,7. In this case, a value of 0,98 is obtained.



Figure 191: pile up phenomena in Nanoindentation

With KINETICS 8000 gun from HSU, two spray conditions were established for spherical powder. The previous experience with this material have shown that temperature has a higher influence in coating obtention than pressure, that's why pressure has kept constant and two different temperatures have been tested. Table 71 shows the performed spraying parameters.

Temperature (°C)	900	1000
Pressure (bar)	38	
Spraying distance (mm)	40	
Spraying angle (°)	90	
Nozzle speed (mm/s)	235	
Powder feeding rate (rpm)	5	

Table 71: HSU spraying conditions for spherical SS316L

Figures 192 and 193 shows the obtained coatings at 900 and 1000°C.



Figure 192: Spherical SS316L coating at 900°C and 38 bar



Figure 193: Spherical SS316L coating at 900°C and 38 bar

The properties of the obtained coatings are shown in table 72

Spraying Conditions	Efficiency %	Thickness µm	Porosity %
900°C, 38 bar	75 ± 1	849 ± 24	0,43 ± 0,05
1000°C, 38 bar	89 ± 7	997 ± 31	$0,14 \pm 0,02$

Table 72: Spherical SS316L coatings properties

As it can be observed, efficiencies are in the same range than the ones obtained at 780°C, thickness has increase a 70% for the coating obtained at 900°C and it has doubled for the coating obtained at 1000 °C.

Porosity has been also reduced to values lower than 0,5% for both cases.

Abrasive wear - Rubber-wheel

The abrasive wear was evaluated according to the ASTM G65-00 standard ^[12] with a rubber-wheel equipment. This test measures the weight or volume lost from a test sample in a controlled environment.

The assay consists in a rotating rubber wheel at a constant speed of 139 rpm onto the piece to test. A normal force is applied on the wheel to press it against the sample and an abrasive agent, in this case, Silica - SiO_2 , falls through the rubber wheel and the sample, wearing them.

	Abrasive wear rate (mm ³ /Nm)		
t (min)	Aluminium	Irregular	Spherical
1	3,53E-04	2,00E-04	1,11E-04
2	3,43E-04	1,99E-04	1,14E-04
3	3,44E-04	1,77E-04	1,11E-04
4	3,48E-04	1,84E-04	1,09E-04
5	3,49E-04	1,81E-04	1,07E-04
6	3,45E-04	1,77E-04	1,06E-04
7	3,35E-04	1,76E-04	1,05E-04
8	3,25E-04	1,72E-04	1,03E-04
9	3,22E-04	1,69E-04	1,01E-04
10	3,17E-04	1,67E-04	1,00E-04
15	2,98E-04	1,57E-04	9,47E-05
20	2,93E-04	1,52E-04	9,16E-05
25	2,86E-04	1,48E-04	8,87E-05
30	2,78E-04	1,45E-04	8,70E-05

The obtained results are shown in the following table.

Table 73: Abrasive wear rates for Al-7075-T6 substrate and 316L coating

Spherical SS316L coating has an abrasive wear rate 3,2 times lower than AI-7075-T6 and irregular SS316L coating has an abrasive wear rate 1,9 times lower than AI-7075-T6 as it can be appreciated in figure 194.



Figure 194: Abrasive wear rate comparative

The obtained values are:

Material	Abrasive wear rate (mm ³ /Nm)	
AI-7075-T6	$2,78 \cdot 10^{-4} \pm 0,7 \cdot 10^{-4}$	
Irregular SS316L coating	$1,45\cdot10^{-4} \pm 0,4\cdot10^{-4}$	
Spherical SS316L coating	$8,70\cdot10^{-5} \pm 0,4\cdot10^{-5}$	

Table 74: Abrasive wear rates

Higher hardness and good intersplat cohesion are the reason for better wear resistance.

CHAPTER 5

SS316L COATINGS

5.3. AZ31 substrate

The following coatings have been obtained under the spraying conditions of table 19 with irregular SS316L.



Figure 195: SS316L coatings onto AZ31

The first thing that was noticed is the multiple cracks that the coatings have. Adherence seems to be really but the thicker and less porous coating is the one obtained at 780°C and 38 bar.

Table 75 shows the efficiency and the thickness of the obtained coatings. Like in all previous cases, as the temperature and the pressure increases, efficiency does it. The optimum coating in terms of efficiency and Thickness is the one obtained at the highest conditions.

Spraying Conditions	Deposition Efficiency %	Thickness µm
780°C, 30 bar	64 ± 6	224 ± 23
780°C, 34 bar	74 ± 4	329 ± 6
780°C, 38 bar	82 ± 4	362 ± 20
730°C, 30 bar	66 ± 5	262 ± 24
730°C, 34 bar	66 ± 6	331 ± 20
730°C, 38 bar	78 ± 4	266 ± 13
680°C, 30 bar	45 ± 5	191 ± 11
680°C, 34 bar	55 ± 5	232 ± 30
680°C, 38 bar	61 ± 4	299 ± 17

Table 75: deposition efficiency and Thickness of 316L coatings onto AZ31

As with AI-7075-T6, KINETICS 8000 gun from HSU has been used with the same spraying parameters shown in table 71.

Figures 196 and 197 shows the obtained coatings at 900 and 1000°C.



Figure 196: Spherical SS316L coating onto AZ31 at 900°C and 38 bar



Figure 197: Spherical SS316L coating onto AZ31 at 1000°C and 38 bar

The properties of the obtained coatings are shown in table 76.

Spraying Conditions	Efficiency %	Thickness µm	Porosity %
900°C, 38 bar	72 ± 4	902 ± 41	<0,25
1000°C, 38 bar	80 ± 1	1013 ± 124	<0,25

Table 76: Spherical SS316L coatings properties

Deposition efficiency is in the same range than before but thickness is extremely increased. It must be taking into account that there is one more layer than before and the powder feeding rate is 5 to 3. Nonetheless, thickness has a 12% increase for the coating obtained at 900°C and a 25% increase for the coating obtained at 1000°C.

Porosity has been reduced to values lower than 0,3%.

Due to the high temperature, impinging particles are more ductile and they can be more deformed, closing the existing pores and reducing the porosity.

CHAPTER 5

5.4. Adherence test

In order to determine the bond strength of the coatings, Tubular Coating Tensile strength test has been realized under the following spraying conditions

Temperature (°C)	900	1000
Pressure (bar)	38	
Spraying distance (mm)	60	
Spraying angle (°)	90	
Nozzle speed (mm/s)	4	
Powder feeding rate (g/min)	39	
Sample rotation speed (mm/s)	250	
Sample material	Aluminum	

Table 77: TCT test spraying conditions for spherical SS316L

The obtained values for both samples are:

Conditions	900°C, 38 bar	1000°C, 38 bar
TCT test (MPa)	125 ± 10	161 ± 6
TS value (MPa)	200 ± 16	258 ± 9

Table 78: TCT and TS values for SS316L coatings

As it can be observed, the obtained coatings at 1000°C has a 30% higher tensile strength than the obtained coating at 900°C. Particles are more ductile, they are able to deform more at impact moment and therefor the coating is more compact.

Figure 198 shows a comparative of the tensile/deformation graphic for both conditions.


Figure 198: tensile/deformation graphic for Spherical SS316L samples

SS316L COATINGS

5.5. Corrosion test

The corrosion resistance of the obtained coatings onto AI-7075-T6 and AZ31 was evaluated by means of electrochemical measurements according to ASTM D-1411 standard. Open-circuit potential-time curves for the two substrates and as-sprayed coatings in aerated and unstirred chloride solution are shown in figure 199.

The electrochemical tests were conducted onto polished samples (below 1µm roughness) because corrosion properties are also assumed to be considerably affected by the surface roughness since the roughness of the coatings promotes a better solution contact in certain areas.



Figure 199: E_{OC} potential for substrates and coatings

As it can be observed, after 24 hours test, no electrolyte has arrived to the substrate surface. E_{OC} potential provides information about the evolution and degradation of the coatings and substrates For all samples, the E_{OC} has been stabilized after 2 hours without significant oscillations.

As more positive the potential is, more resistant is the material to corrosion (is less active, less anodic). As it has been observed before with the obtained curves for Ti6Al4V

coatings, AZ31 has the lowest potential, being also the most susceptible to corrosion, followed by AI-7075-T6 substrate. In all cases, the coated substrates are over the substrates potentials, the coating is less susceptible of corroding. This test also showed that the obtained coatings are fully dense.

In order to estimate the corrosion current density, potentiodynamic curves have been done and anodic and cathodic curves were recorded around the corrosion potential (E_{corr}). From the intercept between the anodic and cathodic linear plots and, by extrapolating to the y and x axis, both E_{corr} and i_{corr} are respectively estimated. According to these Tafel-plots, the observed corrosion potentials are fairly similar to those obtained from the E vs. time curves.



Figure 200: Potentiodynamic curves of Ti6Al4V coatings onto the three substrates.

This means that the cathodic polarization did not cause appreciable change to the electrode surface.

Table 79 shows a comparative of the different obtained data of the curves.

	Substrates		SS316L coatings onto	
	AI-7075-T6	AZ31	AI-7075-T6	AZ31
E _{OC} (V)	-0.774	-1.519	-0,350	-0,438
E _{CORR} (V)	-0,780	-1,510	-0,345	-0,444
i _{CORR} (mA/cm ²)	10 ⁻⁶	5·10 ⁻⁶	6,3·10 ⁻⁷	3,2·10 ⁻⁶
R _p (ohm cm ²)	35,23	0,27	21,28	4,89

Table 79: Corrosion parameters for the analysed substrates/coatings

As it can be observed in table 79, E_{OC} and E_{CORR} are the same for every analysed sample.

5.6. System comparison

Comparing both SS316L systems, spherical and irregular spraying powders, higher deposition efficiencies were obtained with spherical powder as it can be observed in figure 201



Figure 201: Deposition efficiencies depending on spraying conditions for the three substrates

As it can be observed, the best results are obtained with spherical SS316L spraying powder onto Ti6Al4V followed by Al-7075-T6 substrate with the same spraying powder. The lowest efficiency values are obtained with irregular SS316L spraying powder onto Al-7075-T6 substrate (\checkmark).

The combination of AI-7075-T6 passivation layer with the high oxidation of the powder difficult to achieve critical speed and trigger Cold gas spray bonding mechanisms.

Once seen the obtained results, taking into account the efficiency of the process, coating thickness, density, homogeneity and the final hardness, one can conclude that

the optimum coatings are those made at the highest temperatures and pressures (780 °C and 38 bar) for spherical and irregular spraying powder.

Comparing the obtained results at the same pressure and varying temperature, efficiency increase as temperature rises, as well as thickness, while the hardness does not vary considerably.

At the same temperature and varying the pressures, efficiency increases with increasing pressure, but its effect is lower than in the case of temperature, the same way as occurs with the thickness.

Cold Gas Spray process with SS·16L as spraying powder was having better results when spherical powder is used.

Although bibliographically it is said that irregular morphology is better than the spherical morphology for Cold Gas Spray technology that would be under the exactly same properties of the spraying powders. That means, of course, leaving aside the morphology, hardness, size distribution and primarily oxidation level of the powder.

Coatings microhardness is very similar for the optimal coatings onto the three substrates independently of the spraying powder.

For those coating obtained with spherical SS316L spraying powder the obtained microhardness was 358 ± 36 HVN while for irregular SS316L spraying powder, the obtained hardness was 368 ± 35 HVN.

Compared with powder hardness, on the coatings obtained with the spherical 316L powder, hardness has doubled, while on the coatings obtained with the irregular 316L powder, hardness has multiplied per 2.3.

In terms of nanohardness, the variability is much more differentiated, due to the pile-up processes that has been developed onto the optimal coating obtained from irregular 316L spraying powder

5.7. Publications derived from this section

From the obtained results in this section, the following articles have been proposed:

"Optimization of 316L stainless steel coatings on light alloys using cold gas spray"

M. Villa*, S. Dosta, J.M. Guilemany

Surface and Coatings Technology. SURFCOAT-D-13-00086R2. Pending for publication

Optimization of 316L stainless steel coatings on light alloys using cold gas spray

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Keywords : Cold Gas Spray, 316L Stainless steel, Coating Optimization

ABSTRACT

Spherical 316L stainless steel powder was deposited onto light alloys by Cold Gas Spray (CGS). The main objective was to obtain thick coatings and thus improve the wear resistance of the light alloy substrates while maintaining the high oxidation resistance that characterizes 316L stainless steel. To optimize the coatings, the pressure and temperature of the streaming gas were varied in an experimental design matrix. The physico-chemical properties and deposition efficiency of cold-sprayed 316L stainless steel coatings were studied. Deposition efficiency, porosity and wear resistance properties of the coatings were analysed. The coatings achieved under the highest pressure and temperature were denser, thicker and with a higher wear resistance than those obtained under lower energy. The hardness and wear resistance of the

light alloy substrate were improved over those obtained by conventional spraying techniques.

1. INTRODUCTION

The use of light alloys in aerospace, transport and biomedical industries has increased exponentially in recent years, as has surface engineering technologies to enhance the properties of these alloys for a specific end use.

Light alloys and specifically aluminum alloys have a not very high creep resistance and its wear resistance is very low.

316L stainless steel offers higher creep resistance, stress to rupture, and tensile strength at elevated temperatures, and it can be hardened by cold working, which can also result in increased strength [1].

This stainless steel is commonly used in the following: food preparation equipment,

particularly in chloride environments; pharmaceuticals; marine applications; architectural applications; medical implants; and fasteners.

316L coatings have been previously obtained by thermal spray techniques, containing a relatively high amount of oxides. Three thermal spray techniques (HVOF, APS and SPS) to obtain 316L stainless steel coatings have been compared by Zhao et al. [2].. The HVOF coating was the only one with an oxygen content of around 1%, with a hardness value in the range between 240 and 315 HV. Other authors also used HVOF [3,4,5]; for example, T.C.Totemeier even obtained a porosity lower than 1%, with high efficiency and a higher hardness than the wrought material; however, these coatings also had a high oxygen content (4-6.5%) and showed relatively high dislocation densities, more than two orders of magnitude greater than the starting powder [4]. In addition, the ones performed by K. Dobler et al., also with HVOF but with a low oxygen content to achieve low particle temperature, showed to result in detrimental bonding and cohesive strength of the coating [3].

The use of atmospheric thermal spraying for this material leads to the formation of oxides, thus reducing corrosion resistance and mechanical properties. The ability to control the oxygen content of the coating is therefore essential to achieve maximum corrosion resistance. In that case, Cold Gas Spraying (CGS) can be actually useful since it can be employed for oxygen sensitive materials.

Using CGS, K. Spencer et al. have obtained 316L stainless steel coatings onto AZ91E magnesium alloy. Different particle size distributions have been used in order to optimize the obtained coatings, reaching a corrosion resistance behaviour close to SS316L bulk material; however, they have low deposition efficiencies (25-30%) [6]

Cold gas spray (CGS) is a solid-state spraying technique that produces coatings by exposing a substrate to a high-pressure gas stream (nitrogen or helium) that contains powder particles with a certain size distribution. These particles acquire high kinetic energy, thus allowing them to reach speeds between 300 and 1200 m/s, depending on several parameters, namely the pressure and temperature of the streaming gas, powder material, particle size and morphology, and the geometry of the nozzle.

The mechanism behind this process is based on high kinetic energy, localized plastic deformation of the particles and the substrate (depending on its properties), and adiabatic shear instabilities. The study and control of the parameters involved in CGS, namely pressure, temperature, particle speed, standoff distance, powder morphology, feedstock rate, gun angle, and substrate roughness, allows the production of a coating from particles in solid state.[7] Given that high temperature is not involved in CGS, this technique is appropriate for the

deposition of temperature-sensitive materials, such as nanophased and amorphous substances. Furthermore, many deleterious phenomena caused by high temperatures, such as grain growth, which happens during thermal spraying, or oxide formation, are minimized or even prevented by CGS. Therefore the potential to produce nanostructures by Cold Spray technology using nanostructured powders is much higher than when using other methods. Other typical advantages of coatings this technique obtained by include compressive rather than tensile stresses, wrought-like microstructure, near theoretical

density, oxides, and inclusion-free structures [8].

The oxygen content of coatings is dramatically reduced or even absent when high oxygen reactive materials like titanium, aluminium or copper are deposited by CGS, as shown by N. Cinca et al. for titanium grade 2 coatings on aluminium alloy [9].

Upon impact of these particles with the substrate surface, plastic deformation occurs. Depending on the substrate and the powder characteristics, this deformation can take place in the powder, in the substrate, or in both. Only when the impact velocity of the particles reaches a critical value is a coating obtained [10].

CGS allows material cost reduction, the minimization of surface treatments, the possibility to increase machinery lifetime, and the reduction of problems associated with material melting. These features make it an efficient, more ecological and

economically more affordable technique than conventional thermal spray and deposition methods.

The main objective of the present study was to apply CGS technique to obtain high density 316L stainless steel coatings onto aluminum 7075-T6 alloy to increase its wear resistance. For this purpose, a 3² factorial experiment was designed to reduce the number of tests varying pressures and temperatures of the streaming gas. The optimal coating was obtained considering three response variables (deposition efficiency, thickness and porosity) under the influence of each parameter.

Coating microstructures were characterized by standard metallographic approaches, optical microscopy, scanning electron microscopy, and X-ray diffraction. Coating hardness studied was by the microindentation and nanoindentation techniques. Abrasive wear resistance of the optimal coating was also examined and compared with that of the original light alloy used as substrate.

MATERIAL AND METHODS

AI-7075-T6 alloy was used as substrate.

The surface of the alloy was grinded with 220 SiC paper before the spraying process to remove superficial oxidation.

Spherical 316L stainless steel powder (Sandvik Osprey Ltd.,UK) with a particle size distribution of 10-50 μ m was used as feedstock. The powder was sieved to obtain the desirable particle size (20-40 μ m).

Particle distribution was measured using a laser diffraction analyser. X-ray diffraction of the sieved powder and the coating showed that the microstructure was an austenitic phase with an FCC structure without oxide formation.

The density of the powders was measured following the ASTM B-238 standard.

The coatings were achieved using a CGS KINETICS 4000 system from Cold Gas Technology Gmbh (Germany). Nitrogen was used as streaming gas and the gas nozzle temperature was set between 600°C and 800°C and pressure between 20 and 40 bars. Other parameters, such as spraying distance, nozzle transverse speed, feed-rate and spray angle, were kept constant.

Deposition efficiency is a function of many variables, but experimentally it can be determined by the following equation:

$$DE = \frac{\Delta S_w}{\sum P_w}$$

Where:

ED= Deposition efficiency Δ Sw = Sample weight change

Pw= Theoretical deposited mass with 100% deposition efficiency

Theoretical deposited mass was calculated from the spraying powder feed rate (g/min) in relation to the required time (min) to produce a coating on a sample with known surface area.

Deposition efficiency can also give an indication about the number of particles which have an impact velocity equal or above critical velocity.

This study was aimed at improving the mechanical properties of AI-7075-T6 alloy. Thus a rubber wheel test was used to measure the abrasive wear resistance of the coating, following the ASTM G65-04 standard.

Coating microhardness was measured using a MATSUZAWA MXT- α device, following the ASTM E384 - 11e1 standard.

A NANO INDENTER XP (Agilent Technologies) was used to measure the nanohardness of the powder and of the coatings, thus facilitating later comparison.

To observe the microstructure of the powders and coatings, surface must be properly prepared. After having cut and a piece of sample was mounted into an epoxy resin grinding papers from P120 to P1200 were used before polishing the surface of the sample with 6-µm and 1-µm diamond paste. Polishing was completed using a colloidal silica suspension with a particle diameter of 60 nm, and oxalic acid 10% w/w was used to reveal the microstructure, which was observed under an optical microscope. Particle morphology (free surface and cross-sectional area) and the semi-quantitative

composition of the powder, as well as the thickness, porosity and semi-quantitative composition of the coatings, were measured by means of scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1 Feedstock powder

20-40-µm spherical 316L stainless steel powder was used as feedstock. As shown by

X-ray diffraction, the powder had an FCC structure consistent with austenitic stainless steel (gamma phase iron: γ -Fe) (Fig 1), as did the coating



Fig.1: (1a) X-ray diffraction of 316L spherical powder (1b) X-ray diffraction of 316L coating.

As received powder had a wide particle size distribution (d10=11, 7µm - d90= 33,8 µm) with a high proportion of fines and a mean size of 20,1 µm. This distribution generates different particle velocities during spraying due to the different radios and mass of the particles. To reduce this effect, as received powder was sieved with 20, 40 and 63 microns mesh with Retsch equipment, obtaining a narrower size distribution with a mean particle size of 31,5 µm and a d10d90 of 24,5 µm-40,3 µm. Particle velocities are more uniform than before due to a similar size distribution of the powder. Figure 2 shows the particle size distribution of the original and the sieved powder done by Laser scattering technique.



Fig.2: particle size distribution profiles of As received and sieved powder

The critical speed of particles of the same size and morphology was reached at the same time, thus allowing better optimization of the spraying parameters.

Particle morphology is one of the main parameters to take into account in CGS [11]. Particle flight behaviour, critical velocity, and impact behaviour, among others, differed depending on the morphology. Powder-free surface was observed by scanning electron microscopy (Fig. 3a). Small protuberances were observed on the surface of the particles, produced during the atomization process. Figure 3b shows an optical microscope micrograph of the powder microstructure after etching the crosssectional surface with 10% w/w oxalic acid. The powder was observed to have a dendritic microstructure, which is the natural cooling microstructure of stainless steels where grains grow in the crystallographic direction which is the energetically favourable and predominant.



Fig. 3: a. Spraying powder free surface observed by scanning electron microscopy. b. spraying powder cross section after etching observed by Optical microscopy.

Since 316L stainless steel can be hardened by cold working, hardness of the feedstock powders was obtained by the

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nanoindentation technique. A hardness of 180 ± 45 HV was achieved for this powder. This result was later compared with the coating hardness. The latter was observed to show an increase in hardness as a result of the plastic strain deformation of the particles. The apparent density of the feedstock powder was 3.91 g/cm³ (obtained under ASTM B-212-89 standard)

3.2. Coatings

A 3² experimental design, shown in Figure 4, was followed to obtain the maximum information on the response variables, therefore allowing minimization of the number of experiments required to achieve an optimal coating.

The coatings obtained with the parameters specified by the experimental design are shown in Figure 4. In all cases, standoff distance, spray angle, powder federate and gun transversal speed were kept constant. Thus, only the influence of pressure and temperature on the coating was examined. Three levels of temperature and pressure were tested.

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		and the second
20KU X100 1 100PH 299511	2010 ×100 2 1004h 299532	20KU X100 3 100MH 299551
With the Alling Annual		
20kU ×100 4 100mm 299713	20KU X100 5 100MR 299728	20KU X100 6 100Mm 299745
and the second s	in all in all we	2
2010 ×100 7 100Ph 314704	20kU X75 8 100×n 314734	20KU X150 9 100PH 314742

Fig. 4: Spherical powder coatings under a range of conditions 1:Th Pl; 2: Th Pm; 3: Th

Ph; 4: Tm Pl ; 5: Tm Pm; 6: Tm Ph; 7: Tl Pl; 8: Tl Pm; 9: Tl Ph

Temperature/pressure ratio: 20,5 to 22,7 °C/bar Standoff distance: 40 mm Powder feeding rate: 33 g/min Gun speed: 500 mm/s Spraying angle: 90°

Where h is the highest parameter, m the medium parameter value and I the lowest value in a range of parameters

The temperature variation was observed to have a larger influence on the coating than pressure variation.

Figures 4.7, 4.8 and 4.9 shows the obtained coatings at the lowest temperature but with an increase of pressure. If the temperature is not high enough, particles does not deform plastically and as long as the pressure increases the substrate or previous formed coating erode, obtaining a lower thickness, more porous and with a very poor cohesion particles coating. At low between temperature and medium and high pressures, no coating was formed. This finding is attributed to the fact that powders with a certain particle size distribution and morphology have a critical velocity above which the particles adhere to the substrate. If the spraying conditions are not powerful enough, a lower percentage of the particles reach this critical velocity, thus adherence is lower [12].

According to the numerical approach developed by T.Schmidt et al. [7], every

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spraying powder has a window of deposition delimited by the critical and the erosion velocity of the particles. To obtain a coating, particles should be inside this window of deposition. The numerical approach can be graphed applying the following equation

$$v_{crit}^{th,mech} = \sqrt{\frac{F_1 \cdot 4 \cdot UTS \cdot \left(1 - \frac{T_i - T_R}{T_m - T_R}\right)}{\rho}} + F_2 \cdot c_p \cdot (T_m - T_i)$$

Equation 1: Critical and erosion velocity equation

Nomenclature for calculations:

F ₁	Constant
F_2	Constant
UTS	Ultimate Tensile Strength
T _i	Impact temperature
T _R	Room temperature
T _m	Melting temperature
ρ	Density
Cp	Specific heat

Table 1: equation 1 nomenclature

Observation of SEM images of Figure 4 and taking into account equation 1, indicate that, at the same temperature, the particle impact velocity increases with the spraying pressure. Theoretically, particles are situated more in the centre zone between the line of critical velocity and the line of erosion velocity, implying that a higher percentage of particles reached the critical velocity and adhered to the substrate. When the temperature is not high enough, an increase in pressure will not result in a coating, because the particles do not reach the v_{crit} The highest deposition efficiency achieved was approx. 90%. This result implies that most of the particles reached the substrate with a velocity equal or higher to the critical velocity, and thus bonded to the substrate or to the underlying surface.

In all cases, coating hardness was about double that of the powder. This result confirms that the hardness increased as a result of the work hardening of the upon impact. The hardness, deposition efficiency and thickness of the coatings produced in all the spraying conditions are shown in Table 1. To obtain table 1 values, three different samples have been analysed for every spraying condition. Deposition efficiency was observed to decrease as the temperature and pressure decreased. Thickness was greater at the highest temperature and decreased as this parameter fell. The influence of pressure was smaller than that of temperature.

Spraying Conditions	Efficiency %	Thickness µm	Hardness (HVN)
T _h °C, P _l bar	79,7 ± 4,2	463 ± 20	338 ± 44
T _h °C, P _m bar	88,4 ± 3,8	458 ± 17	340 ± 66
T _h °C, P _h bar	89,2 ± 3,5	495 ± 17	358 ± 36
T _m °C, P _l bar	74,5 ± 5,0	463 ± 32	353 ± 72
T _m °C, P _m bar	74,0 ± 4,3	479 ± 19	314 ± 58
T _m °C, P _h bar	84,1 ± 2,8	474 ± 18	333 ± 57
T _I °C, P _I bar	58,2 ± 6,2	336 ± 33	310 ± 61
T _I °C, P _m bar	19,0	-	-
T _l °C, P _h bar	22,5	-	-

Table 2: Deposition efficiency, thickness and Vickers hardness for each coating.

Temperature influences CGS in several manners. Higher temperature causes an

increase in carrier gas velocity and therefore in the impact velocity of particles. Consequently, the particles reach their critical speed sooner. The elastic and plastic properties of materials depend on the temperature. An increase in the temperature of the materials could enhance thermal softening, which is important for the bonding mechanism [13] because it facilitates particle deformation on impact and also surface activation. An increase in temperature of the carrier gas leads to greater speed and allows higher compaction of the coating.

The optimal coating was obtained at the highest temperature and pressure, as shown by the response variables (Fig. 5).



Fig. 5: Optimal coating.

The nanoindentation technique was used to compare the hardness of the coatings with that of the initial powders. An indentation matrix on the optimal coating before etching distinguishes the limits of the particles (Fig. 6). Differences between the indentations were detected. In this case, the differences were caused by the indentation location. For the coating, the load used and indentation depth were higher than in the case of the powder. Therefore the grain limits of the micro-structure did not have a great influence on the hardness. Here the large difference was between indentations inside the particle or those within the particle limits. Indentations within a single particle differed depending on the degree of deformation grade of the microstructure. The greater the deformation, the greater the hardness is. hardness corresponded Lower to nanoindentations made on the particle limits where cohesion between particles was weak or occurred in a pore. In contrast, higher hardness corresponded to inner particles or zones where the cohesion between particles on impact was high. Severe deformation was observed in these zones (Fig. 6).





Fig. 6: Nanoindentation matrix on the optimal coating.

316L stainless steel can be hardened by cold working, which can also result in increased strength. The hardness of the optimal coating was 358 ± 36 HVN. This value was

almost double than that of the initial powder. Taking into consideration that light alloys are softer than stainless steels, the substrate undergoes severe plastic deformation, while the first impinging particles maintain their microstructure as it can be seen in figure 7



Fig. 7: Particle/Substrate deformation.

Regarding resistance the wear tests performed on the optimum coating, it showed as expected a lower abrasive wear rate than the substrate. The abrasive wear resistance increased more than 300% with respect to that of the aluminium substrate (the abrasive wear rate was 2.8*10⁻⁴ mm³/Nm vs. 0.9*10⁻⁴ mm³/Nm for the 316L coating)(Fig 11). M. Torrell et al. studied stainless steel coatings deposited by HVOF and their abrasive wear resistance. The value for the 316L coating was 1.32*10⁻⁴ mm³/Nm when sprayed with hydrogen and 1.60*10⁻⁴ mm³/Nm

with propylene. These results show [13] that although the hardness of the 316L HVOF coating was similar to that obtained by CGS and, in the former, the absence of oxides on the particle surface provides greater interparticle bonding with higher toughness and wear resistance.

CONCLUSIONS

- Spherical 316L stainless steel powder was deposited successfully onto light alloys by Cold Gas Spray technique
- Given the efficiency of the process, and the thickness, density, homogeneity and final hardness of the coatings, it can be concluded that the optimum coating is obtained at the highest temperature and pressure in CGS
- There was an absence of oxides in the coating. DRX of figure 1, as well as the micrographies of figure 4, shows the absence of oxides on the coating.
- Coating hardness is approximately double of the powder hardness. After coating etching, the deformation zones at the particle limits can be clearly seen, thereby supporting the notion of hardening caused by particle deformation.
- As the temperature increases, the plasticity of the sprayed material increases, as does surface activation, thus allowing the deposition of the material on the substrate.
- An increase of carrier gas pressure leads to larger particle velocities, thus allowing to surpass the critical particle velocity and to a higher particle deformation at the impact moment, both required for satisfactory deposition. If a minimum temperature is not reached or the material has low plasticity, an increase in

the pressure causes erosion of the substrate upon particle impact. At the same temperature, an increase in pressure produces greater deformation of the particles, which leads to an increase in the hardness of the coating.

 The abrasive wear resistance of the coating is 300% greater than that of the substrate, and this parameter is in the same order of magnitude as that of coatings produced by HVOF.

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REFERENCES

- Various authors, ASM Handbook, vol. 1: Properties and Selection: Irons, Steels, and High-Performance Alloys, ASM International, 1993
- [2] L. Zhao, E. Lugscheider Surf. Coat. Technol. 162 (2002) 6–10
- [3] K. Dobler, H. Kreye, and R. Schwetzke J. Therm. Spray Technol. 9 (2000) 407-413
- [4] T.C. TotenmeirJ. Therm. Spray Technol vol. 14 /3 (2005) 369-372

- [5] M. Torrell, S. Dosta, J. R. Miguel and J. M. Guilemany
 Corros. Eng., Sci. Technol, 45/1 (2010) 84-93
- [6] K. Spencer, M.-X. ZhangSurface & Coatings Technology 205 (2011) 5135–5140
- [7]H. Assadi, F. Gärtner, T. Stoltenhoff, H. Kreye Acta Mater. 51 (2003) 4379-4394
- [8] R. Ghelichi, M. Guagliano
 Frattura ed Integrità Strutturale, 8 (2009) 30-44
- [9] N. Cinca, M. Barbosa, S. Dosta, J.M. Guilemany
 Surf. Coat. Technol. 205/ 4 (2010) 1096-1102.
- [10] T.Schmidt, F. Gärtner, H. Assadi, H. KreyeActa Mater. 54 (2006) 729–742
- [11] V.K. Champagne, The cold spray materials deposition process: Fundamentals and applications, Woodhead Publishing Itd, England, 2007
- [12] H. Assadi, T. Schmidt, H. Richter, J.-O.Kliemann, K. Binder, F. Gärtner, T.Klassen, H. Kreye
 - J. Therm. Spray Technol 20 (2011) 1161– 1176
- [13] S. V. Klinkov, V. F. Kosarev, M. Rein Aerosp. Sci. Technol. 9 (2005) 582–591

CHAPTER 6: DISCUSSION

The previous two chapters explained the results obtained with Ti6Al4V and SS316L metallic powders onto three different light alloys and discussed in detail the problems involved.

This chapter covers all the obtained coatings and gives a global discussion in terms of spraying powders, achieved coatings and properties.

<u>Pre-deposition</u>

The manufacturing process, by which the raw powder material is obtained, has a strong influence on the process and therefore on the final coating.

The supplied spherical Ti6Al4V and spherical SS316L spraying powders were manufactured by gas-atomizing, which gives an spherical shape to the powder. Ti6Al4V was atomized in Argon medium and leads to the obtention of very pure powder, free of ceramic impurities and with low oxygen contents. The high speed of solidification leads to a fine microstructure.

SS316L was atomizing in inert gas medium obtaining very pure powder, free of ceramic impurities and with low oxygen contents. The obtained microstructure is austenitic with dendritic structure.

The supplied irregular Ti6Al4V spraying powder was obtained by *Hydride/Dehydride* process, which gives an angular shape with fine $\alpha+\beta$ microstructure. Irregular SS316L was obtained by water atomization which gives an irregular shape of austenitic stainless steel with fine dendritic microstructure.

Both processes for irregular powders obtention, creates high oxidation levels on powder particles surface, which has a strong influence in powder's flight behavior and at impact moment, on particles bonding mechanism.

Oxidized particles have lower velocity in flight than non-oxidized ones, so it might happen that they could not adhere to the surface because its critical velocity has not been reached.

At the impact moment, the oxide layer difficult the bonding formation because:

The energy released at the impact moment is transformed in deformation of the impact zone (particle, substrate or both) and heat, which increases impact zone temperature and may even cause microfusions. If part of the energy released at the impact moment is used in breaking the oxide layer that covers particles surface, is possible that the remaining energy is not enough to deform the area and increase the temperature of the impact zone sufficiently to create adiabatic shear instabilities and form a bond.

If in addition to powder oxide layer, the substrate material is also oxidized, the remaining energy after impact is even lower. For this reason in Cold Gas Spray this factor can be reduced or even eliminated by grinding or grit blasting the substrate.

All the above powders show a compact structure that leads to a temperature gradient from the external surface to the core during the spraying process. It should be taken into account that particles remain in gas flow tens of nanosecond, even so, it is possible to reach temperatures of 500 degrees at impact moment. Particle's impact temperature depends on the spraying gas temperature and of the pressure of the streaming gas. It is a combination of gas temperature and time into the flow before impact.

Non-oxidized particles reach higher temperatures than oxidized ones, simply because they do not have a protective layer which has a low thermal conductivity and thermal expansion coefficient.

The acquired temperature leads to ductility increase which allows later a higher deformation

The used substrates are Ti6Al4V, aluminum alloy AI-7075-T6 and magnesium alloy AZ31. In addition to their difference in composition, which is obvious, there is between 100 and 150 HVN difference between them. Besides the hardness, thermal conductivity is a factor that must be taken into account. High thermal conductivity materials will lead to lower temperatures on impact zone. It cannot be said that higher thermal conductivity material will lead to worst coating or the opposite. Everything depends on the sprayed and the substrate material.

For Ti6Al4V spraying powders, the high thermal conductivity of Al-7075-T6 and AZ31 has a negative effect on coating formation, because dissipates the heat fast enough to hinder the formation of adiabatic shear instabilities.

DISCUSSION

<u>As-sprayed coatings</u>

In line with the references found in the literature, and the previous experience of the Thermal Spray Center Ti6Al4V powders were sprayed by CGS onto the three substrates and different spraying parameters were tested.

With KINETICS 4000 gun these tests consisted on modifying pressure and temperature of the spraying gas based on a 3² experimental design, which gives a wide range of temperatures and pressures (50°C and 4 bar difference between points).

With KINETICS 8000 these tests consisted on modifying pressure and temperature of the spraying gas based on a reduced 3² experimental design (100°C and 12bar difference between points). With KINETICS 8000 other nozzle, which generates higher particle velocities because of its length, was used, and also Helium as propellant gas, which due its mass, allows much higher particles velocities at lower temperature and pressure of the gas.

Using nitrogen as propellant gas, as higher the temperature and pressure of the streaming gas is, better coatings are obtained.

Deposition efficiencies are higher as well as thicknesses, while porosity is lower when temperature and pressure increase. Particles, due to higher temperature are more ductile and due to pressure the are able to deform more at the impact moment, closing existing pores and compacting the already formed coating.

Maximum efficiencies reached with Ti6Al4V irregular powder are around 50% while with spherical Ti6Al4V efficiencies are over 80%. Porosity is reduced as temperature increase but is always over 1%.

For irregular Ti6Al4V powder, efficiencies are always very similar independently of the temperature and pressure of the streaming gas. The variation in this case comes from the porosity level or what is the same, the compaction of the coating. With more energetic parameters, coating is more compacted. Although particles does not adhere to the surface, they are compacting it, and this compaction, reduces porosity and this will be reflected on future adherence of the coating.

Temperature variation it seems to have a higher influence on deposition efficiency than the pressure until a maximum point, where is the pressure which has a higher influence. With Helium, 100% deposition efficiency and porosities lower than 0,1% were reached for spherical Ti6Al4V powder.

SS316L coating followed the trend lines than Ti6Al4V coatings. Irregular powder has a higher oxidation level than spherical one, and this is reflected on the much lower deposition efficiency. It can arrive to 40% difference depending on the substrate.

As the temperature and the pressure increase, deposition efficiencies are better for both powders. As in previous case higher temperature increases powder ductility and due to pressure the are able to deform more at the impact moment, closing existing pores and compacting the already formed coating.

At 1000°C and 38 bar pressure, fully dense coatings have been achieved. Porosity levels are under 0,2% and deposition efficiencies are over 97% independently of the used substrate.

Mechanical properties

Tensile strength

Tensile bond strength has already been defined as the adhesion between a substrate and a coating and the cohesion between the particles. The strength of adhesion of the impinging particle to the substrate is dependent on mechanical, metallurgical-chemical and physical mechanisms.

An impinging particle is mechanically bonded when it flattens and conforms to a suitably prepared surface; subsequently, bonding mechanism may occur, (physical bonding results from particle adhesion to the substrate by mechanical anchoring or microfusions.

The obtained results of cavitation test, has given an idea of the bond strength between single particles and substrate without the influence of subsequent compaction. The obtained curves of % of bonded particles with respect to cavitation time showed that Ti6Al4V powder adheres stronger to Ti6Al4V substrate followed by Al-7075-T6

substrate and finally AZ31 substrate. With Ti6Al4V substrate material transfer between particles and substrate has been also observed, confirming T. Schmidt simulation of bonding mechanism (Figure 97) and arising a hypothesis of the existence of possible microfusions due to the observed images of substrate's footprints and detached particles as well as rupture zone of TCT test.

Apart from the deposition process employed, bond strength also depends on the cleanliness (without oxides and other foreign elements), adequate roughness and adhesion to a substrate surface, along with the plastic deformation of the particle on it. Optimization of the deposition process is thus important, to ensure that both the bond and cohesive strengths of the coating are at a maximum, thus producing a quality coating.

The results of the adhesion test demonstrate that, in all cases, glue strength (85 ± 5) is much higher than bond strength (coating-substrate interface) or cohesive strength (within the coating). The obtained values in order of magnitude are 76 \pm 7, 45 \pm 2 and 39 \pm 5 MPa for Ti6Al4V, AI-7075-T6 and AZ31 respectively.

TCT-Test

It follows similar principles than tensile strength. When the obtained TCT values at the highest conditions for both powders are compared (1000°C and 50 bar), the obtained coatings with irregular powder (248 \pm 13) have a 16% higher TCT values than the spherical powder coatings (213 \pm 13). These higher values are mainly because:

- Higher compaction of the coating: although less particles are adhering to the surface, its impact energy compacts the coating.
- Higher area of union between particles: irregular particles orientate in a gas flux. At impact moment, particles reorientate and deposit on the coating forming layers.
- Particles are much more intertwined: the formed layers are very interlaced requiring more energy to separate them.

Wear resistance

- Sliding wear

The microscopic mechanisms that are involved are: adhesion, mechanical interaction of surface asperities, ploughing of one surface by asperities on the other, deformation and/or fracture of surface layers such as oxides and interference and local plastic deformation caused by third bodies, mainly agglomerated wear particles, that are trapped between the moving surfaces.

It must be also remembered that local contact areas may be heated by friction to temperatures that cause significant softening or even recrystallization, and that may promote local oxidation.

The obtained results, might be a cause of the porosity and low interparticle adherence of tested samples. Friction coefficient is a 15% higher on the irregular Ti6Al4V coating and the volume loss is more than a 50% higher.

Abrasion

Abrasive wear occurs due to the contact in the presence of hard particles (third-body abrasion). A variety of material characteristics, such as hardness, elastic modulus, yield strength, crystal structure, microstructure and composition, either form a correlation with abrasive wear or have some effect on it.

It has been proved experimentally according to the obtained results that SS316 L has lower abrasion damage than the AI-7075-T6 substrate (between 2 and 3 times lower for the coating depending on the spraying powder). It has been proved experimentally and theoretically that the hardness of a material correlates with its abrasion rate. SS316L is also cold-hardened due to CGS process, making even higher the difference between substrate and coating. The obtained value for spherical powder is $8,70\cdot10^{-5}$ mm³/Nm, for the irregular is $1,45\cdot10^{-4}$ mm³/Nm and for the AI-7075-T6 substrate is $2,78\cdot10^{-4}$ mm³/Nm.

In the case of Ti6Al4V, the abrasive wear rate is similar than the obtained for Al-7075-T6. As in previous case with friction wear, the obtained results, might be a cause of the porosity and low interparticle adherence of tested samples.

CHAPTER 7: CONCLUSIONS

In the present thesis, coatings based on Ti6Al4V and Stainless Steel 316L have been successfully obtained by means of Cold Gas Spray Technologies onto three different light alloys (Ti6Al4V, Al-7075-T6 and AZ31) improving their properties with respect to wear and corrosion resistance.

From this study, the following assumptions can be concluded:

WITH REGARD TO POWDER RAW MATERIALS AND SPRAYING PARAMETERS

- 1. Irregular powders reach higher in flight velocities than the spherical ones due to drag coefficient, and despite both powders have the same hardness, the deposition efficiencies of the spherical powders are higher. Irregular powders are more oxidized due to production process (gas atomization vs. hydride-dehydride and water atomization) and this reduces the DE.
- 2. When oxidized and non-oxidized spherical Ti6Al4V powders are compared, deposition efficiencies between 15 and 30% higher are obtained with non-oxidized powder.
- 3. Better coatings in terms of efficiency, porosity and wear resistance are obtained through the use of spherical powders onto all the studied substrates.
- 4. As the spraying temperature increases, deposition efficiency does it also because more particles are reaching its critical velocity. In addition, porosity reduces because particles are more ductile due to the temperature and they are able to deform more.
- 5. As the pressure increase, coatings are denser because particle's impact velocity is higher, deforming more the particles and the substrate and closing the existing pores of the coating.

CONCLUSIONS

WITH REGARD TO BONDING MECHANISM

- 6. When spraying powder on substrate with the same or similar nature, as it has been seen with Ti6Al4V spraying powder and Titanium or Ti6Al4V substrate, microfusions are produced due to impact, making strong the bond between particles and substrate. Ti6Al4V adhesion values onto Ti6Al4V is an 80% higher than onto Al-7075-T6 and a 95% higher than onto AZ31.
- 7. When spraying powder and substrate has different nature and properties (hardness, ductility, thermal conductivity, crystal structure, deformation mechanism), as it has been seen with Ti6Al4V as spraying powder and Al-7075-T6 and AZ31 as substrates, mechanical bonding is produced by anchoring. No fusion zones are founded.
- 8. Coating adhesion values for irregular Ti6Al4V powder were 76 \pm 7 MPa for Ti6Al4V, 45 \pm 2 MPa for Al-7075-T6 and 39 \pm 5 MPa for AZ31.
- 9. The obtained results of cavitation test, have helped to identify experimentally CGS bonding mechanisms as a function of particle/substrate nature. The order in bonding strength is Ti, Ti6Al4V, Al-7075-T6 and finally AZ31. These results are in accordance to those obtained with adhesion tests.

WITH REGARD TO COATINGS ACHIEVEMENT

- 10. Independently of spraying powder morphologies, higher impact velocities generate better coatings for the studied systems. In general, higher velocities are obtained when temperature and pressure of the propellant gas is increased, being a function of convergent-divergent nozzles. obtention
- 11. An increase of carrier gas pressure leads to higher particle velocities, thus allowing to surpass the critical particle velocity and to a higher particle deformation at the impact moment, both required for satisfactory deposition. If a minimum temperature is not reached or the material has low plasticity, an increase in the pressure causes erosion of the substrate upon particle impact.

- 12. Through the use of interaction diagrams and Pareto charts allows the study of spraying parameters influence by comparing the response variables. It can be concluded that temperature has a higher influence in coating obtention than pressure, with the exception of irregular Ti6Al4V powder where the pressure's influence is higher.
- 13. For structural applications where the light alloy structures would undergo to wear and corrosion processes, coatings must be thick and dense. Fully dense coatings have been obtained using He as propellant, gas protecting the substrates against corrosion, but He is more than 4 times expensive than N₂.

WITH REGARD TO TI6AI4V SYSTEM

- 14. Comparing both systems, spherical Ti6Al4V and irregular Ti6Al4V spraying powders, higher deposition efficiencies are obtained with spherical powder, arriving to 140% higher on the optimal spraying conditions.
- 15. For every parameter, those coatings obtained with spherical Ti6Al4V powder onto Ti6Al4V substrates are the ones with highest deposition efficiencies (over 80%) followed by the same powder onto AZ31 substrate (over 65%) and then Al-7075-T6 (over 45%).
- 16. As it has been observed in cavitation test, both powder morphologies behave similar. Onto Titanium, footprints with a ring shape are left by the particles after cavitation test, showing the creation of microfusions at the adiabatic shear instabilities zones due to the impact.
- 17. When changing the streaming gas (replacing N₂ by He) spraying particles are even faster and the best results are obtained. With N₂ maximum obtained DE are 83, 70 and 65% for Ti6Al4V spraying powder onto Ti6Al4V, AI-7075-T6 and AZ31 substrates respectively and between 98 and 99% DE for Ti6Al4V spraying powder onto all substrates for Helium.

- 18. When N₂ is used as propellant gas, coating porosities can be reduced to values lower than 2% but when the propellant gas is changed to Helium, porosity is reduced to ~0,1% for spherical Ti6Al4V powder onto the three substrates.
- 19. Using D24 nozzle, maximum obtained DE are the same than those described on conclusion 17 when N₂ is used and increased to 87, 82 and 70% DE for Ti6Al4V spraying powder onto Ti6Al4V, AI-7075-T6 and AZ31 substrates respectively when D50 nozzle is used.
- 20. TCT values of the irregular powder coatings are between 15 and 45% (between 30 and 60 MPa) higher than those obtained for spherical powder.
- 21. Concerning TCT tests, irregular powder coatings have stronger intersplat bonding than spherical ones. particles have higher velocities and non-adhered particles compact the already formed coating. The bonded area on irregular particles is higher than on spherical ones and they are more interwined, which implies that higher energy is needed to separate them
- 22. Concerning to corrosion resistance, the obtained Ti6Al4V coatings onto the three substrates, using He as propellant gas, are fully resistant to corrosion. After 24 hours testing, no electrolyte has reached substrate surface showing fully resistance and ensuring the accomplishment of ASTM D-1411 standard.

WITH REGARD TO 316L SYSTEM

- 23. Spherical and irregular morphology stainless steel 316L spraying powders were deposited successfully onto light alloys by Cold Gas Spray technique
- 24. Coating hardness is approximately double of the powder hardness (100% higher for those coatings obtained with the spherical powder, and 130% higher for the ones obtained with irregular powder). After coating etching, the deformation zones at the particle limits can be clearly seen, thereby supporting the notion of hardening caused by particle deformation.

- 25. Comparing the obtained results at the same pressure and varying temperature, efficiency increase as temperature rises, as well as thickness, while the hardness are on the same orders of magnitude.
- 26. At the same temperature and varying the pressures, efficiency increases with increasing pressure, but its effect is lower than in the case of temperature, as it has been seen with the obtained Pareto charts and interaction diagrams.
- 27. The abrasive wear rate of the spherical SS316L coating is 220% lower than the abrasive wear rate of AI-7075-T6 substrate and for irregular SS316L coating this value is reduced to 190%.
- 28. Concerning to corrosion resistance, the obtained SS316L coatings onto AI-7075-T6 and AZ31 substrates, using N_2 as propellant gas, are fully resistant to corrosion, following ASTM D-1411 standard

CHAPTER 8: BIBLIOGRAPHY
- [1] The science and engenieering of thermal spray coatings, second edition, Lech Pawlowski © 2008 John Wiley & Sons
- [2] Handbook of Thermal Spray Technology,© 2004 ASM International, Edited by J.R.Davis, Davis & Associates
- [3] H. ASSADI, F. GÄRTNER, T. STOLTENHOFF, H. KREYE, Acta Mater. 51 (2003) 4379–4394
- [4] G. BAE, S. KUMAR, S. YOON, K. KANG, H. NA, H-J. KIM, C. LEE., Acta Mater. 57 (2009) 5654–5666
- [5] F. GÄRTNER, T. STOLTENHOFF, T. SCHMIDT, H. KREYE,J. Therm. Spray Techn. ,Volume 15, Number 2, 223-232
- [6] R. GHELICHI, M. GUAGLIANOR. GHELICHI ET ALII, Frattura ed Integrità Strutturale, 8 (2009) 30-44
- [7] T. HUSSAIN, D. G. MCCARTNEY, P. H. SHIPWAY, D. ZHANGJ. of Therm. Spray Technology. September 2009, Volume 18, Issue 3, pp 364-379
- [8]T. HUSSAIN Key Engineering Materials Vol. 533 (2013) pp 53-90
- [9] F. GÄRTNER, T. STOLTENHOFF, T. SCHMIDT, H. KREYE Journal of Thermal Spray Technology June 2006, Volume 15, Issue 2, pp 223-232
- [10] N. CINCA, M. BARBOSA, S. DOSTA, J.M. GUILEMANY Surf. Coat.Technol. . Vol. 205, Issue 4. Pp. 1096-1102. (2010)
- [11]T.SCHMIDT,F.GÄRTNER, H.ASSADI, H.KREYE Acta Mater.54 (2006) 729–742

[12] A.N. PAPYRIN,

European Summer University, ENISE, St-Etienne, France, September 11-15, 2006

- [13] M. GRUJICIC, C.L. ZHAO, W.S. DEROSSET, D. HELFRITCH , Mater. Design.25 (2004) 681–688
- [14]W-Y. LI, C. ZHANG, X. GUO, C-J. LI, H. LIAO, C. CODDET, Appl. Surf. Sci.254 (2007) 517–526
- [15] S. VLADIMIROVICH, V. FEDOROVICH, M. REIN Aerosp. Sci. Technol. 9 (2005) 582–591
- [16] T. SCHMIDT, F. GA"RTNER, H. ASSADI, H. KREYE, Acta Mater. 54 (2006) 729–742
- [17], M.M. HYLAND, Y.-C.LAU, C.-J. LI, R.S. LIMA, G. MONTAVON,(Ed.) B.R. MarpleISBN: 978-0-387-77285-1
- [18] B. JODOIN, L. AJDELSZTAJN, E. SANSOUCY, A. ZÚÑIGA, P. RICHER, E.J.LAVERNIA Surf. Coat.Tech. 201 (2006), Pags. 3422–3429
- [19] E. IRISSOU, J.-G. LEGOUX, C. MOREAU, BOUCHERVILLE, A. N. RYABININ, International Thermal Spray Conference & Exposition 2008: Thermal Spray Crossing Borders (DVS-ASM). 2008 Pg. 613-619
- [20]M. GRUJICIC, C.L. ZHAOA, C. TONGA, W.S. DEROSSET, D. HELFRITCH, Mater. Sci. Eng. A368 (2004) 222–230
- 21 S. VLADIMIROVICH KLINKOVA,, V. FEDOROVICH KOSAREV, M. REIN Aerospace Science and Technology 9 (2005) 582–591
- [22]A.N. PAPYRIN, S.V. KLINKOV , V.F. KOSAREV, ITSC 2005: Thermal Spray connects: Explore its surfacing potential (DVS-ASM) Pages: 145-150
- 23 H. ASSADI, F. GÄRTNER, T. STOLTENHOFF, H. KREYE

Acta materialia 51 (2003) 4379-4394

- [24] T. SCHMIDT, F. GÄRTNER, H. ASSADI, H. KREYEActa Materialia Volume 54, Issue 3, February 2006, Pages 729–742
- [25] LI GANG, WANG XIAO-FANG, LI WEN-YA, Trans. Nonferrous Met. SOC. China 17(2007) 116-121
- [26] J. PATTISON **□**, S. CELOTTO, A. KHAN, W. O'NEILL, Surf.Coat. Tech. 202 (2008) 1443–1454
- [27] P. C. KING, M. JAHEDI,Appl. Surf. Sci.256 (2010) 1735–1738
- [28] K. TAYLOR, B. JODOIN, J KAROV, P. RICHER,J. Therm. Spray Tech., Volume 15(2) June 2006, 273-279
- [29]M. GRUJICIC, C.L. ZHAOA, C. TONGA, W.S. DEROSSET, D. HELFRITCH, Mater. Sci. Eng. A368 (2004) 222–230

[30]A.N. PAPYRIN, S.V. KLINKOV , V.F. KOSAREV, ITSC 2005: Thermal Spray connects: Explore its surfacing potential (DVS-ASM) Pages: 145-150

- [31] LI GANG, WANG XIAO-FANG, LI WEN-YA, Trans. Nonferrous Met. SOC. China 17(2007) 116-121
- [32] J. PATTISON, S. CELOTTO, A. KHAN, W. O'NEILL Surf.Coat. Tech. 202 (2008) 1443–1454
- [33] P. C. KING, M. JAHEDI,Appl. Surf. Sci.256 (2010) 1735–1738
- [34] K. TAYLOR, B. JODOIN, J KAROV, P. RICHER,J. Therm. Spray Tech., Volume 15(2) June 2006, 273-279

- [35] T. SCHMIDT, H. ASSADI, F. GÄRTNER, H. RICHTER, T. STOLTENHOFF, H. KREYE, AND T. KLASSEN Journal of Thermal Spray Technology December 2009, Volume 18, Issue 5-6, pp 794-808,
- [36] W.-Y. LI, C. ZHANG, X.P. GUO, L. DEMBINSKI, H. LIAO, C. CODDET Thermal Spray 2007: Global Coating Solutions
- [37] J. PATTISON, S. CELOTTO, A. KHAN, W. O'NEILL Surface and Coating Technology 202 (2008) 1443-1454
- [38] W.-Y. LI, C. ZHANG, X.P. GUO, G. ZHANG, H.L. LIAO, C.-J. LI, C. CODDET Materials and Design 29 (2008) 297–304
- [39] D. HELFRITCH AND V. CHAMPAGNE U.S. Army Research Laboratory, Aberdeen Proving Ground, MD
- [40] P. RICHTER, B. JODOIN, K. TAYLOR, E. SANSOUCY, M. JOHNSON, L. AJDELSZTAJN Thermal spray 2005:Thermal spray connects pp 193-198
- [41] K. TAYLOR, B. JODOIN, J KAROV AND P. RICHER Journal of Thermal Spray Technology June 2006, Volume 15, Issue 2, pp 273-279
- [42] C.-J.LI, W.-Y.LI, Y.-Y.WANG.
 Thermal Spray 2003: Advancing the Science & Appliying the Technology (Ed.) C. Moreau and B. Marple
 Published by ASm International, Materials Park, Ohio, USA, 2003
- [43] K.-R. ERNST, J. BRAEUTIGAM, F. GAERTNER, AND T. KLASSEN JTTEE5 22:422–432
- [44] P. RICHER, B. JODOIN, L. AJDELSZTAJN.Journal of Thermal Spray TechnologyJune 2006, Volume 15, Issue 2, pp 246-254

- [45] D. ZHANG, P. H. SHIPWAY, D. G. MCCARTNEYJournal of Thermal Spray TechnologyMarch 2005, Volume 14, Issue 1, pp 109-116
- [46] S. KUMAR, G. BAE, C. LEEApplied Surface ScienceVolume 255, Issue 6, 1 January 2009, Pages 3472–3479
- [47] P. RICHER, B. JODOIN, K. TAYLOR, E. SANSOUCY, M. JOHNSON, AND L. AJDELSZTAJN,
 Thermal Spray 2005: Thermal Spray connects: Explore its surfacing potential! (DVS-ASM) 2005, pp. 193-198
- [48] S. KUMAR, GYUYEOLBAE, CHANGHEE LEE Applied Surface Science 255 (2009) 3472–3479
- [49] L. AJDELSZTAJN, E. J. LAVERNIA, B. JODOIN, P. RICHER, E. SANSOUCY Journal of Thermal Spray Technology December 2006, Volume 15, Issue 4, pp 495-500
- [50] FRANÇOIS RALETZ, MICHEL VARDELL, GUILLAUME EZO'O Surface and Coatings Technology Volume 201, Issue 5, 25 October 2006, Pages 1942–1947
- 51 Value Stream Analysis of Casting. *COLD SPRAY TECHNOLOGY: INTERNATIONAL STATUS AND USA EFFORTS.* Prepared by J. Karthikeyan.ASB Industries Inc.
- [52] M. GRUJICICA, V. SELLAPPANA, M.A. OMARA, N. SEYRB, A. OBIEGLOB, M. ERDMANNC, J. HOLZLEITNERC Journal of Materials Processing Technology Volume 197, Issues 1–3, 1 February 2008, Pages 363–373
- [53] M. GRUJICIC, V. SELLAPPANA, L. MEARSA, X. XUANA, NORBERT SEYRB, MARC ERDMANNC, JOCHEN HOLZLEITNERC,

J. Mater. Process. Tech.198 (2008) 300-312

- [54] Light Alloys, Fourth Edition: From Traditional Alloys to Nanocrystals [Hardcover] Ian Polmear Butterworth-Heinemann; 4 edition (December 15, 2005)
- [55] Light alloys: metallurgy of the light metalsI. J. PolmearJohn Wiley & Sons Australia, Limited, 1995, 362 pages

[56] Standard Test Method for Apparent Density of Free-Flowing Metal Powders Using the Hall Flowmeter Funnel, ASTM B212-99, ASTM International, West Conshohocken, PA, <u>www.astm.org</u>.

- [57] Standard Test Method for Flow Rate of Metal Powders.
 ASTM B213 03, ASTM
 International, West Conshohocken, PA,
 www.astm.org.
- [58] Standard test method for Microindentation Hardness of Materials.ASTM E384-07,Book of Standards 03.01.ASTM International, 2007.
- [59] W. OLIVER, G. PHARRJournal of Materials Research, Vol. 7 (1992) pp. 1564-1583.
- 60 Standard test method for Adhesion or Cohesion Strength of thermal spray coatings. ASTM C633-01, Book of Standards 03.01. ASTM International, 2001.
- [61] T. SCHMIDT, F. GÄRTNER, H. ASSADI, H. KREYE, Acta Materialia 54 (2006) 729 – 742.

[62] T. SCHMIDT, F. GÄRTNER, H. KREYE, Journal of Thermal Spray Technology, 15(4), 2006, S. 488-494.

- [63] Test Method for Wear Testing with a Pin-on-Disk Apparatus.ASTM G99-03, ASTMInternational, West Conshohocken, PA,www.astm.org.
- [64] Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus. ASTM G65-00,ASTM International, West Conshohocken, PA, <u>www.astm.org</u>.
- [65] Standard Test Method for Cavitation Erosion Using Vibratory Apparatus
 ASTM G32 10
 ASTM International, West Conshohocken, PA,
 www.astm.org.
- [66] J. LU, K-H ZUM GAHR, J. SCHNEIDER Wear 265 (2008) 1680–1686
- [67] J.D. ESCOBAR, E. VELÁSQUEZ, T.F.A. SANTOS, A.J. RAMIREZ, D. LÓPEZWear Volume 297, Issues 1–2, 15 January 2013, Pages 998–1005

68 Standard Test Methods for Water-Soluble Chlorides Present as Admixtures in Graded Aggregate Road Mixes.
ASTM D-1411-04,
Book of Standards 03.01. ASTM International, 2004

[69] J.V. BERNIER, J.-S. PARK, A.L. PILCHAK, M.G. GLAVICIC, M.P. MILLER Metallurgical and Materials Transactions A December 2008, Volume 39, Issue 13, pp 3120-3133,

[70] "Powder Metallurgy Science"

Second Edition,

R.M. German, MPIF.

- [71]. F.J. GIL , M.P. GINEBRA, J.M. MANERO, J.A. PLANELL Journal of Alloys and Compounds 329 (2001) 142–152
- [72]. Ian Polmear*Light Alloys: From Traditional Alloys to Nanocrystals*Four edition (2006), Ed. Butterworth-Heinemann
- [73] VIRGINIA M. OSTERMANIndustrial Heating;May2008, Vol. 75 Issue 5, p75Solar Atmospheres, Souderton, Pa
- [74] H. FUKANUMA, N. OHNO, B. SUN, R. HUANGSurface and Coatings TechnologyVolume 201, Issue 5, 25 October 2006, Pages 1935–1941
- [75] T. SESHACHARYULU, S.C. MEDEIROS, W.G. FRAZIER, Y.V.R.K. PRASAD Materials Science and Engineering: A Volume 325, Issues 1–2, 28 February 2002, Pages 112–125
- [76]T. SCHMIDT, H. ASSADI, F. GÄRTNER, H. RICHTER, T. STOLTENHOFF, H. KREYE, T. KLASSEN
 Journal of Thermal Spray Technology
 December 2009, Volume 18, Issue 5-6, pp 794-808,
- [77] MILOŠ JANEČEK AND FRANTIŠEK CHMELÍK
 Materials Science and Engineering: A
 Volume 462, Issues 1–2, 25 July 2007, Pages 311–315
 International Symposium on Physics of Materials, 2005

[78] SHU-BO XU, ZHEN QIN, TING LIU, CAI-NIAN JING, GUO-CHENG REN

Transactions of Nonferrous Metals Society of China Volume 22, Supplement 1, October 2012, Pages s61–s67

- [79] T. SCHMIDT, F. GÄRTNER, H.KREYE,Journal of Thermal Spray Technology, 15(4), 2006, S. 488-494.
- [80]Various authors, ASM Handbook, vol. 1:Properties and Selection: Irons, Steels, and High-Performance Alloys, ASM International, 1993
- [81] L. ZHAO, E. LUGSCHEIDERSurf. Coat. Technol. 162 (2002) 6–10
- [82] K. DOBLER, H. KREYE, AND R. SCHWETZKEJ. Therm. Spray Technol. 9 (2000) 407-413
- [83] T.C. TOTENMEIRJ. Therm. Spray Technol vol. 14 /3 (2005) 369-372
- [84] M. TORRELL, S. DOSTA, J. R. MIGUEL AND J. M. GUILEMANY Corros. Eng., Sci. Technol, 45/1 (2010) 84-93
- [85] K. SPENCER, M.-X. ZHANG Surface & Coatings Technology 205 (2011) 5135–5140

RESUMEN

Esta tesis se centra en el uso de la tecnología de Cold Gas Spray para proyectar polvos micrométricos sobre diferentes aleaciones ligeras con el fin de aumentar su resistencia al desgaste y a la corrosión.

El creciente interés por parte de la industria en reducir al máximo los costes (consumo de combustible, duración maquinaria, o la seguridad personal) ha fomentado la necesidad de investigar las posibles aplicaciones que las aleaciones ligeras pueden ofrecer.

La reducción de peso es una razón por la cual los metales ligeros y sus aleaciones se han asociado con fuertes industrias como el transporte o la industria aeroespacial.

Sin embargo, los aspectos de ahorro de peso no debe ocultar el hecho de que los metales ligeros poseen otras propiedades "tecnológicas" como la alta resistencia a la corrosión y alta conductividad eléctrica y térmica del aluminio, la mecanizabilidad de magnesio y la resistencia a la corrosión extrema de titanio.

Hay que tener en cuenta que a pesar de estas propiedades de importancia tecnológica, debido a su densidad el aluminio y magnesio tienen una baja dureza y una baja resistencia al desgaste, lo que provoca la necesidad de mejorar sus propiedades superficiales.

El objetivo principal ha sido la obtención y optimización de recubrimientos de Ti6Al4V y de acero inoxidable 316L sobre aleaciones ligeras a través del uso de la proyección fría, que permite obtener recubrimientos densos y sin rastros de oxidación, manteniendo la microestructura original de los polvos de proyección.

Se han obtenido recubrimientos de Ti6Al4V y SS316L sobre sustratos de Al-7075-T6, AZ31 y Ti6Al4V.

1. INTRODUCCION

En ingeniería de superficies, una de las ramas más importantes para proteger las estructuras contra cualquier tipo de daño externo son las tecnologías de obtención de recubrimientos.



Figura 1: Esquema de los procesos de obtención de recubrimientos en ingeniería de superficies

De ellas, los procesos de proyección térmica son unos de los más rentables y de alta calidad.

Las tecnologías de proyección térmica convencionales son procesos de obtención de recubrimientos en los que partículas fundidas o semi-fundido se depositan sobre un sustrato.

El material a depositar es sometido a un fuerte calentamiento y acelerado antes entrar en contacto con la superficie del sustrato. Las propiedades y la microestructura de los recubrimientos dependerán de los fenómenos que se producen durante el vuelo. Estas técnicas requieren tratamientos pre- y post- proyección. Los tratamientos previos a la proyección consisten principalmente en la limpieza de la superficie, del sustrato así como su activación para permitir la adherencia de las partículas.

Los tratamientos posteriores a la obtención del recubrimiento son la clave para la optimización y el acabado. Los principales tratamientos existentes son:

- Tratamiento térmico
 - o Tratamiento electromagnéticos que implican la sinterización con microondas y los tratamientos con láser
 - o Prensado isostático en caliente (HIP)
 - o La re-fusión por combustión de llama
- Impregnación para cerrar la porosidad de los recubrimientos
- Acabado

Pero al igual que cualquier otra técnica, las tecnologías de proyección térmica tienen limitaciones. Los principales son:

- Oxidación del material metálico de partida
- La modificación química durante el vuelo de las partículas proyectadas, como descarburación, oxidación o reducción
- Las partículas en estado líquido pueden evaporarse y reducir su tamaño
- Aumento de las tensiones a tracción
- Modificación de la microestructura del sustrato debido al calor y el impacto

Estas limitaciones existentes en los procesos de proyección térmica han impulsado el desarrollo de técnicas de proyección donde los bajos costes y las altas eficiencias de deposición son esenciales.

La reducción de costes, la disminución de los tratamientos superficiales (pre-y postproyección), y la reducción de los problemas asociados con la fusión de material (oxidación, la corrosión, las tensiones de tracción, el cambio microestructura), han hecho de la Proyección Fría (CGS) una técnica eficiente, competitiva, limpia y económicamente viable. El principal objetivo de esta tecnología, así como de las técnicas de proyección térmica más convencionales, es la obtención de recubrimientos que mejoren la superficie del material, para la aplicación deseada. La eficiencia de la deposición, la adherencia o la estructura final depende de muchos factores que, al mismo tiempo, dependen del material proyectado y del sustrato.

1.1. Procesos de proyección térmica (PT)

La proyección térmica son un grupo de procesos que utilizan la energía térmica generada por métodos eléctricos o químicos para fundir o ablandar un material y acelerarlo a velocidades de entre 50 y 1000 m/s. La alta temperatura y la velocidad alcanzada por las partículas, da como resultado una alta deformación de las partículas al impactar contra la superficie del sustrato obteniéndose los denominados "splats", que son las unidades básicas de formación de un recubrimiento. Un flujo continuo de partículas fundidas o semi-fundidos impacta sobre la superficie del sustrato, solidificándose y formando capas. Tras el impacto, las partículas se enfrían rápidamente formando recubrimientos uniformes, de grano muy fino y policristalino.



Figura 2: Obtención de recubrimientos por proyección térmica

La principal ventaja de estos procesos es la amplia variedad de materiales que pueden ser utilizados para producir recubrimientos. Otras ventajas son la capacidad de producir recubrimientos sobre sustratos con una entrada de calor muy bajo o la capacidad de reparar piezas sin cambiar las propiedades o dimensiones La Figura 3 muestra las tres categorías principales de procesos de proyección térmica.. Cada proceso desarrolla ciertas propiedades específicas en los recubrimientos, tales como la fortaleza del enlace, la porosidad, la dureza o la formación de óxidos.



Figura 3: Procesos convencionales de proyección térmica

La Tabla 1 muestra una comparativa entre los principales procesos de proyección térmica en términos de gas transportador, la materia prima y las propiedades del recubrimiento obtenido.

Attribute	Flame spray	High-velocity oxyfuel	Detonation gun	Wire arc	Air plasma	Vacuum plasma	Radiofrequency plasma
Jet							
Jet temperature, K Jet velocities, m/s (ft/s)	3500 50–100 (160–300)	5500 500–1200 (1600–4000)	5500 >1000 (>3300)	>25,000 50–100 (160–300)	15,000 300–1000 (1000–3300)	12,000 200–600 (700–2000)	10,000 20–80 (70–300)
Gas flow, sLm Gas types Power input, kW equiv.	100–200 O ₂ , acetylene 20	400–1100 CH ₄ , C ₃ H ₆ , H ₂ , O ₂ 150–300	N/A O ₂ , acetylene N/A	500–3000 Air, N ₂ , Ar 2–5	100–200 Ar, He, H ₂ , N ₂ 40–200	150–250 Ar, He, H ₂ 40–120	75–150 Ar, He, H ₂ 40–200 (plate)
Particle feed							
Particle temperature (max), °C (°F)	2500 (4500)	3300 (6000)	N/A	>3800 (>6900)	>3800 (>6900)	>3800 (>6900)	>3800 (>6900)
Particle velocities, m/s (ft/s)	50-100 (160-300)	200–1000 (700–3300)	N/A	50–100 (160–300)	200-800 (700-2600)	200–600 (700–2000)	20-50 (70-160)
Material feed rate, g/min	30-50	15-50	N/A	150-2000	50-150	25-150	20-50
Deposit/coating							
Density range (%)	85-90	>95	>95	80-95	90-95	90-99	95-99
Bond strength, MPa (ksi:)	7-18 (1-3)	68 (10)	82 (12)	10-40 (1.5-6)	<68 (<10)	>68 (>10)	>68 (>10)
Oxides	High	Moderate to dispersed	Small	Moderate to high	Moderate to coarse	None	None

Tabla 1: comparativa de los procesos de proyección térmica

En general, sólo aquellos materiales que son estables a altas temperaturas son adecuados para los procesos de proyección térmica, estos incluyen la mayoría de los metales y sus aleaciones, cerámicas, cermets y algunos polímeros.

Las aplicaciones más comunes de los recubrimientos obtenidos por proyección térmica son:

- Protección contra el desgaste
- Aislamiento térmico
- Resistencia a la corrosión
- Materiales desgastables y abrasivos
- Conductores eléctricos
- Recubrimientos con resistencia eléctrica / aislantes
- Restauración
- Recubrimientos de aplicaciones médicas
- Recubrimientos poliméricos

La proyección fría es una técnica que no está limitada a industrias altamente tecnológicas como la militar o la aeronáutica, sino que debido a su asequibilidad y la amplia gama de materiales que se pueden utilizar, ha permitido su aplicación en industrias tan comunes como la automoción o los productos de consumo.

Uno de los mayores atractivos de ésta tecnología es la posibilidad de obtener recubrimientos con propiedades únicas, las cuales no son alcanzables a través de tecnologías de proyección térmica convencionales. Esto es debido al hecho de que la deposición de material tiene lugar en estado sólido. El material no está expuesto a alta temperatura, de modo que no llegan a su temperatura de fusión. Como resultado, las reacciones de descomposición u oxidación indeseables son virtualmente eliminadas manteniéndose las propiedades deseables de los materiales de partida.

1.2. LA PROYECCIÓN FRÍA

La proyección fría es un proceso de obtención de recubrimientos mediante la exposición de un sustrato a un haz supersónico de gas comprimido que contiene partículas de pequeño tamaño como materia prima (desde tamaños nanométricos a tamaños micrométricos) que son aceleradas a velocidades comprendidas entre los 300 y los 1200 m/s. El mecanismo de este proceso se basa en la combinación de las diferentes propiedades físico-químicas de la partícula que permitan proyectar a la menor temperatura y presión posible. El estudio y control de estas variables permite la obtención de recubrimientos a partir de partículas en estado sólido.

Hay una diferencia básica entre las técnicas convencionales de proyección térmica y la denominada Proyección fría. Mientras que en las primeras el sistema necesita una elevada energía térmica así como una energía cinética para formar el recubrimiento, en el caso de la Proyección fría la energía cinética adquiere un papel principal y mayoritario en el proceso.



Figura 4: Esquema del sistema de proyección fría

Las principales ventajas que el proceso conlleva:

 Disminución de la porosidad y los óxidos en los recubrimientos. El efecto compresivo de las partículas que llegan a alta velocidad al sustrato, tienden a cerrar los pequeños poros y huecos existentes en las capas subyacentes de material.

- Existe una alta eficiencia en la deposición (60-90%) con capacidad para obtener recubrimientos de alta densidad y dureza.
- Debido principalmente a que las partículas no se encuentran en estado fundido cuando llegan al sustrato las tensiones a tracción existentes en los recubrimientos generados por proyección térmica son sustituidas en su mayoría por tensiones de tipo compresivo.
- La química, la composición de las fases, y la estructura cristalina de los materiales de partida se mantiene.
- Capacidad de obtener recubrimientos con alta conductividad eléctrica/térmica.
- Capacidad de proyectar materiales temosensibles
- Necesidad de preparación del sustrato mínima.
- Posibilidad de recolección y reutilización de las partículas (utilización de polvo de hasta el 100% de reciclaje).
- Incremento de la seguridad operacional debido a la ausencia de un haz de gas de alta temperatura, radiación o gases explosivos.

Variables del proceso

Las condiciones en la que se realiza la proyección varían en función del tipo de material proyectado, el sustrato, sus composiciones, sus propiedades físico-químicas, etc... Estas condiciones determinan la optimización del recubrimiento basado en las necesidades establecidas por la aplicación para la cual se desea obtener dicho recubrimiento (nivel de porosidad, espesor, adherencia recubrimiento-sustrato, microestructura...).

La unión de las partículas al sustrato está influenciada por diversos factores. Estos factores van desde los parámetros geométricos, como la superficie de contacto y su rugosidad, hasta los parámetros termo-mecánicos como la deformación plástica, la tensión de fluencia, la presión y la temperatura en la interfase.

Las principales variables que se deben tener en cuenta a la hora de llevar a cabo una proyección son:

Velocidad de la partícula:

Las primeras partículas que inciden sobre el sustrato activan la superficie debido a la creación de una elevada concentración de dislocaciones en la capa superficial. Los

puntos donde se concentran estas dislocaciones pueden ser centros para el inicio de la interacción química entre la partícula y el sustrato.

El tiempo transcurrido desde que se producen los primeros impactos sobre la superficie del sustrato hasta que comienzan a adherirse las primeras partículas es el denominado "tiempo de inducción".

Distancia de Proyección

La velocidad de la partícula se incrementa fuera de la boquilla y disminuye durante el vuelo. Esta velocidad puede seguir reduciéndose debido a la onda de choque que resulta del choque del flujo de gas con la superficie del sustrato ("Bow Shock"). Debido a ello, a distancias de separación cortas, cuando la fuerza del Bow Shock es grande, el rendimiento de la deposición se reduce, mientras que a largas distancias, cuando éste efecto ha desaparecido, la deposición continúa sin obstáculos.

Morfología del polvo de proyección

En general un rango de distribución de partículas estrecho y menor suele tener una velocidad media de las partículas mayor. Esto es debido a que la aceleración que le imprime el gas a las partículas es inversamente proporcional al diámetro de la misma. Sin embargo se debe tener en cuenta que, del mismo modo que las partículas de menor tamaño se aceleran más fácilmente, también su deceleración es más rápida, mientras que las partículas de mayor tamaño, mantienen la velocidad durante un mayor periodo de tiempo.

Tasa de alimentación del polvo de proyección

El espesor aumenta linealmente con el aumento de la tasa de alimentación, hasta un máximo que indica que existen demasiadas partículas impactando en la superficie del sustrato dando lugar a un exceso de tensiones residuales que provocan que el recubrimiento se desprenda ("Efecto Peeling").

Ángulo de la pistola de proyección

En función del tipo de material existe un ángulo de impacto crítico por debajo del cual no se produce deposición de material. La relación entre el ángulo de proyección y la eficiencia relativa de deposición puede dividirse en tres rangos:

- Rango de máxima deposición
- Rango de transición
- Rango de no deposición



Figura 5: Angulo de proyección

Temperatura de partícula, sustrato y gas transportador

La temperatura influye en el proceso de proyección fría de diferentes maneras. En primer lugar, aumentando la temperatura del gas transportador, aumenta su velocidad, y como consecuencia de ello, la velocidad de las partículas y por lo tanto su velocidad de impacto.

En segundo lugar, las propiedades elásticas y plásticas de los materiales dependen de la temperatura. A mayor temperatura, la elasticidad y la plasticidad de los materiales aumenta.

Rugosidad de la superficie

Una de las teorías existentes para explicar los mecanismos de unión está basada en el anclaje mecánico que se forma entre la partícula que incide y el sustrato, por lo tanto, es razonable suponer que un aumento de la rugosidad del sustrato favorecerá la formación de enlace partícula/sustrato debido a la existencia de una mayor superficie específica donde las partículas pueden adherirse. Estas partículas son sometidas posteriormente a una compactación adicional como consecuencia del impacto sucesivo de partículas sobre el sustrato.

Material de partida

Con sustratos blandos y materiales de proyección duro, los primeros impactos deformarán el sustrato y tras una primera capa de partículas no deformadas, los siguientes impactos provocaran una deformación tanto en el sustrato como en las partículas que impactan.

Materiales con estructuras cristalinas FCC tienen el mayor número de planos de deslizamiento, los cuales son responsables de su alta plasticidad. Metales con estructura HCP contienen un menor número de planos de deslizamiento, lo que se traduce en un menor grado de plasticidad. Aquellos compuestos cuya estructura cristalina sea BCC, tendrán una muy baja plasticidad.

Eficiencia de la deposición

La eficiencia de la deposición está en función de un gran número de variables, y da una indicación sobre el número de partículas que tienen una velocidad de impacto igual o superior a la velocidad crítica.

2. MATERIALES

Los polvos de proyección seleccionados fueron Ti6Al4V y acero inoxidable 316L, con dos morfologías diferentes (esférica e irregular). Estos materiales se proyectaron sobre tres tipos de sustratos: Ti6Al4V, Al-7075-T6 y AZ31.

Los proveedores de cada material fueron:

- Polvo esférico de Ti6Al4V: Technik GmbH & Co. KG Spezialpulver en Alemania
- Polvo irregular de Ti6Al4V: Phelly Materiales de EE.UU
- Polvo esférico de Acero inoxidable 316L: Sandvik Materials Technology de Alemania
- Polvo irregular de Acero inoxidable 316L: Ames en España
- Sustrato de Ti6Al4V: Robert ZappWerkstofftechnik GmbH de Alemania
- Sustrato de Al-7075-T6: Lumetal Plastic en España.
- Sustrato de AZ31: Air Craft Materials UK de Reino Unido

3. PROCEDIMIENTO EXPERIMENTAL

Morfología:

Se ha empleado un microscopio JEOL 5510 equipado con un detector de electrones secundarios, un detector de electrones retro-dispersados ROBINSON y un detector EDS. También se ha usado un microscopio electrónico Quanta 650 de la empresa FEI Company, equipado con dos modos de vacío (alto y bajo), detector de electrones secundarios y retrodispersados y detector EDS.

Distribución de partículas:

Este análisis permite la obtención de la distribución granulométrica del polvo inicial y el estudio de su morfología a partir de imágenes de SEM.

La obtención de la distribución granulométrica se realiza a través de un análisis por difracción láser con un equipo BECKMAN COULTER LS.

Este equipo utiliza un láser con una potencia de 5mW y con una longitud de onda de 750nm El rango de tamaño de partícula que permite analizar esta comprendido entre los 200nm y los 2 mm.

Densidad:

La densidad es una magnitud que expresa la relación existente entre la masa y el volumen de un cuerpo (g/cm3). En el caso de los polvos de proyección existen 3 tipos de densidad:

- Densidad aparente: Se calcula mediante la norma ASTM B-212-89.
- Densidad Vibrada: Se calcula mediante la norma ASTM B-527-85.
- Densidad real: Se calcula por la norma ASTM B-238.

<u>Fluidez</u>

Determinado de acuerdo con la norma ASTM B-213-30.

Composición de fases:

El análisis de fases de ha realizado a través de diferentes técnicas:

Difracción de rayos X: El equipo utilizado es un SIEMENS D500 tipo Bragg-Brentano $\theta/2\theta$ que utiliza una radiación Cu K α_{1+2} (α_1 =1.54060 y α_2 =1.54443) a 40 kV y a una corriente de 30 mA.

Microscopia óptica: Para ello se ha utilizado un equipo de la marca *Leika DMI* 5000 *M* invertido.

EDS: Se ha usado un detector RÖNTEC que permite detectar elementos con un numero atómico mayor al del Boro (B) y con una resolución de 109 eV con respecto a la línea K_{α} del Mn.

Análisis ICP (Inductively coupled plasma mass spectrometry (ICP-MS))

Es un tipo de espectrometría de masas que es capaz de detectar varios metales y no metales en concentraciones tan bajas como una parte en 10^{12} .

Equipos de Proyección Fría

Los sistemas de proyección que se han utilizado han sido KINETICS 4000 de la empresa CGT y la KINETICS de 8000 de la Compañía CGT modificado por la Universidad Helmut Schmidt en Hamburgo. Ambos equipos consisten esencialmente en:

- Sistema de control o consola
- Fuente de alimentación
- Sistema de dosificación de gas
- Tolva de alimentación de polvo

• Pistola

La potencia máxima es 34 kW: Este valor puede alcanzar la presión de gas máxima de 40 bar y temperaturas de hasta 800 ° C en la KINETICS 4000 y 60 bar y temperaturas de hasta 1100 ° C con la KINETICS 8000. Se necesita una cantidad mínima de polvo de proyección de 200 cm³ para poder realizar la proyección.

Propiedades mecánicas

<u>Dureza</u> ha sido evaluado para sustratos mediante un penetrador CENTAUR con cargas variables.. El dispositivo proporciona una medición directa de la dureza Rockwell, transformando a la dureza Vickers a través de tablas de conversión.

<u>Microdureza</u> se ha llevado a cabo siguiendo la norma UNE 7-423/2 (ASTM E384-99 estándar). El equipo empleado ha sido un microdurómetro Matsuzawa MXT- α . Se usan cargas variables de entre 10 y 1000 gramos.

<u>Nanoindentación</u> Se utilizó un nanoindentador XP de Agilent Technologies, con cargas máximas de 500 mN y profundidades de penetración de 2.000 nm.

<u>Adherencia de los recubrimientos</u>: La adherencia del recubrimiento ha sido obtenida siguiendo la norma ASTM. C-633.

Tubular Coating Tensile strength test. Esta prueba se ha desarrollado en el Instituto de Tecnología de Materiales de la Universidad Helmut Schmidt de Hamburgo, Alemania. Los resultados obtenidos se pueden transformar en resistencia a la tracción multiplicándolos por un factor de 1,5-1,7 dependiendo del material.

<u>Desgaste</u>

Por fricción. Ball-on disc test. Bajo la norma ASTM G99-03

<u>Test de abrasión. Rubber wheel</u>: Se evaluó de acuerdo con la norma ASTM G65-00. <u>Test de cavitación</u> Se llevó a cabo bajo la norma ASTM G32-10. Este método de ensayo se utiliza para estimar la resistencia relativa de los materiales a la erosión por cavitación.

Test electroquímico

La resistencia a la corrosión de las muestras se evaluó por medio de mediciones electroquímicas en 80 ml de una disolución de NaCl al 3,4% según la norma ASTM D-1411.

4. OBTENCION DE RECUBRIMIENTOS

La optimización de los parámetros de proyección para cada polvo se realizó en función de la aplicación teórica final del recubrimiento. Un objetivo general de la tecnología de Proyección fría es asegurar que todas las partículas que impactan sobre el sustrato están en estado sólido y han adquirido una velocidad mínima necesaria (V_{critica}) con el fin de formar un recubrimiento denso.

Para determinar los parámetros de proyección, además de la bibliografía estudiada, se ha tenido en cuenta la experiencia previa del Centro de Proyección Térmica (CPT) con polvos de proyección de similar naturaleza.

Al buscar una buena resistencia a la oxidación y al desgaste el objetivo es obtener recubrimientos con baja porosidad, buena adherencia y alta espesor. Puesto que ningún material fundido o semi-fundido está involucrado, los niveles de oxidación serán los mismos en el recubrimiento que en el polvo de proyección.

Se utilizó un diseño de experimentos 3², donde las variables eran la Temperatura y la Presión del gas transportador, con el fin de obtener la máxima información posible a través de las variables respuesta, con un número mínimo de experimentos. El rango de condiciones fue el mismo para los tres sustratos.



Se llevaron a cabo nueve experimentos diferentes bajo los parámetros que se muestran en el diseño experimental. Los tres sustratos fueron desbastados para eliminar las impurezas y la capa de óxido superficial, así como comenzar a activar la superficie de sustrato.

Las condiciones de proyección fueron:

Temperatura (°C)	680	730	780
Presión (bar)	30	34	38
Distancia de proyección (mm)	40		
Angulo de proyección (º)	90		
Velocidad de la pistola (mm/s)	500		
Tasa de alimentación (rpm)	3		
Pre-cámara (°C)	450		

Tabla 2: Parámetros de proyección KINETICS 4000

En proyección fría, la primera capa del recubrimiento no se comporta como las siguientes. Se deseaba obtener un recubrimiento denso con un espesor medio-alto en un solo paso, sin la necesidad de cambiar las condiciones de proyección de una capa a otra.

En la HSU, con el equipo KINETICS 8000 modificado, se utilizó un diseño de experimentos reducido que definía las condiciones de proyección. Se establecieron cuatro condiciones de proyección diferentes para los polvos de proyección de titanio y 2 condiciones diferentes para los polvos de proyección de SS316L.

	Temperatura (°C)	Presión (bar)
Condición A	780	38
Condición B (SS316L)	900	38
Condición C (SS316L)	1000	38
Condición D	1000	50

Tabla 3: condiciones de proyección KINETICS 8000

Las otras variables fueron:

Distancia de proyección (mm)	60
Angulo de proyección (º)	90
Velocidad de la pistola (mm/s)	235
Tasa de alimentación (rpm)	3

Tabla 4: Parámetros de proyección KINETICS 8000

Hay que tener en cuenta que la morfología de polvo es un parámetro que influye en el mecanismo de unión y las propiedades del recubrimiento obtenido.

El comportamiento en vuelo y el impacto así mismo como la velocidad y la temperatura de la partícula son, son propiedades altamente dependientes de la morfología.

Las partículas con morfología angular tienen coeficientes de arrastre mayores que las esféricas. Este hecho es positivo ya que las partículas alcanzan más rápido su velocidad crítica y alcanzan velocidades mayores en vuelo, cumplimiento de uno de los principios necesarios para producir la adhesión con el sustrato.

Uno de los principales problemas es que el toda el área superficial de la partícula irregular no adquiere la misma temperatura, como ocurre con las partículas esféricas que se adquiere de forma homogénea. Algunas áreas de la partícula irregular adquirirán cierta temperatura más rápidamente que otros, por lo que tendrán diferentes niveles de deformabilidad, que influyen en la eficiencia de deposición.

4.1 Recubrimientos de Ti6Al4V

Bajo el diseño de experimentos realizado para el sistema KINETICS 4000 los recubrimientos óptimos tanto para el polvo esférico como para el irregular se obtuvieron a 780°C y 38 bares de presión. Como se comentó anteriormente, se desea obtener un recubrimiento óptimo sin variar las condiciones de proyección entre capas.

Las figuras 7 y muestran la evolución de la eficiencia en función del número de capas depositadas sobre los 3 sustratos.



Figura 7: Variación de la ED en función del Nº de capas de Ti6Al4V esférico



Figura 8: Variación de la ED en función del Nº de capas de Ti6Al4V irregular

Como puede observarse, a mayor número de capas, la eficiencia se va estabilizando y el sustrato no tiene tanta influencia.

El sustrato de Al-7075-T6 tiene la eficiencia de deposición más baja. La influencia del sustrato es mucho más alto en Al-7075-T6 que en AZ31 seguido de Ti6Al4V donde el sustrato apenas tiene una influencia remarcable.

En el caso del Ti6Al4V irregular, Se puede observar en el gráfico que las eficiencias de deposición sobre substrato de Ti6Al4V son los más altos, seguidos por AZ31 sustrato y luego sustrato de Al-7075-T6.

A pesar de aumento de la temperatura y la presión, la ED apenas varía para todos los sustratos. Se cree que el polvo irregular tiene un alto nivel de oxidación debido al proceso de obtención y el envejecimiento sufrido por el ambiente. Esta capa de oxidación reduce la velocidad de las partículas y también evita un contacto íntimo en el momento de impacto reduciendo la eficiencia del proceso.

Las partículas que no se adhieren, compactan el recubrimiento, por lo que la porosidad se reduce cuando aumenta la temperatura y la presión.

Vistos las eficiencias obtenidas se realizaron experimentos de cavitación sobre "splats" para ver la fortaleza del enlace partícula-sustrato. Se usaron 4sustratos distintos, los tres bajo estudio más un sustrato de Titanio grado II.

Cuando se compara la fuerza de unión entre las partículas y los diferentes sustratos a través de% de partículas unidas en función del tiempo de prueba de la cavitación se obtiene que sobre Titanio de grado II y Ti6AIV tienen la unión más fuerte debido a una mayor deformación de las partículas y la existencia de microfusiones que aumentan la adherencia. En contrario, sobre el AI-7075-T6 y AZ31, la adherencia de las partículas es baja para ambos casos. Las partículas no se deformen tanto como antes, y la conductividad térmica del sustrato impide el desarrollo de los mecanismos de unión.



Figura 9: % de partículas esféricas adheridas en función del tiempo de cavitación

Además se analizaron las huellas dejadas por las partículas sobre la superficie de los sustratos así como las partículas recuperadas de los experimentos de cavitación.



Figura 10: partícula recuperada de cavitación y una huella sobre el sustrato de Titanio

Como puede observarse, la unión de las partículas se ha producido en la zona que rodea el punto de impacto, donde se han alcanzado mayores temperaturas. Los análisis EDS que se realizaron a posteriori confirman la existencia de un anillo de Titanio puro en la partícula, demostrando la formación de microfusiones en la zona de enlace.

Para el sustrato de Al-7075-T6 y de AZ31 no se pudieron recuperar partículas y debido al carácter destructivo de los test de cavitación las huellas sobre los sustratos eran inexistentes

La comparación de la sección transversal de los splats de polvo esférico de Ti6Al4V sobre los sustratos de Ti6Al4V y Al-7075-T6, confirman los mecanismos de enlace descritos para ambos sustratos.



Figura 11: sección transversal de los splats

Se puede observar la diferencia en el mecanismo de unión entre Ti6Al4V y el sustrato Al-7075-T6. Adiabatic shear instabilities junto con microfusiones para el sustrato de Ti6Al4V y un componente mayoritario de anclaje mecánico para los sustratos más blandos. En los primeros, el punto de impacto de la partícula con el sustrato no está adherido a la superficie corroborando las huellas encontradas sobre el sustrato y la estructura de partículas desprendidas, en los segundos no se observan zonas de fusión y es más una unión mecánica en lugar de la unión metalúrgica.

Con Al-7075-T6 y AZ31 sustratos, la alta energía cinética que las partículas contienen al momento del impacto, se distribuye en deformación del sustrato (principalmente) y de partículas y la otra parte se dispersa preferentemente en forma de calor a través del sustrato debido a su mayor conductividad térmica (Al-7075-T6TC = 130 W / mK, AZ31TC = 98 W / mK y Ti6Al4VTC = 6,7 W / mK).

Los recubrimientos de Ti6Al4V esférico mejoran sus propiedades con el aumento de la temperatura y la presión, independientemente del sustrato proyectado.

En los experimentos realizados con el sistema KINETICS 8000, comparando los 3 sistemas que se han estudiado, independientemente del polvo utilizado y de las condiciones, las mejores eficiencias y porosidades más bajas se han logrado sobre el sustrato Ti6Al4V.



Figura 12: ED KINETICS 8000 con el polvo esférico y el irregular de Ti6Al4V

Como puede apreciarse, las mayores eficiencias han sido obtenidas con el Ti6Al4V esférico.

Para todas las condiciones de proyección, a partir de 680 ° C y 30 bar hasta 1.000 ° C y 50 bares, los mejores recubrimientos en términos de eficiencia de deposición, porosidad y la adherencia se han obtenido siempre sobre el sustrato Ti6Al4V.

Cuando se comparan AI-7075-T6 y AZ31, la eficiencia de deposición es mayor sobre AZ31, así como espesores de capa, independientemente de las condiciones de proyección. Las primeras partículas que inciden endurecen fuertemente el AZ31 o, lo que permite una mayor deformación en las siguientes partículas desencadenando mecanismos de unión.

Además de variar la presión y la temperatura del sistema 8000, también se ha cambiado el gas propelante y se trabajó con Helio en vez de con Nitrógeno. Se obtuvieron eficiencias por encima del 98% y porosidades por debajo del 0,2% para todos los sustratos.



Figura 13: Recubrimientos de Ti6Al4V esférico con Helio

Cuando se tienen en cuenta los valores de adherencia obtenidos, los valores obtenidos para Ti6Al4V son mejores. Si comparamos el Al-7075-T6 y el AZ31, a pesar de la tendencia de aluminio a oxidarse, la unión es más fuerte que con el magnesio. El, AZ31 se deforma principalmente a través de dos mecanismos, dislocaciones y maclas. Estos mecanismos, además de endurecer el sustrato y reducir la plasticidad, aumentan la tensión en la estructura evitando la recuperación del material, dificultando el contacto íntimo entre las partículas y el sustrato y evitando los mecanismos de unión de CGS.

Con respecto a los TCT test, los mayores valores se han obtenido en aquellos parámetros que permiten una mayor velocidad de partícula.

Si se comparan los valores obtenidos con el polvo esférico y el polvo irregular, son muy similares, ya que a pesar de una mayor oxidación de las partículas irregulares, y que las
eficiencias de deposición son menores, existe una gran compactación y una mayor superficie de contacto en las partículas irregulares que en las esféricas. Además, el recubrimiento está más entrelazado dificultando así su ruptura.

4.2. Recubrimientos de SS316L

Comparando ambos polvos de SS316L, esférico e irregular se han obtenido mayores eficiencias de deposición con el polvo esférico como puede observarse en la figura 14.



Figura 14: ED de los polvos de SS316L sobre todos los sustratos

Los mejores resultados se obtienen sobre el sustrato de Ti6Al4V seguido por el sustrato Al-7075-T6. Los valores de rendimiento más bajos se obtuvieron con el polvo irregular sobre el sustrato Al-7075-T6.

La combinación de la capa de pasivación del Al-7075-T6 junto con la alta oxidación del polvo irregular hace difícil que se alcance la velocidad crítica y se desencadenen los mecanismos de unión.

Una vez visto los resultados obtenidos, teniendo en cuenta la eficiencia del proceso, el espesor de los recubrimientos, la densidad, la homogeneidad y la dureza final, se puede concluir que los recubrimientos óptimos son los realizados en las más altas temperaturas y presiones (780 ° C y 38 bar) para ambos polvos.

Comparando los resultados obtenidos a la misma presión y cambiando la temperatura se observa que la eficiencia aumenta a medida que aumenta la temperatura, así como de espesor, mientras que la dureza no varía considerablemente.

A la misma temperatura y variando las presiones, la eficiencia aumenta con el aumento de la presión, pero su efecto es menor que en el caso de la temperatura.

La microdureza de los recubrimientos es muy similar para los recubrimientos óptimos sobre los tres sustratos independientemente del tipo de polvo.

Para aquellos recubrimientos obtenidos con polvo esférico, la microdureza obtenida fue de 358 \pm 36 HVN mientras que para el polvo irregular la microdureza obtenida fue de 368 \pm 35 HVN.

Si se comparan estas durezas obtenidas con los polvos de partida, los recubrimientos obtenidos con el polvo esférico, duplican la dureza del polvo mientras que en los recubrimientos obtenidos con el polvo irregular, la dureza se ha multiplicado por 2,3. En términos de nanodureza, la variabilidad es mucho más diferenciada, debido a los procesos de *pile-up* que se ha desarrollado sobre el recubrimiento óptimo obtenido del polvo irregular.

De los experimentos realizados con el equipo 8000, los mejores recubrimientos han sido aquellos obtenidos a 1000°C y 38 bar (figura 15) con unas eficiencias por encima del 95%, porosidad por debajo del 0,3% y unos valores de adherencia de 258 ± 9 MPa.



Figura 15: micrografías de microscopia óptica de los recubrimientos óptimos de 316L sobre Al-7075-T6 y AZ31

5. CONCLUSIONES

En esta tesis se han obtenido con éxito recubrimientos de acero inoxidable 316L y Ti6Al4V a través del uso de la Proyección fría sobre tres aleaciones ligeras (Ti6Al4V, Al-7075-T6 y AZ31). Se han mejorado sus propiedades de resistencia al desgaste y a la corrosión. La mejora de sus propiedades en materia de resistencia al desgaste ya la corrosión.

A partir de este estudio, se puede concluir:

CON RESPECTO A POLVOS DE PROYECCION Y LOS PARAMETROS DE PROYECCION

- Los polvos irregulares alcanzan mayores velocidades de vuelo que los esféricos debido al coeficiente de arrastre, y a pesar de que los dos polvos tienen la misma dureza, las eficiencias de deposición de los polvos esféricos son más altas. Los polvos irregulares tienen un mayor nivel de oxidación debido al método de obtención lo que reduce la ED.
- 2. Cuando se compara el polvo esférico oxidado y no oxidado de Ti6Al4V, las eficiencias son entre un 15 y un 30% mayores con el polvo no oxidado.
- Se han obtenido mejores recubrimientos en términos de eficiencia, porosidad, y resistencia al desgaste con los polvos de proyección esféricos sobre todo los sustratos.
- 4. A medida que aumenta la temperatura de proyección, también lo hace la ED ya que existen un mayor número de partículas que alcanzan su velocidad crítica. Además, la porosidad disminuye ya que la ductilidad de las partículas es mayor y son capaces de deformarse más debido al impacto
- A medida que aumenta la presión, los recubrimientos son más densos debido a la velocidad de impacto de las partículas. Éstas se deforman más al impactar y cierran los poros existentes en el recubrimiento,

CON RESPECTO AL MECANISMO DE ENLACE

- 6. Cuando el polvo de proyección y el sustrato tienen una naturaleza similar, como ya se ha visto con el polvo de Ti6Al4V sobre sustratos de Titanio y Ti6Al4V, se pueden llegar a producir microfusiones debido al impacto, fortaleciendo el enlace. . Los valores de adherencia de Ti6Al4V sobre Ti6Al4V son un 80% mayores que sobre AI-7075-T6 y un 95% mayores que sobre AZ31.
- 7. Cuando el polvo de proyección y el sustrato tienen distinta naturaleza y propiedades (dureza, ductilidad, conductividad térmica, estructura cristalina, mecanismos de deformación) se produce una unión mecánica. No se encontraron zonas de fusión o de enlace metalúrgico.
- 8. Se obtuvieron unos valores de adherencia de 76 \pm 7, 45 \pm 2 y 39 \pm 5 MPa para Ti6Al4V, sobre los sustratos de Ti6Al4V, Al-7075-T6 y AZ31 respectivamente
- 9. Los resultados obtenidos de las pruebas de la cavitación, han ayudado a identificar experimentalmente los mecanismos de unión de CGS como una función de la naturaleza de la partícula / sustrato. El orden en la fuerza de unión es Ti, Ti6Al4V, Al-7075-T6 y finalmente AZ31. Estos resultados están de acuerdo con los obtenidos con los ensayos de adhesión.

CON RESPECTO A LA OBTENCION DE RECUBRIMIENTOS

- 10. Independientemente a las morfologías de los polvos de proyección, mayores velocidades de impacto dan lugar a mejores recubrimientos para los sistemas estudiados. En general, se obtienen mayores velocidades cuando se aumenta la presión y la temperatura del gas portador.
- 11. Un aumento de la presión del gas portador genera mayores velocidades de partícula, permitiendo de este modo superar la velocidad crítica y aumentando la deformación de las mismas en el momento del impacto. Pero si no se ha

alcanzado una temperatura mínima o el material tiene una baja plasticidad, un aumento en la presión puede provocar la erosión del sustrato por impacto.

- 12. A través del uso de los diagramas de interacción y diagramas de Pareto se puede estudiar la influencia de los parámetros de proyección mediante la comparación de las variables respuesta. Se puede concluir que la temperatura del gas portador tiene una mayor influencia en la obtención del recubrimiento que la presión, con la excepción de polvo irregular de Ti6Al4V donde la influencia de la presión es mayor.
- 13. Para aplicaciones donde las estructuras de aleaciones ligeras se sometería a procesos de desgaste y corrosión, los recubrimientos deben ser densos y con un espesor medio-alto. Se han obtenido recubrimientos completamente densos usando tanto N₂ como Helio como gas portador. Se tiene que tener en cuenta que el He es 4 veces caro que el N₂.

CON RESPECTO AL SISTEMA TI6Al4V

- 14. Se han obtenido mayores ED con el polvo esférico que con el irregular, llegando incluso a valores de un 140% mayores para las condiciones óptimas de proyección.
- 15. Para todas las condiciones de proyección, los recubrimientos obtenidos con polvo esférico sobre Ti6Al4V tienen las mayores eficiencias (por encima del 80%) seguidos por los obtenidos con el mismo polvo sobre AZ31 (sobre el 65%) y por ultimo sobre Al7075-T6 (sobre el 45%)
- 16. Como se ha observado en los test de cavitación, ambas morfologías del polvo se comportan de forma similar. Tras la cavitación se han observado huellas con forma circular en la superficie de los sustratos dejadas por las partículas, dando pie a pensar que se han producido microfusiones en las zonas de unión debido a la alta energía existente en el momento del impacto.

- 17. Cuando se cambia el gas portador (N₂ por He) las partículas aumentan su velocidad y se obtienen mejores resultados. Con N₂ la máxima eficiencia obtenida es de un 83, un 70 y un 65% sobre Ti6Al4V, Al-7075-T6 y AZ31 respectivamente, en cambio, con He, las eficiencias son prácticamente del 100% sobre todos los sustratos.
- 18. Cuando se usa nitrógeno como gas portador, la porosidad de los recubrimientos se reducen hasta valores menores al 2% pero si el gas portador se cambia por Helio, la porosidad de los recubrimientos se reduce por debajo del 0,2% para todos los sustratos.
- 19. Si se comparan las dos boquillas usadas, con la D24 las máximas eficiencias obtenidas sobre Ti6Al4V, Al-7075-T6 and AZ31 son las mismas que las de la conclusión 17, en cambio, usando el D50, estas eficiencias aumentan hasta un 87, 82 and 70% respectivamente
- 20. Los valores de los TCT test para los recubrimientos obtenidos con el polvo irregular tienen entre 30 y 60 MPa más que para los recubrimientos obtenidos con el polvo esférico. Las partículas irregulares están más entrelazadas y su área de contacto es mayor, por lo que se necesita una mayor energía para separarlas.
- 21. Los recubrimientos obtenidos con el polvo esférico y usando He como gas portador son completamente resistentes a las corrosión del sustrato al que protegen.

CON RESPECTO AL SISTEMA SS316L

- 22. Se han obtenido recubrimientos de acero inoxidable 316L sobre aleaciones ligeras usando la Proyección fría.
- 23. La dureza de los recubrimientos es aproximadamente el doble que la de los polvos de proyección (un 100% superior en el caso del polvo esférico y un

130% superior en el caso del polvo irregular). Este aumento en la dureza es debido al endurecimiento por deformación en frio, la cual puede verse claramente al revelar la microestructura de los recubrimientos tras el ataque químico.

- 24. Comparando los resultados obtenidos a la misma presión y variando la temperatura, la eficiencia aumenta a medida que aumenta la temperatura, así como el espesor, mientras que la dureza permanece en el mismo orden de magnitud.
- 25. Manteniendo la temperatura constante y variando la presión, aumenta la eficiencia con el aumento de la presión, pero su efecto es menor que en el caso de la temperatura, como se ha visto con los diagramas de Pareto y los diagramas de interacción obtenidos.
- 26. La tasa de desgaste por abrasión del recubrimiento de SS316L esférico es un 220% menor que la tasa de desgaste abrasivo del sustrato de AI-7075-T6 y para el recubrimiento de SS316L irregular este valor se redujo al 190%con respecto al sustrato.