

Development of Ti-6Al-4V coating onto Ti-6Al-4V substrate using Low Pressure Cold Spray and Pulse Gas Dynamic Spray

By

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Abstract

The objective of this study is to successfully deposit Titanium Ti-6Al-4V layers onto Ti-6Al-4V substrate using two new commercially available Cold Spray processes such as Low Pressure Cold Spray (LPCS) and Pulsed Gas Dynamic Spray (PGDS). The second objective of this work is to develop a technique to repair Titanium parts since there is currently no repair technique commercially available. It is envisioned that commercial cold spray systems could be used to repair gashes on Titanium components. The examination of both feedstock powders and coatings were performed by different techniques such as optical microscopy and Scanning Electron Microscopy (SEM). Porosity, hardness, adhesion strength, flattening ratio, wipe test, fracture surface, wear test, XRD and chemical composition of the coatings using EDS have been evaluated. Cold spray has shown to be a promising technique for the deposition of heat sensitive particles such as titanium. LPCS and PGDS both produced high quality coatings. Low porosity, high hardness, adhesion strength over 40 MPa, metallurgical bonding, similar to bulk material wear rate, no oxide and nitride phases inside coating were measured.

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List of Symbols

Nomenclature

A	Cross-sectional flow area of the nozzle	$\dot{m}$	Mass flow
B	Load on indenter	P	Gas pressure
c	Speed of sound	T	Gas temperature
k	Specific heat ratio	w	Indenter width length
HV	Vickers hardness	ρ	Gas density
M	Mach number		

Subscripts and Superscripts

0	Flow stagnation properties
01	Initial state at stagnation
02	Final state at stagnation
1	Initial state

- 2 Final state
- 25 Load of 245 mN
- 300 Load of 2.942 N
- * Nozzle throat conditions
- e Nozzle exit area conditions

Abbreviation

CGDS	Cold gas dynamic spray
HPCS	High pressure cold spray
LPCS	Low pressure cold spray
PGDS	Pulse gas dynamic spray
SCFH	Standard cubic feet per hour

Chemical compounds

BaF ₂ -CaF ₂	Barium Fluoride –Calcium Fluoride in powder form is used in thermal as an abradable seals.
CoNiCrAlY	Alloy composed of Cobalt, Nickel, Chrome, Aluminum, and Yttrium And it is used as a bond coat material.
CP Ti	Commercially pure titanium (99% Ti)
FeO-TiO ₂	This one of the basic composition of titanium found in earth crust. Also named ilmenite
HF	Hydrofluoric acid is used in the etching process of Titanium
HNO ₃	Nitric acid is used in the etching process of Titanium
Ti-6Al-4V	Titanium alloy grade 5 is the most common titanium alloy used in the industry
TiCl ₄	Titanium tetrachloride is an inorganic compound obtain during the purification process of Titanium
TiO ₂	Titanium dioxide is one of the basic compositions of titanium found in earth crust. Also named rutile.

Chapter 1 – Introduction

1.1 Background

Since the introduction of thermal spray by Schoop [1] in 1910, there has been a constant evolution as the deposition process and its applications. Schoop's patent presents the basis of a technology consisting in heating solid particles and propelling them on to a substrate. After the particles strike the substrate, they deform and solidify to form a dense coating. Coating thickness and properties may vary depending upon the particles' material and the process parameters. Ceramics, cermets, pure metals and alloys are typically used as feedstock materials [1–3]. These materials are usually introduced into the spray process in powder or wire form.

The purpose of the coating is to protect the substrate against various type of degradation such as corrosion, wear and oxidation, and to prevent thermal deterioration. Coatings are widely used by aerospace and biomedical industries [1–3]. Coatings are also used in the pulp and paper industries as well as for automotive parts to produce wear protection coatings for their cylinders [1–4]. Thermal barriers produced by the coatings are vastly used in power generation turbines [1–3].

Following Schoop's patent, many researchers and engineers have worked toward the improvement of the initial concept. The first research path explored the increase of the propellant gas temperature to enhance particle melting. The process developed to reach that goal used electric arc beam. Subsequently, works have been done to further increase the propellant gas temperature using plasma jets. Following this, important research and development efforts were made on increasing the particles velocity, leading to high-velocity oxy-fuel (HVOF) process. Recently, research

on thermal spray processes aiming at reducing the propellant gas temperature below the particle melting point while increasing the propellant gas velocity were undertaken. This low particle's temperature combined with its high-velocity processing is named cold gas dynamic spray or CGDS. By keeping the gas temperature lower than the particle melting point, coatings with similar properties than those of the sprayed bulk material are produced [5,6]. Furthermore, materials that can experience oxidation during heating, such as Titanium can potentially be sprayed using CGDS.

Within CGDS process, three systems were developed using high velocity and low temperature principle. They differ by their powder injection point and the particle acceleration techniques. Low pressure cold spray (LPCS) and high pressure cold spray (HPCS) accelerated a continuous flow at high velocity using a de Laval nozzle. In LPCS process, the powder is injected in the diverging section of the nozzle instead of the converging in the HPCS. Pulsed gas dynamic spray (PGDS) does not require a nozzle but shock wave instead. In order to create shock waves, the PDGS processes use intermittent propellant gas flow.

These two processes could be used to create coating made of Titanium particles. The utilization of Titanium is increasing each year since it can decrease the mass of critical parts. In 2011, near 7 million tons of Titanium dioxide was mined around the globe. Using Titanium dioxide in combination with the Kroll process, Titanium can be obtained. The production of this metal was of 186,000 tons in its sponge form in 2011 [7]. In the aircraft industry, 50% of the Titanium components are made of Ti-6Al-4V [8]. This Titanium alloy is used in various parts of the aircraft such as the engine, the wings and the landing gear [8].

1.2 Motivation of Research and General Objectives

The present study was motivated by the improvement of the potential of the LPCS and PGDS processes to develop engineered coatings with desired properties. The specific purpose of this research is to explore and expand the range of applicability of the LPCS and PGDS processes by spraying Ti-6Al-4V grade 5 powder. Few coatings have been investigated with LPCS and PGDS processes with this type of powder material. Moreover, the mechanical properties of LPCS and PGDS Ti-6Al-4V coatings have not yet been evaluated. In order to achieve this objective, a number of specific goals will need to be performed as follows:

- Explore the feasibility of LPCS and PGDS processes with Ti-6Al-4V particles
- Conduct studies on the experimental parameters of the LPCS and PGDS coating techniques with the systems available
- Characterize the microstructure of the coating and correlate it to the process parameters chosen.
- Evaluate the mechanical properties of the coating and correlate them to the microstructure.
- Evaluate the potential for repairing Titanium parts by using Ti-6Al-4V coating.

1.3 Outline of the Thesis

Chapter 1 introduces the thermal spray process from its origin to the latest research in the field. Moreover, motivation of the research and the outline of the thesis are mentioned.

Chapter 2 explains the transformation process of titanium and its utilization in the different industries. Details on the evolution of thermal spray and related methods to achieve spraying of particles on to a substrate are then presented. This is followed by an overview of the LPCS and PGDS physics and process functioning principles. Powder manufacturing techniques for the material of interest (Ti-6Al-4V) are also explained. Finally, Ti-6Al-4V coatings spray and analysis by other researchers are presented to complete the subjects considered in the literature review.

Chapter 3 presents the main objectives of this research and the potential for commercial coatings obtained by LPCS and PGDS techniques.

Chapter 4 defines all the experimental systems and measurement methods used in this research along with a description of the equipment.

Chapter 5 synthesizes the characteristics of feedstock and milled Ti-6Al-4V powders.

Chapter 6 covers the spray testing for both systems using baseline spray parameters. Following this step, each parameter was optimized sequentially by varying each of them and selecting the value providing the best coating. Therefore, the optimized value for the first parameter was used during the performance of the optimization of the second one, then both optimized values of these

parameters were used in the optimization of the third one and so forth until all parameters were optimized.

Chapter 7 presents the results of the coatings obtained for each process using the best parameters, as described in the previous chapter. The values and observations obtained from different technical analyses, such as porosity, hardness, adhesion strength and oxide content, are then presented to compare the results between LPCS and PGDS processing methods.

Chapter 8 summarizes all the major results obtained during this research.

Chapter 9 describes future development and studies to improve each process and their applications.

Chapter 2 –Literature Review

2.1 Preamble

A literature review of the thermal spray processes constitutes the first part of this chapter. This will be followed by the description of the Low Pressure Cold Spray (LPCS) and Pulse Gas Dynamic Spray (PGS) processes. The critical particle velocity will then be introduced since it is the dominant parameter ensuring coating formation. A review of the bonding mechanisms occurring at impact for CGDS processes will be the next subject presented. Since this research is about the development of Titanium coatings and repairs, Titanium transformation and powder manufacturing processes are also briefly described. A summary of the studies conducted by other researchers in the area of sprayed Ti-6Al-4V coatings will then be presented to conclude this chapter.

2.2 Thermal Spray Processes

Schoop introduced in 1910 [1] a new coating manufacturing process. Since then, new techniques have been developed and classified in four different categories used in the thermal spray industry. Each category corresponds to a different method to heat and accelerate the particles leading to the production of the coating. The thermal spray processes will be presented going from a process featuring a high temperature and low velocity towards a low temperature and high velocity process. Figure 2.1 illustrates all the processes which will be briefly covered in this section. The processes highlighted in grey have been used in the present study, therefore they will be discussed more details.

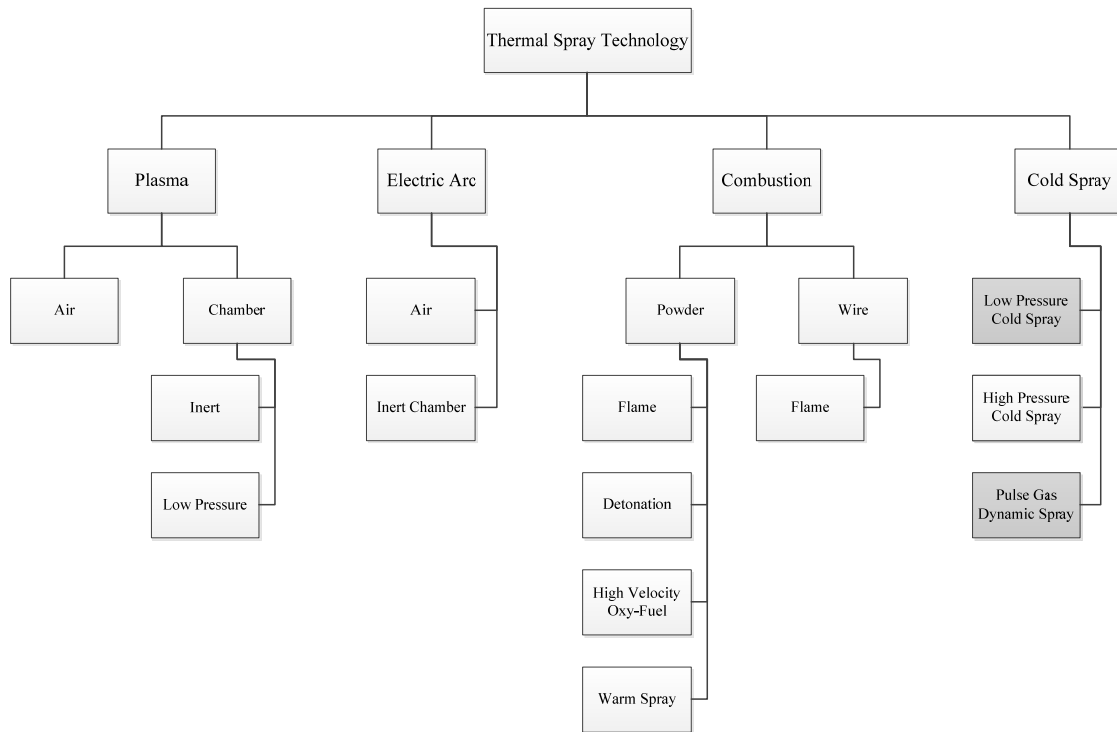


Figure 2.1 :Thermal spraying processes (adapted from [1])

For each type of heating method presented above, sub-categories representing variations or evolutions of each of them are indicated. The first type consists of using thermal plasma to heat the feedstock particles above their melting point. The second type uses an electric arc to heat the feedstock particles at a temperature lower than in plasma spraying; but still above their melting point. In the third category, the powder is heated by combustion. The combustion typically heats the particles above the melting point, with the exception of warm spray. In the last category, particles temperatures are below their melting point but their velocity is much higher compared to the previous categories. Each process contained in the sub-categories will be explained in the next sub-sections.

2.2.1 Plasma Spraying

Plasma spraying is the most common thermal spray process used in commercial coating applications [1]. The plasma gas is typically a mixture of nitrogen (N_2) or argon (Ar) with hydrogen (H_2) or helium (He) to improve the gas thermal conductivity. The carrier gas goes through an electric arc created between an anode and cathode that heats it up to 25000 K [9] approximately. The plasma gas heats the powder above 4500K [1,10] and accelerates them to a velocity up to 600 m/s [10]. The resulting molten powder solidifies after impacting the substrate to form the coating.

A schematic of a plasma spraying gun is shown in Figure 2.2. Plasma spraying generates enough heat to melt any type of materials including ceramic and refractory materials. It can produce a coating in different spray environments. The most common, known as Air-Plasma Spraying (APS), is carried out under an atmospheric environment. It is possible to spray in vacuum or an inert gas chamber when oxidation is an issue. Plasma sprayed coatings have porosity levels from 1 to 40% and bond strength between 10 and 45 MPa [1,11].

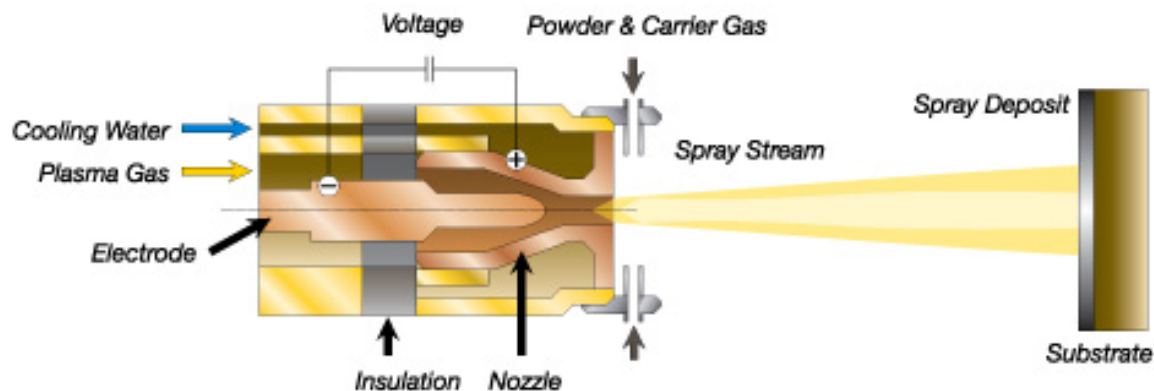


Figure 2.2 : Schematic of a plasma spray gun [12]

2.2.2 Electric Arc Spraying

The working principle of this process is based on the use of two metallic wires with opposite electrical charges fed into the arc gun. When the tips of the wires are in contact, enough heat is created to melt the wires. The material from the molten wires can reach temperatures up to 4000K [1] and it is projected on the substrate at a velocity up to 240 m/s [9] using compressed air. A schematic of an electric arc spraying gun is shown in Figure 2.3. A drawback of this process is the requirement to use conductive materials because of the required use of an electric charge. Ceramics and polymers cannot therefore be deposited using this method. This process works very well with aluminum alloys, zinc, copper and stainless steels. It is possible to spray in an inert gas chamber when oxidation is an issue. The resulting coatings have porosity levels from 5 to 20% and bond strength between 10 and 40 MPa [1].

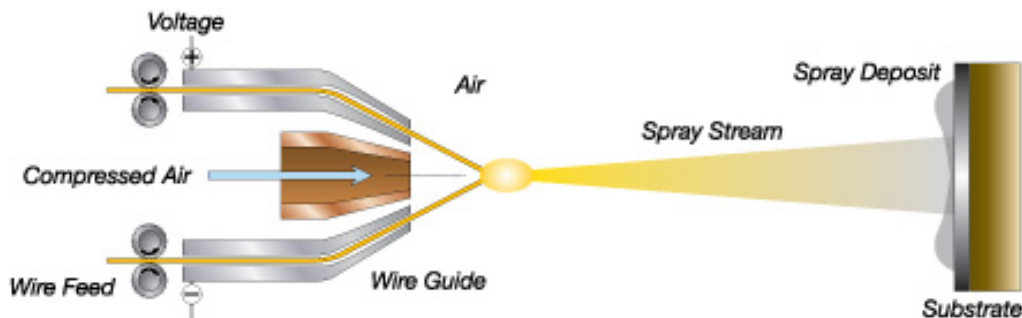


Figure 2.3 : Schematic of electric arc gun [12]

2.2.3 Combustion Spraying

The combustion of fuel in an oxygen rich environment to heat the particles represents the working principle of the process in this category. Four processes are included in this category.

2.2.3.1 Flame spray

Flame spray uses combustion of hydrogen, acetylene or propane in an oxygen rich environment, in order to heat wires or powders coating materials. These materials are fed in axial or radial direction and accelerated to velocities between 30 and 180 m/s [1]. This process can be used to spray low melting point metals such as tin or lead. A schematic of a flame spray gun is shown in Figure 2.5. Since the particles velocity is low, the coating porosity is high and the adhesion obtained is under 30 MPa [11].

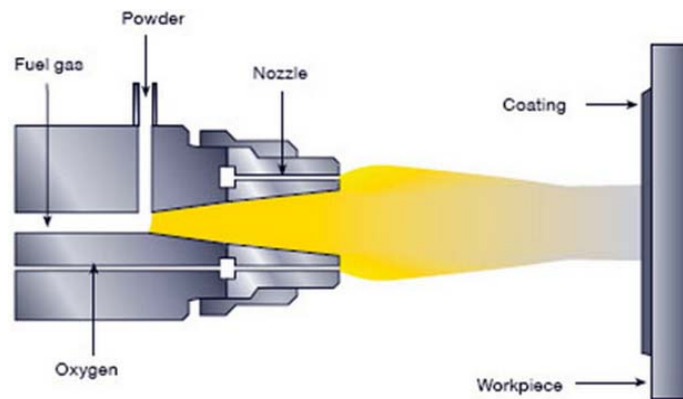


Figure 2.4 : Schematic of a flame spray [13]

2.2.3.2 Detonation Gun

The detonation gun (D-Gun), as its name indicates, uses detonations to accelerate and heat powder particles. A gas mixture of fuel (acetylene) and oxygen is injected into the acceleration tube while the coating material in powder form is introduced in the barrel. The detonation is created by igniting the mixed gases with a spark. This reaction accelerates the powder material to a velocity of up to 1050 m/s [11] while heating the powder. This cycle is repeated many times per seconds. A dense and strong coating is produced by the hot powder particles when they impact the substrate because of their high kinetic energy. Ceramics and high melting point metals can be sprayed using

this technique. A schematic of a detonation spraying gun is shown in Figure 2.5. The resulting coatings present porosity levels under 0.5% and bond strengths up to 70 MPa [11]; thus providing highly improved results compared to the techniques presented before.

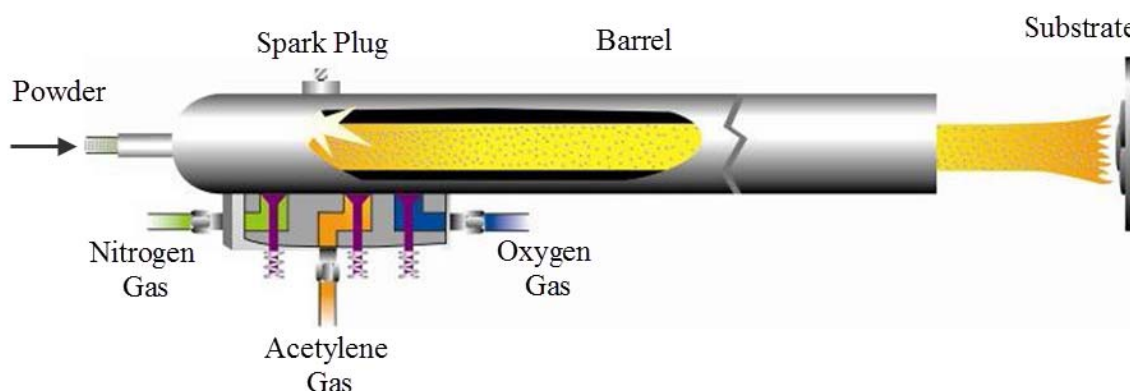


Figure 2.5 : Schematic of detonation gun [14]

2.2.3.3 High velocity oxy-fuel (HVOF)

High velocity oxy-fuel (HVOF) was commercialized in the 1980s. This process uses heat from continuous combustion that can reach a flame temperature up to 3000K [11]. It is created by a mixture of fuels (hydrogen, propylene, propane, acetylene or kerosene) with oxygen. The combustion gases go through a converging-diverging (De Laval) nozzle that accelerates them. The powder is fed axially into the combustion chamber and accelerated to a velocity up to 1000 m/s [1]. The molten or semi-molten particles are plastically deformed upon impact on the substrate. A schematic of a HVOF gun is shown in Figure 2.6. The resulting coatings have porosity levels between 1 and 40% with bond strength up to 83 MPa [11].

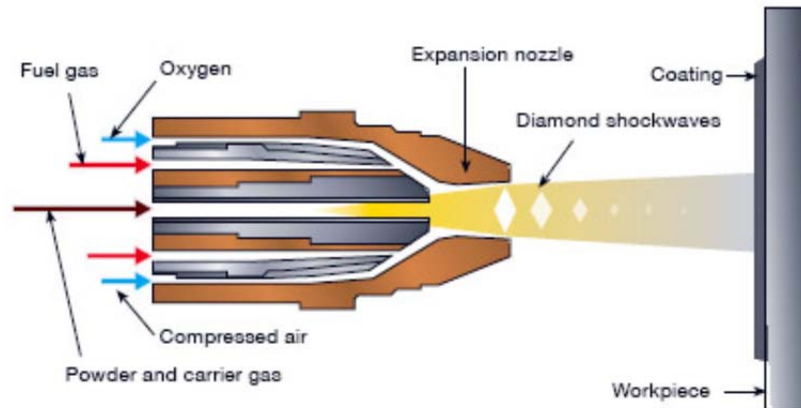


Figure 2.6 : Schematic of high velocity oxy-fuel gun [12]

2.2.3.4 Warm Spray

A modified version of the HVOF process, known as Warm Spray (WS), was recently developed [15].

The injection of nitrogen in a post-combustion mixing chamber located before the converging-diverging nozzle enables the reduction of the gas temperature from 3000°C to 500°C [15]. This process has been successfully used to spray heat sensitive materials such as Titanium and polymers [15,16]. A schematic of a warm spray gun is shown in Figure 2.7.

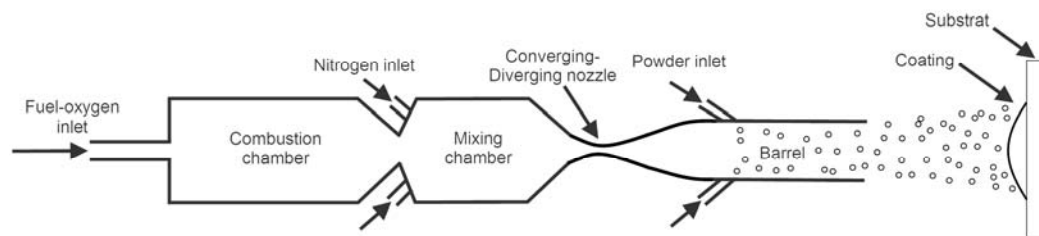


Figure 2.7 : Schematic of warm spray gun

2.2.4 Cold Spray

Cold Gas Dynamic Spray (CGDS), is the last sub-category of thermal spray methods and includes: low pressure cold spray (LPCS), high pressure cold spray (HPCS) and pulse gas dynamic spray (PGDS). More details on the first and last ones will be presented in sections 2.3 and 2.4 respectively since these processes were used in this research. The low thermal energy provided to the feedstock particles in all of the processing methods in this sub-category lead to a powder temperature lower than its melting point. In order to compensate for this lower powder temperature, a converging-diverging nozzle also named a De Laval nozzle is used to produce higher carrier gas velocity to accelerate the particles to reach velocities between 200 and 1200 m/s [17]. The coating formation is produced only through the plastic deformation of the high-velocity impact of the particles on the substrate [18]. The difference between LPCS and HPCS lies in the location of the powder injection into the system. In LPCS, powder injection is carried out in the low pressure region after the nozzle throat while it is injected before the throat, in the high pressure area, in the case of HPCS. These two processes use a continuous gas flow to accelerate the particle. The gas stream is pulsed and does not use a De Laval nozzle to accelerate the gas flow in the case of PGDS. The powder used in all of these processes must be ductile. However, brittle or hard material can be mixed with ductile matrix material to produce composite coatings [19]. Porosity level from 0.5 to 20% [1] and bond strength between 20 and 70 MPa [20] have been reported.

2.2.5 Summary of the Thermal Spray Processes

In order to quickly compare the different thermal spray methods presented in sections 2.2.1 to 2.2.4, a summary of the values for the important working characteristics for each process is presented in Table 2.1 below.

Table 2.1 : Characteristics of the various thermal spray processes (from [1,9,15,17,21,22])

Spray Process	Particle Velocity (m/s)	Particle Temperature (K)	Materials applicability
Plasma	10-600	1200-4500	Metal, ceramic
Electric arc	240	4000	Metal
Flame Spray	30-180	2000	Metal
Detonation Gun	400-1050	Up to 2500	Metal, cermet ceramic
HVOF	600	2500	Metal, cermet ceramic
Warm Spray	600	Up to 900	Metal
Cold Spray	200-1200	Up to 900	Metal and Polymer

As it can be observed in this table, the plasma spray process has the lowest particle velocity but the highest particle temperature. This process is used for the deposition of ceramic and metallic coatings. On the other end of the particle velocity and temperature spectrum, there is cold spray. It is used to spray low melting temperature and heat sensitive materials. In the middle of this spectrum, combustion spray offers a compromise between high particle velocity and temperature.

Table 2.2 : Characteristics of the various thermal spray processes (from [1,11,16,23])

Spray Process	Porosity range (%)	Oxide content	Adhesion Strength (MPa)
Plasma	1-40	Moderate-High	10-45
Electric arc	5-20	Moderate-High	10-30
Flame Spray	1-40	High	15-30
Detonation Gun	1-40	Moderate	Up to 80
HVOF	1-40	Moderate	Up to 80
Warm Spray	0.5-20	Low	Above 50
Cold Spray	0.5-20	Minimal	20-70

Table 2.2 above shows the relationship between the particle velocity and the porosity level in the coating. It is observed that a higher particle velocity has a higher impact energy which produces higher deformation of the particles resulting in the creation of a denser coating. Furthermore, it is possible to conclude that high particle temperature increases the oxide content in the coating. Oxides are formed when the high temperature particles are in contact with air.

2.3 Low Pressure Cold Spraying (LPCS)

Details on the low pressure cold spray system working principles are presented in this section. A review of the history of this technology is first presented followed by discussion of the general process characteristics. The basic gas dynamic principles involved in the LPCS process are then reviewed followed by the presentation of the advantages and limitations of this technology.

2.3.1 Background

In the late 1980's, Cold Gas Dynamic Spray (CGDS) was introduced as a new thermal spray process [24]. This technology was first developed at the Institute of Theoretical and Applied Mechanics of the Siberian division of the Russian Academy of Science in Novosibirsk. At that time, researchers observed that a metallic coating was created on the leading edges of models in a supersonic wind tunnel when they were using metallic powder tracer [25]. They showed that it was possible to create an aluminum coating if the particle velocities were above 400 m/s [25]. In the mid 1990's, a US patent was filed explaining the principle behind this process with the powder injection located before the throat of the de Laval nozzle; this method is also known as high pressure cold spray (HPCS). Another powder injection point on the nozzle was developed during the 2000's to provide control over the powder temperature and enable work at a lower temperature. This process was named low pressure cold spray or LPCS. Nowadays, there are many commercial systems using either of the injection points. In addition, in-house systems are under development in many laboratories all over the world to further study and improve this technology [5].

2.3.2 General Process Overview

Low Pressure Cold Spray is a solid-state process mainly relying on the sprayed particle kinetic energy to produce the coatings. This process uses driving gases such as nitrogen or helium to accelerate

particles between 200 m/s and 1200 m/s using a de Laval nozzle [1,26–31]. The gas temperature is increased using an electric heater providing the following advantages: avoidance of hazardous gasses used in the combustion process as well as absence of combustion products; easier control compared to a combustion process, capability to characterize precisely and thus optimize the temperature; possibility to use inert gas and lower gas temperature. The nozzle converts thermal energy into kinetic energy in order to accelerate the particle above their critical velocity, as explained in section 2.5 [32]. This system, as oppose to HPCS, presents the advantage of eliminating clogging/fouling at the throat because the powder is injected after it. Furthermore, this technique involves feedstock powder temperatures below their melting points thus providing the capability to work with heat sensitive material. This system can also integrate an electric powder heater in order to precisely control powder temperature fed in the nozzle. The schematic of this process is shown in Figure 2.8.

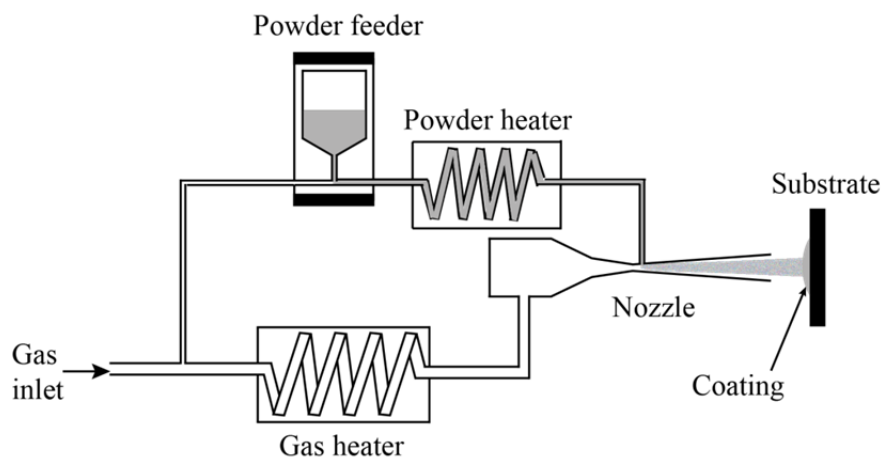


Figure 2.8 : Schematic of the LPCS technique.

2.3.3 Gas Dynamic Principles Involved in LPCS

The nozzle accelerating the gas stream to supersonic velocity is the most important part of this process. The basic gas dynamic principles govern the nozzle design as well as the effect of pressure, temperature and area ratio change in the gas stream. These principles will be discussed in this section.

2.3.3.1 Assumptions in LPCS calculations

Some assumptions must be made in order to simplify gas dynamics calculation. The first one is that the nozzle flow is isentropic. This yields to consider an adiabatic and reversible flow thus resulting in absence variation of energy into the system. In addition, the driving and carrier gases are inert; they can therefore be assumed as calorically perfect. A steady state flow is also assumed. The last assumption is a one-dimensional flow inside the nozzle which presumes small variations of the flow properties in the radial direction.

2.3.3.2 Compressible Flow

Since gases are compressible, their density can vary. This phenomenon can be analysed considering a simple pressure wave traveling at the speed of sound through a stagnant gas. Using the continuity and momentum equations on both sides of the pressure wave two equations can be derived:

$$\frac{d\rho}{\rho} = \frac{du}{c} \quad (\text{Eq. 2.1})$$

$$c^2 = \left(\frac{dP}{d\rho} \right)_s \quad (\text{Eq. 2.2})$$

Where ρ is the flow mass density, P is the flow local static pressure, u the flow velocity and c is the speed of sound on that point. Eq. 2.2 can be further simplified assuming the perfect gas law thus resulting in the following equation to compute the speed of sound in the gas of interest:

$$c = \sqrt{kRT} \quad (\text{Eq. 2.3})$$

In this equation k is the specific heat ratio, R the specific gas constant and T the local static temperature. It can be observed that the speed of sound depends upon the nature of the gas and his temperature. Therefore, it is possible to compare different gases as a function of the speed of sound in them. Such values at standard atmospheric pressure are presented in Table 2.3.

Table 2.3 : Speed of sound for different gasses at standard atmospheric pressure

Gas	Speed of sound (m/s)
Carbon dioxide	269
Argon	322
Air	346
Nitrogen	351
Helium	1016
Hydrogen	1315

This table shows that lower speeds of sound are observed for higher molecular weight gases. It is therefore preferable to use hydrogen or helium as the driving gas since higher velocities are preferable in the process.

Another equation can be developed to compute the Mach number (M). This number is the ratio between the velocity of the flow (u) and the speed of sound (c):

$$M = \frac{u}{c} = \frac{u}{\sqrt{kRT}} \quad (\text{Eq. 2.4})$$

The Mach number is used as a reference to determine the flow regime. For example, a computed Mach number below 0.3 for the flow is considered incompressible since the density is not much affected. A Mach number between 0.3 and 1 is named subsonic and the flow is compressible. A sonic flow is traveling at the speed of sound i.e. $M=1$ while a supersonic flow travels above the speed of sound ($M>1$). For compressible flow ($M>0.3$), the effects on the change of density must be considered in the calculations.

2.3.3.3 Flow through a Section of Variable Area

In order to simplify the combination of the conservation of energy and Gibbs equations, the flow passing through the nozzle was considered one dimensional, steady and isentropic flow hence resulting in [33]:

$$\frac{du}{u} = - \frac{dA}{A} \frac{1}{(1-M^2)} \quad (\text{Eq. 2.5})$$

In this equation, A is the area of the nozzle section and u is the velocity of the flow. Based on Eq. 2.5 it can be concluded that the velocity and section area vary in opposite directions for subsonic flow ($M < 1$) and in the same direction for supersonic flow ($M > 1$) therefore subsonic flow is accelerated with a converging section while supersonic flow is accelerated with a diverging section. In order to accelerate a flow above supersonic from a subsonic one, the combination of a converging nozzle to accelerate the flow until $M=1$ and a diverging section to further increase the velocity of the flow must be used.

Eq. 2.5 was combined with continuity equation to derive the following equation in order to define the effect of the Mach number on the density of flow:

$$\frac{d\rho}{\rho} = \frac{dA}{A} \frac{M^2}{(1-M^2)} \quad (\text{Eq. 2.6})$$

This equation shows that the density and the area change in the same direction for subsonic flows ($M < 1$) while they vary in opposite directions for supersonic flow ($M > 1$).

2.3.3.4 Fluid Stagnation Properties Definition

The calculation of the fluid stagnation pressure and temperature will be discussed in this section. Stagnation refers to a parameter at rest ($u=0$) following an isentropic process. These parameters (subscript 0) can be calculated for a perfect gas with the following equations [33]:

$$T_0 = T \left(1 + \frac{k-1}{2} M^2 \right) \quad (\text{Eq. 2.7})$$

$$P_0 = P \left(1 + \left(\frac{k-1}{2} M^2 \right)^{\frac{k}{k-1}} \right) \quad (\text{Eq. 2.8})$$

With these equations, it is possible to compute the Mach number and therefore the velocity of the flow if one knows either the type of gas used along with either the temperature ratio $\left(\frac{T_0}{T}\right)$ or the pressure ratio $\left(\frac{P_0}{P}\right)$. Another equation can be further derived to obtain the density ratio $\left(\frac{\rho_0}{\rho}\right)$ if

Eq. 2.7 and Eq. 2.8 are combined together considering perfect gas law [33]:

$$\frac{\rho_0}{\rho} = 1 + \left(\frac{k-1}{2} M^2\right)^{\frac{1}{k-1}} \quad (\text{Eq. 2.9})$$

2.3.3.5 Compressible Isentropic Flow in a Converging-Diverging Nozzle

Using equations (2.7) and (2.8), it is possible to compute the pressure and the temperature ratio along the flow from any point on a stream line if the Mach number and gas nature are known. The top section of Figure 2.9, shows a schematic of a converging-diverging nozzle. A large reservoir with stagnation pressure P_0 and stagnation temperature T_0 is illustrated on the left side. The reservoir is coupled with a converging-diverging nozzle where the exit pressure is P_e . Finally there is an outlet reservoir at a pressure P_b on the right side.

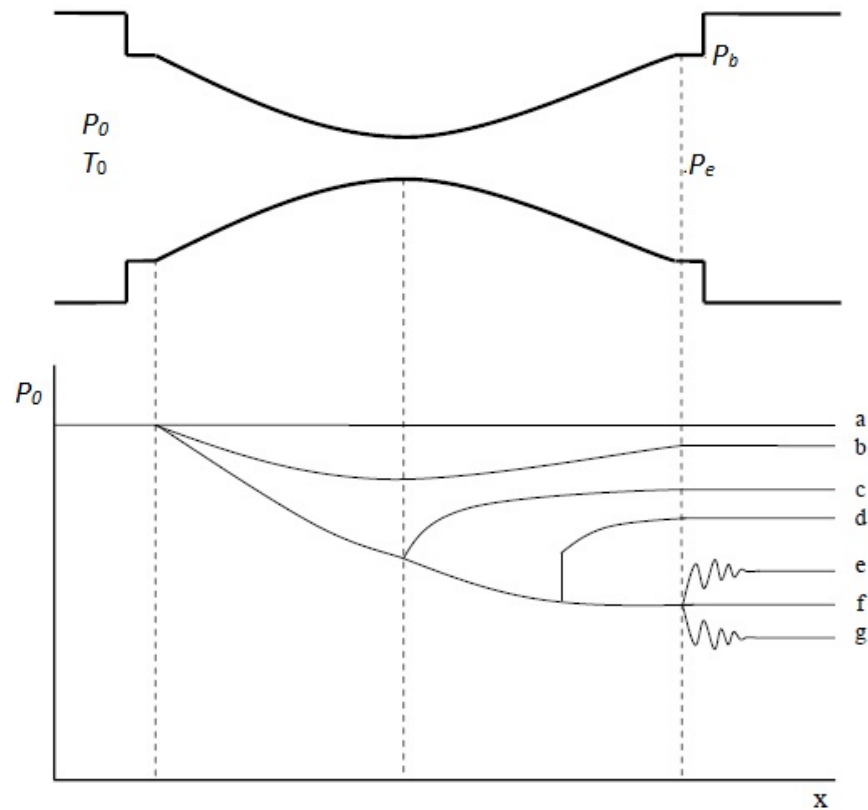


Figure 2.9 : Isentropic flow behaviour in a converging-diverging nozzle as a function of the pressure ratio (adapted from [34])

Gas stream representations for the different cases are illustrated in the curves at the bottom of Figure 2.9. In case "a", the stagnation pressure is equal to the outlet pressure ($P_0 = P_b$) resulting in no acceleration of the flow. The outlet pressure is decreased compared to the stagnation pressure ($P_0 > P_b$) in case "b". In this case, the pressure drops in the converging area, as computed with Eq. 2.8. Furthermore, since the flow is in a subsonic regime at the end of the converging section, there is an increase of pressure and a drop of velocity in the diverging section. In the next case ("c"), the outlet pressure is further dropped thus affecting the pressure in the nozzle, and the velocity is increased to obtain a sonic flow ($M=1$) at the converging section and choking the flow at the throat. This flow is

still not fast enough to be accelerated in the diverging section, resulting in a deceleration in the diverging section. In case "d", the outlet pressure is low enough so the flow is choked, and it is accelerated in the diverging section. At one point in the diverging section, there is a drop of velocity caused by shock wave. This shock wave will be located in the diverging section because the exit pressure must be equal to the back pressure. The velocity after the shock wave is subsonic so the velocity decreases until the end of the diverging section. In the last three cases (e, f, g) a supersonic velocity is present without shock wave inside the nozzle. In case "e" the exit pressure is lower than the outlet pressure resulting in an expansion to return to the outlet pressure, and the nozzle is called "over-expanded". Case "f" is the perfect case since the exit pressure is similar to the outlet pressure so it is named ideally-expanded. In the last case ("g"), the exit is higher than the outlet pressure resulting in expansion waves and oblique shock wave to compensate; it is called under-expanded.

2.3.3.6 Design Parameters of CGDS Nozzles

Using Eq. 2.3, Eq. 2.4, Eq. 2.7 and Eq. 2.9, the mass flow rate and area ratio can be expressed as

$$\frac{\dot{m}}{A} = \frac{P_0 \sqrt{k}}{\sqrt{RT_0}} M \left(\frac{1}{1 + \frac{k-1}{2} M^2} \right)^{k+1/2(k-1)} \quad (\text{Eq. 2.10})$$

The mass flow per unit area is maximized when $M=1$. Considering the properties for $M=1$ (indicated with an asterisk), the maximum flow per unit area is given by:

$$\frac{\dot{m}}{A^*} = \frac{P_0 \sqrt{k}}{\sqrt{RT_0}} \left(\frac{1}{1 + \frac{k-1}{2}} \right)^{k+1/2(k-1)} \quad (\text{Eq. 2.11})$$

The combination of these two last equations then gives

$$\frac{A}{A^*} = \frac{1}{M} \left[\frac{2}{k+1} \left(1 + \frac{k-1}{2} M^2 \right) \right]^{k+1/2(k-1)} \quad (\text{Eq. 2.12})$$

A is the area of the section and A^* is the area at the throat section. This equation shows that two velocity results can be obtained; one will be subsonic while the other one supersonic. The correct velocity can be determined using Eq. 2.8.

2.3.4 LPCS Advantages

LPCS provides the advantage of being a solid-state process where the bulk properties of the particles are still the same after impact. In addition, the jet stream is very small making it a promising technique for precision deposition without the requirement of part masking. This process allows the precise control of gas and powder temperatures, which provides some advantage to enable spraying temperature and oxygen sensitive materials such as Titanium and copper. Another advantage of this process is the ability to deposit thick coating after one pass without affecting the substrate; even with thin substrate [35]. This technique presents the advantage of producing a dense coating coming from the plastic deformation at impact. This deformation helps the bonding between the substrate and the coating resulting in a good adhesion [36]. Since the particle deforms at impact, cold working occurs thus increasing the hardness of the feedstock powder inside the coating [37].

The LPCS capability of spraying typical cold spray materials such as pure aluminum [38,39], copper [40], tin [38], zinc [38], aluminum-alumina mixtures [41,42], Al-WC [43], Cu-WC [43], NiCrAlY [44] has been demonstrated.

It does not require a closed environment to control the pressure, temperature and gas which are required with other thermal spray techniques. It is also possible to recycle the gas and the powder since the gas is not combusted in the process, and the powder is not melted.

2.3.5 LPCS Limitations

One of the limitations of this process comes from the formation of a coating build-up also known as clogging inside the diverging section of the nozzle. It is happening even if the powder is inserted after the throat in the radial axis. When this happens, the deposition rate and the coating quality decrease since the diverging section accelerating the powder is not smooth anymore.

In order to produce a coating, plastic deformation must take place. Brittle materials, such as ceramics, require to be embedded into a ductile matrix to allow to use this method [19].

2.4 Pulse Gas Dynamic Spraying (PGDS)

This section presents the PGDS process background and the physics governing it.

2.4.1 Background

Pulse Gas Dynamic Spray (PGDS) was originally developed at the University of Ottawa Cold Spray Laboratory(Canada) [21] and a patent was filed and licensed to the Supersonic Spray Division of Centerline Ltd (Windsor, Canada). This process is a variation of the cold spray processes where a pulsed flow is used instead of a continuous one. Each pulse creates a shock wave heating and propelling the particles towards the substrate. This process involves limited transfer of the driving gas thermal energy into kinetic energy since it does not use a de Laval nozzle. The accelerating particles are heated up while they are traveling into a high-intensity heat zone just behind the shock wave front [45]. The accelerated particles remain warmer as compare to LPCS and HPCS processes, which promote a higher powder ductility thus enhancing particle deformation[46]. Various metals such as aluminum and copper were successfully deposited using this process [21]. Stainless steel [47], WC-Co [48] and WC-10Co4Cr [48] and amorphous iron coatings [21] were also sprayed successfully with this method.

2.4.2 General Process Overview

The system used for this study is represented schematically in Figure 2.10 below.

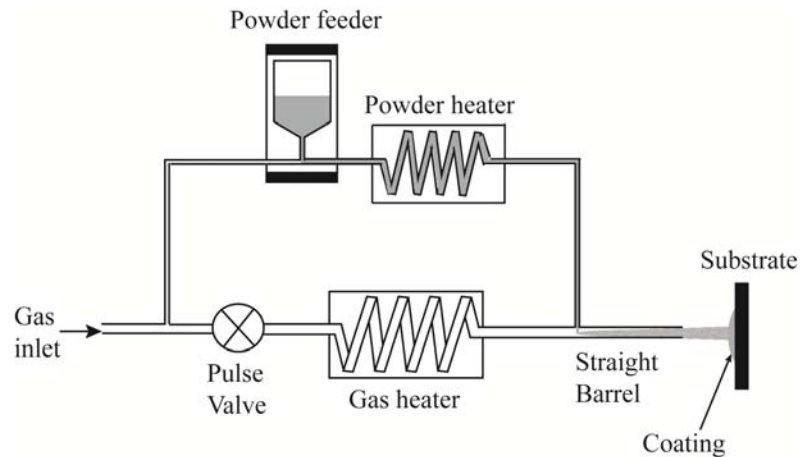


Figure 2.10 : Schematic of the PGDS process.

The PGDS includes an additional valve before the gas heater when compared with the Low Pressure Cold Spray. This valve consists of a small gas reservoir with a fast opening/closing gate mechanism. This quick opening and closing of the valve creates a shock wave traveling into the gas heater which accelerates the particles afterwards. Nitrogen or helium are typical gases used in this process. The gas is warmed with an electric heater thus presenting the following advantages: no hazardous gases used in the combustion, easier direct temperature control leading to well characterized and optimized temperatures compare to a combustion process, absence of combustion product, possibility to use inert gas and lower gas temperature. This technique presents the capability of spraying oxygen sensitive material since the particles temperatures remain below their melting points. This system can integrate an electric powder heater to precisely control powder temperature fed in the barrel.

2.4.3 Gas Dynamic Principles Involved in PGDS

The most important principle involved during this process is the creation of a shock wave that accelerates the gas stream to supersonic velocity.

2.4.3.1 Normal Shocks

In order to understand the physics behind the PGDS operation, the theory of normal shocks will be briefly presented in this sub-section. A shock is a discontinuity in a supersonic flow. It is labelled normal shock if the flow going through the shock is perpendicular (normal) to it. Using the continuity, momentum and energy equations combined with the Mach number and the ideal gas equations, three equations are derived. In these equations, subscripts 1 and 2 represent the initial and the final states respectively. In addition, M represents the Mach number, T is the temperature, P is the pressure and k is the specific heat ratio for the gas involved in the process.

$$\frac{P_2}{P_1} = \frac{M_2}{M_1} \sqrt{\frac{T_2}{T_1}} \quad (\text{Eq. 2.13})$$

$$\frac{P_2}{P_1} = \frac{1+kM_1^2}{1+kM_2^2} \quad (\text{Eq. 2.14})$$

$$\sqrt{\frac{T_2}{T_1}} = \frac{\sqrt{1+\frac{k-1}{2}M_1^2}}{\sqrt{1+\frac{k-1}{2}M_2^2}} \quad (\text{Eq. 2.15})$$

Using these three equations, it is possible to conclude that an increase of pressure and temperature is obtained when going through a normal shock wave. These three equations are also influenced by the nature of the gas used. Elimination of the $\left(\frac{P_2}{P_1}\right)$ and $\left(\frac{T_2}{T_1}\right)$ terms in the previous equations yields an equation of the Mach number after the shock as a function of the Mach number before it and the gas nature (represented by the specific heat ratio).

$$M_2^2 = \frac{M_1^2 + \frac{2}{k-1}}{\frac{2k}{k-1}M_1^2 - 1} \quad (\text{Eq. 2.16})$$

This equation shows the Mach number decreases across a normal shock wave. Further transformations enable the development of an equation to define stagnation pressure.

$$\frac{P_{02}}{P_{01}} = \frac{\left[\left(M_1^2 \frac{k+1}{2} \right) / \left(1 + M_1^2 \frac{k-1}{2} \right) \right]^{\frac{k}{k-1}}}{\left(M_1^2 \frac{2k}{k+1} - \frac{k-1}{k+1} \right)^{\frac{1}{k-1}}} \quad (\text{Eq. 2.17})$$

This equation shows that the stagnation pressure decreases while going through a shock wave. The evolution of the variables describing the steady flow of an ideal gas passing across a normal shock wave is summarized in Table 2.4.

Table 2.4 : Summary of normal shock wave characteristics

Variable	Change across a normal shock wave
Mach number	Decreases
Static pressure	Increases
Stagnation pressure	Decreases
Static temperature	Increases
Stagnation temperature	Constant
Density	Increases
Velocity	Decreases

2.4.3.2 PGDS process working principles

As mentioned earlier, this process involves the use of a valve to produce repeated shock waves. It is assumed in this section, for the sake of simplification, that there is no gas heater after the creation of the shock wave, no powder already traveling in the barrel and that the carrier gas for the powder does not affect the shock wave. At the initial state illustrated in Figure 2.11, the powder is at rest

near the valve. Zones 1 and 4 can be filled with different gasses at different temperatures. Since the end of zone 1 is opened to the environment, this zone is at atmospheric pressure. Based on the results presented in the last section, zone 4 requires to be at a higher pressure than zone 1 to create a shock wave.

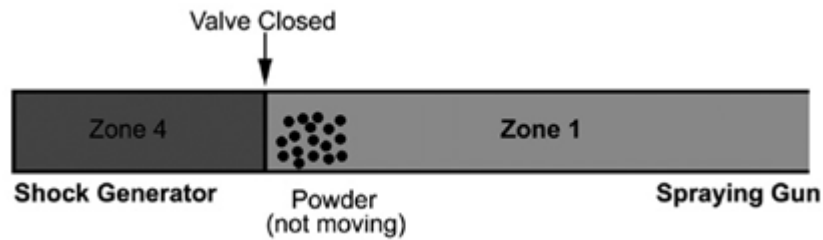


Figure 2.11 : Schematic of the PGDS process at initial state. [21]

The valve gate is opened for a very short period of time, thus resulting in a coalescent normal shock wave moving toward the exit. Using Eq. 2.16, it is possible to compute the velocity of the shock wave traveling along the barrel. During its travel in the zone, the pressure and the temperature behind the shock (zone 2 in Figure 2.12) are increased. Zone 2 represents the accelerating flow zone in the barrel. The powder is also accelerated and heated up but remains under its melting point in this zone; which reduces the critical velocity [49,50]. Zone 3 represents the flow from the valve gas traveling at a lower temperature since no shock wave goes through it. This zone has multiple expansion waves smoothly decreasing the pressure.

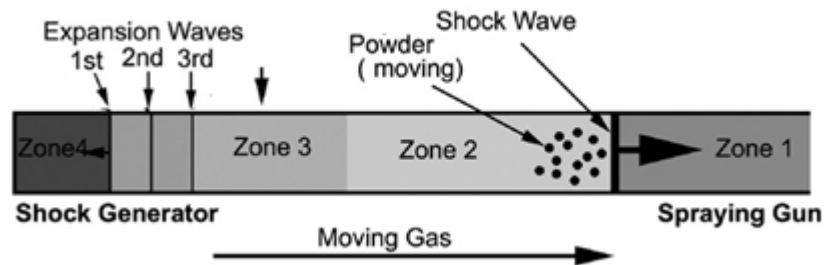


Figure 2.12 : Schematic of the PGDS process after a valve opening [21]

A new cycle in the process is started when the gas in the tube returns to ambient pressure and the powder is injected.

2.4.4 PGDS Advantages

As LPCS, PGDS is a solid-state process where the bulk properties of the particles are still the same after impact. It provides the same advantage of being able to spray heat and oxygen sensitive materials. Although few studies have been published on the PGDS process, it has been shown to successfully produce dense aluminum and copper coatings [21]. The deposition of aluminum alloys mixed with SiC [51] and other harder powders such as stainless steel [47], WC-Co [48,52] and WC-10Co4Cr [48] and amorphous iron coatings [21] is also possible using the PGDS process.

It also shares the same safety features mentioned in section 2.3.4 for LPCS. A specific advantage of this process compared to LPCS is the use of pulsed gas, which decreases gas consumption.

2.4.5 PGDS Limitations

The PGDS process requires to have the powder inserted perpendicular to the gas stream. When the amount of gas carrying the powder is too high, there could be formation of a coating on the opposite wall in the barrel. When this happens, the deposition rate and the coating quality decrease since the paths of the shock waves accelerating the powder are obstructed.

There is also the need to use a ductile matrix to spray brittle materials.

2.5 Critical Particle Velocity

It was observed that a transition point, where a particle impacting the substrate could either create a coating or not, is present. The outcome was related to the particle velocity. In addition, a major change in the deposition efficiency on the substrate is noticeable at this transition velocity; also known as critical particle velocity [17,32]. Deposition efficiency, or DE, is the ratio of the mass of the coating on the substrate divided by the fed powder mass. The occurrence of a second transition velocity where there is a drop of DE and the powder erodes the substrate instead of building a coating was observed at a higher velocity in other studies [17,32]. This transition was named erosion velocity. The next figure presents the DE results as a function of particle velocity along with pictures showing the coating evolution on the substrate at certain velocities for copper deposition.

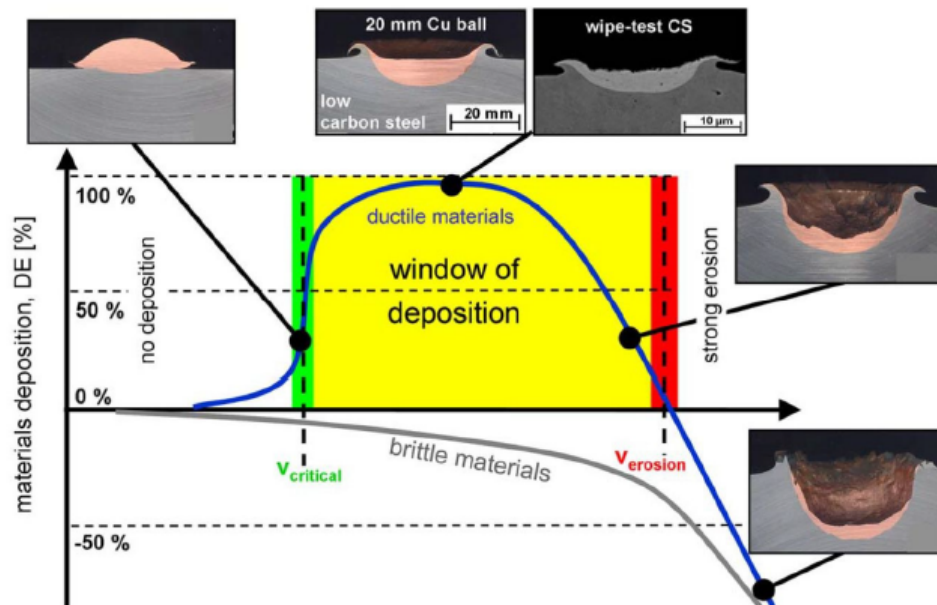


Figure 2.13 : Deposition efficiency of copper as a function of the particle velocity and coating cross-section pictures [17]

Figure 2.13 shows the critical velocity represented by the transition or turning point where DE starts increasing at a high rate. From that point on, the DE rises until some particle starts eroding the coating leading to the decrease of DE down to a transition point labelled erosion velocity in the figure. The velocity being affected by the material nature [17,53], particle size [32,54], temperature at impact [49,50], substrate material [55,56] and powder oxide content [57], all these properties also control the critical and eroding velocities. Typical experimental values of critical velocity for 20 μ m particle observed with different materials are summarized in Table 2.5.

Table 2.5 : Critical velocity for different powder nature for 20 μ m powder (Adapted from [17,53])

Powder nature	Critical velocity (m/s)
Pure Titanium	700-890
Aluminum	620-660
Tin	160-180
Zinc	360-380
Stainless steel (316L)	700-750
Copper	460-500
Nickel	610-680
Tantalum	490-650
CoNiCrAlY	850-900

The ranges of critical velocity for each material depend on the difference in crystallographic structures, alloy composition, melting temperature and mechanical strength [53]. In addition, properties affecting the deformation of the particle also have an effect on critical velocity. The results presented in Table 2.5 show that pure Titanium powder has a high critical velocity than the other materials listed which can mainly be explained by its protective passive layer and its higher hardness. Since Ti-6Al-4V has a higher hardness than pure Titanium, this Titanium alloy critical velocity is higher.

To understand the effect of particle size on the critical velocity for HPCS, Stoltenhoff et al. [50] modeled variations of particle sizes in function of the particle velocity and temperature. This model shows that smaller particles tend to have a higher velocity due to their lower inertia. However, the particle temperature is low because of the cooling phenomena in the nozzle diverging section. Medium size particles tend to remain at a higher temperature due to their higher thermal capacity but their higher inertia decrease their velocity. If the particle diameter is further increased, the heating section is not long enough to heat and accelerate the particle. This has the consequences of decreasing the temperature and velocity of the particle.

As mentioned earlier, the powder temperature at impact influences the critical velocity of the particles. This influence was proven in a model developed by Schmidt et al. [32]. It is possible to monitor the powder temperature before its insertion in the diverging section which is an advantage of the LPCS technique. PGDS process does not require a cooling diverging section to accelerate the flow and a powder heater can be used. The combination of these two characteristics leads to a decrease in the critical velocity since the particles remain hot and with high velocity.

Oxide layer can increase the critical velocity due to the need to break the oxide film and then to deform the particle. This oxide layer is the reason why aluminum presents a high critical velocity

[54]. Another study has concluded the same facts for stainless steel and Monel particles [58]. A study was also performed with copper and showed an increase of critical velocity from 310 m/s to 610 m/s when the oxide content was increased from 0.02% to 0.32% by weight [58].

The substrate material was shown to have influence on the critical velocity. Harder substrate material can affect the deformation mechanism, as confirmed by both numerical study [59] and experimentation [56]. However, the effect from the substrate influences only the first layer of particle since the second layer impacts the first layer composed of sprayed particle and is therefore not governed by the nature of the substrate [60].

Another parameter influencing the critical velocity is the spraying angle or impact angle. This angle is the angle between the nozzle or barrel and the substrate. As shown in Figure 2.14 the DE decreases as a function of the impact angle. This can be explained by the fact that, as the impact angle increases, the particles tend to rebound or ricochet; a well-known effect in impact engineering.

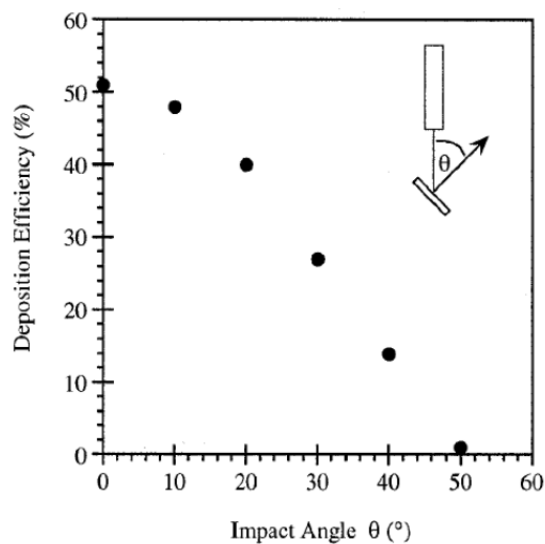


Figure 2.14 : The deposition efficiency in function of the impact angle [from [61]]

2.6 Particles Deformation

Particles' deformation is calculated by computing the average of the flattening ratio of the individual particles in the coating. This ratio has been calculated with multiple methods in the literature. In one of her articles, Goldbaum calculated the ratio of the width over the height of singular splats as seen in Figure 2.15 [62]. This presents the advantage of calculating the deformation after impact, but it does not include the deformation from subsequent layers.

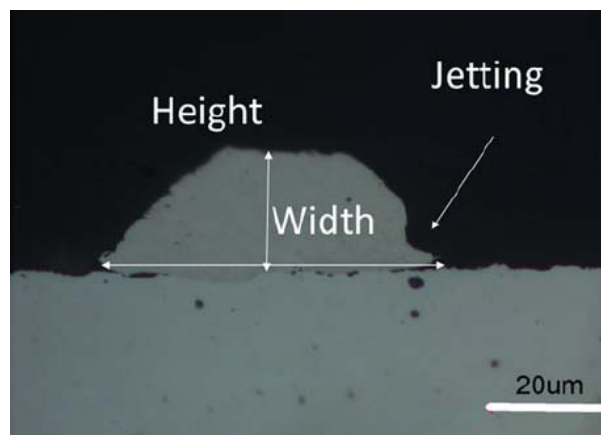


Figure 2.15 : Splat cross-section obtained by optical microscope used to calculate the flattening ratio[from [62]]

Another technique used by Moy defines the flattening ratio as the splat main length (L_f) over the initial mean diameter of the feedstock powder (D_i) [63]. This technique is good for feedstock powder with a small standard deviation and a schematic of the particle deformation is shown in Figure 2.16.

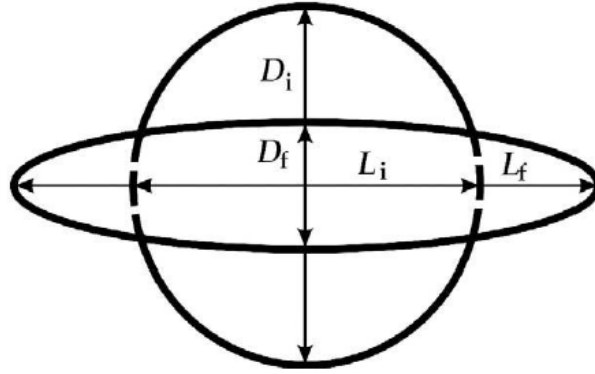


Figure 2.16 : Particle schematic before and after impact [from [63]]

Champagne used the ratio of the splat main length over the initial diameter. To calculate the initial splat diameter, the following equation was developed:

$$d_0^3 = d_a^2 d_b \quad (\text{Eq. 2.18})$$

Where d_0 is the initial diameter, d_a is the splat main length and d_b the splat main height [64]. This ratio takes into account of the various particle diameters hitting the substrate. A schematic representation of the main dimensions used in this equation can be seen in Figure 2.17.

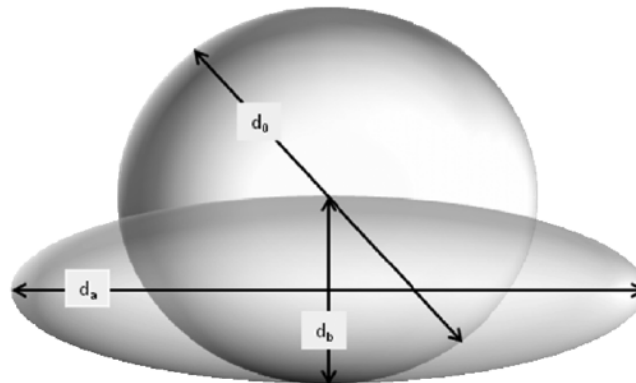


Figure 2.17 : Particle schematic before and after impact [from [64]]

2.7 Bonding Mechanism

As demonstrated in section 2.5, critical velocity affects the deposition of the coating. The vast majority of the researchers agree that this is explained by plastic deformation of the particle and the substrate due to the transfer of kinetic energy to heat during the impact [36,54,59,65–71].

The first type of bonding mechanism reported was plastic deformation. During the deformation, the surface layer around the particle, such as oxides, breaks-up thus allowing bonding due to high pressure [72]. During the impact, a ring of excess material around the zone of impact, also called jetting, is created. The picture at the top of Figure 2.18 shows the jetting ring created experimentally by a copper particle impacting stainless substrate. The bottom picture of the figure presents the sectioned view of the numerical simulation of that impact.

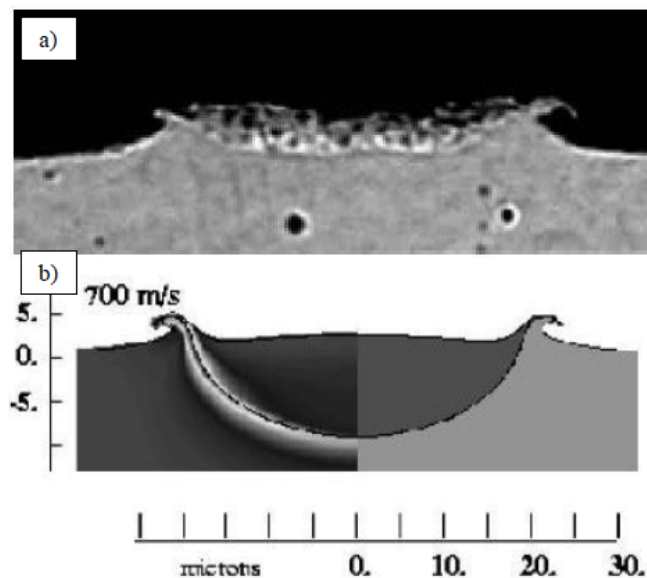


Figure 2.18 : Cross-section of a deformed copper splat with jetting formation after an impact on stainless at 700 m/s a) experimentally and b) numerically (adapted from [36])

Another type of possible bonding mechanism is adiabatic shear instability as presented by Wright [73]. This mechanism was also described by Assadi et al. [65] and Grujicic et al. [67] as an adiabatic increase of material temperature at the impact interface. The temperature is high enough to change solid into a viscous effect. In order to obtain this type of bonding, the transition from high velocity into heat must be adiabatic. This assumption is realistic because the point of impact is very small and occurs in a short duration thus making heat dissipation negligible. Copper particles were numerically simulated by Assadi et al. [65] for different velocities leading to the conclusion that adiabatic shear deformation occurs at high velocity. The main results from that study are summarized in Figure 2.19.

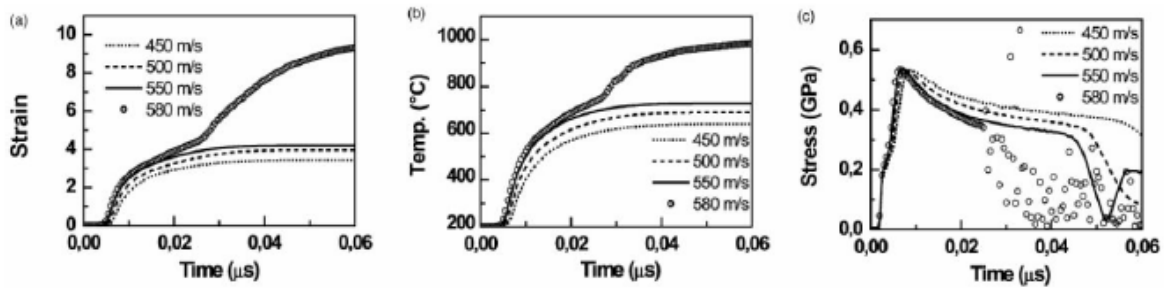


Figure 2.19 : Evolution of the a) strain, b) temperature and c) stress at the impact region in function of the time for a copper particle and various velocities [65]

As it can be observed in Figure 2.19, an increase of 30 m/s from 550 m/s to 580 m/s produces radical changes in the three properties of interest. During this increase, the strain and the temperature increase while the stress decreases. Additionally, the velocity 580 m/s for copper particles is close to the experimental value of the critical velocity for that material thus indicating a relationship between the adiabatic shear mechanism and the critical velocity.

Adiabatic softening is the proposed mechanism for the formation of interfacial jets cleaning the surface at the particle-substrate and at particle-particle interfaces. Intimate contact between these surfaces promotes metallurgical bonding. Experimental evidence of metallurgical bonding and of adiabatic shear bands can be observed experimentally, as presented in Figure 2.20 and Figure 2.21 [57,74], respectively. Metallurgical bonding is represented by material continuity along the interfaces while adiabatic shear bands are denoted by characteristic thin regions around the particle boundaries.

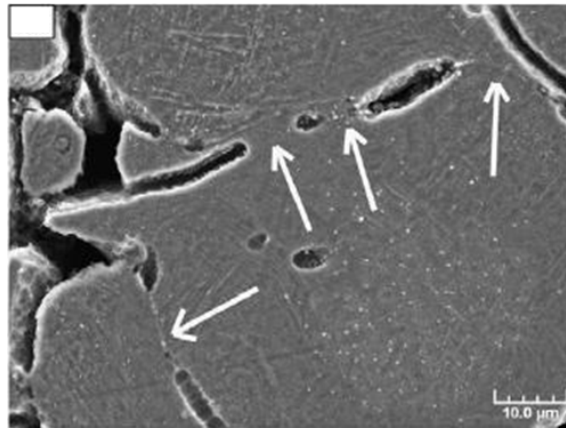


Figure 2.20 : Metallurgical bonding indicated by arrows between Ti-6Al-4V particles
(from [57])

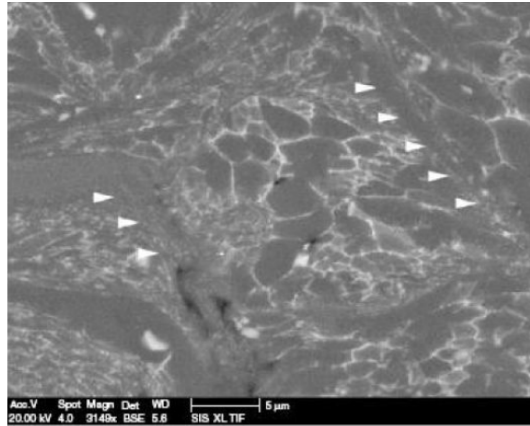
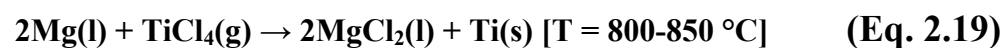


Figure 2.21 : Shear band formation (indicated by the arrows) in Al-alloy coating (from [74])

2.8 Sources of Titanium Powder

Titanium has an atomic number 22 in the periodic table. This element cannot be found in nature as pure metal, but it is typically found in the earth crust as either of the two forms of Titanium oxide, i.e. rutile (TiO_2) and ilmenite ($\text{FeO} \cdot \text{TiO}_2$). Transformation of Titanium oxide to metallic Titanium is achieved by the Kroll process. In a first step, the oxide ore is converted into titanium chloride (TiCl_4) by running chlorine gas over rutile or ilmenite at high temperature. In a second step, the Titanium is condensed and purified during a reduction process of titanium chloride using molten magnesium in an inert gas at a temperature around 800°C . The chemistry of this reduction reaction is presented in Eq. 2.19.



Solid Titanium obtained after purification is porous and looks like a sponge. It is then pressed and melted in an inert gas furnace to obtain ingots. The high cost of this product comes from the requirement for magnesium in the reduction reaction, and the fact that all the processes are performed in an inert gas, which is not needed for other materials such as steel.

Iron, aluminum, vanadium and molybdenum are currently used to produce different alloys with Titanium. These element inclusions help the stabilization of the Titanium phases. In this study, we used the Ti-6Al-4V alloy a biphasic($\alpha+\beta$) alloy where aluminum is inserted for the stabilization of the alpha phase and vanadium for beta phase [75]. This dual phase combines the stronger alpha phase with higher ductility of beta phase. With this association, Ti-6Al-4V is a good compromise between ductility and hardness, suitable for various applications in the biomedical, aerospace and industrial fields [8]. In addition, this alloy is corrosion-resistant, strong and has a low-density.

2.9 Ti-6Al-4V Manufacturing Process

Cold spray processes use powder of various nature and morphologies. Powder manufacturers transform bulk pieces of material into particles. Powder size distribution, oxide content and morphology are known to affect critical velocity [54,57,58,76]. Powder manufacturing process and modification will be discussed in the following sections.

2.9.1 Gas or Water Powder Atomization

This process starts by heating metal by induction or arc furnace until it is melted. The molten metal is accelerated and spread as droplet using different media such as air, water or inert gas. The choice

of media influences the final powder morphology. A schematic of this process is presented in Figure 2.22.

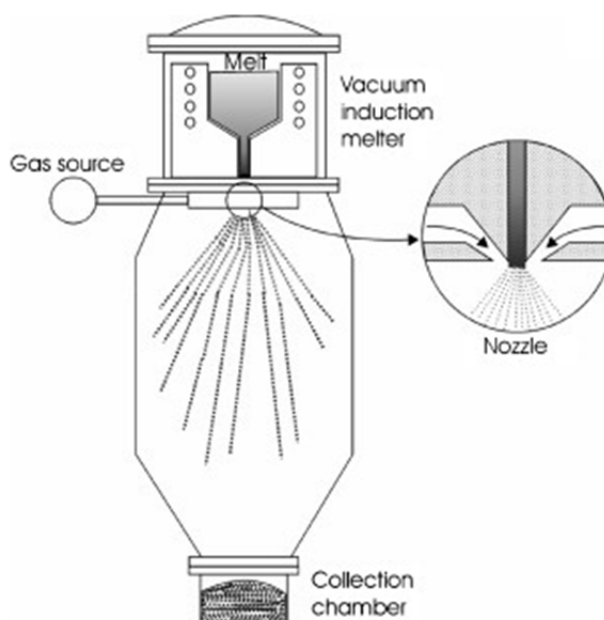


Figure 2.22 : Schematic of a gas atomization system [77]

Gas atomization yields spherical particles while those obtained with water atomization present irregular shapes. Oxide sensitive materials are produced in an inert gas environment. The major drawback of the use of inert gas is the elevated manufacturing cost [78]. CoNiCrAlY powder produced by inert gas atomization is shown Figure 2.23. Figure 2.24 shows a water atomized Barium Fluoride-Calcium Fluoride powder.

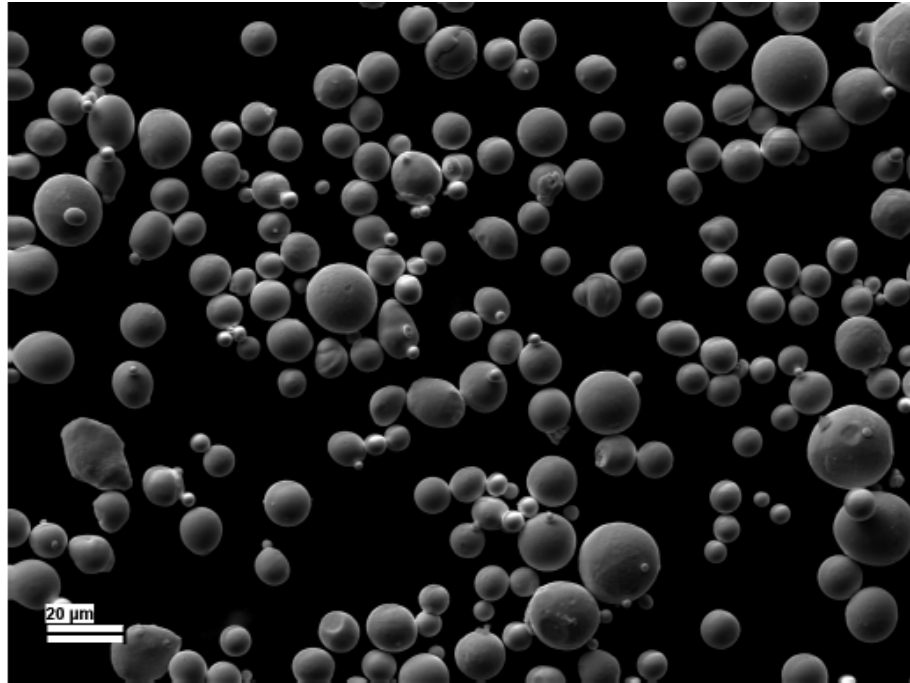


Figure 2.23 : Inert gas atomized of CoNiCrAlY powder

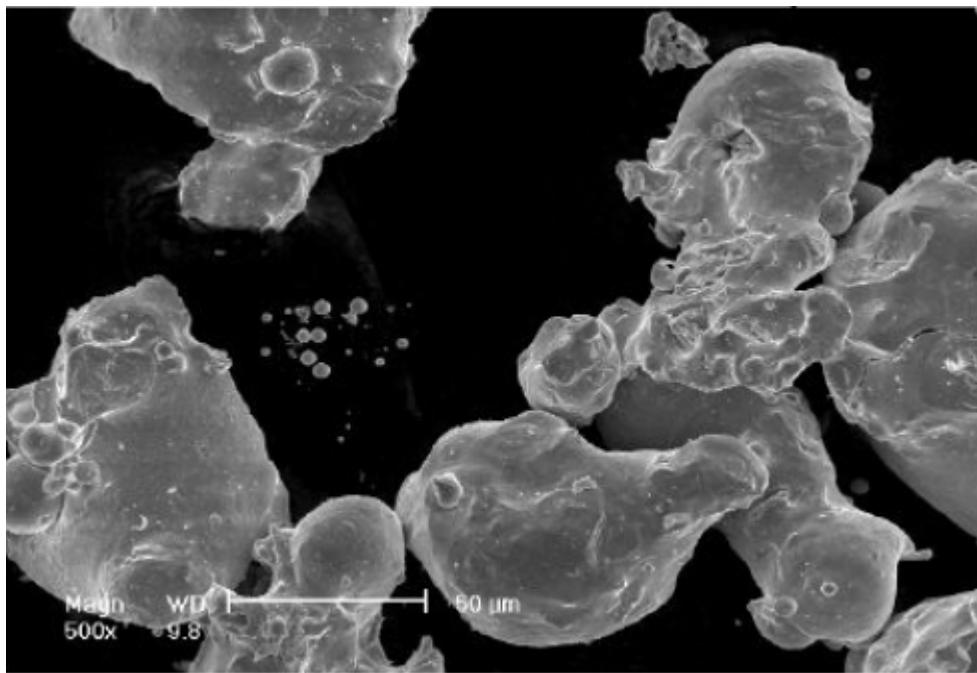


Figure 2.24 : Water gas atomized Barium Fluoride-Calcium Fluoride powder

2.9.2 Plasma Atomized Powder

This technique is similar to gas or water atomization powder manufacturing process. As shown in Figure 2.25, instead of molten material spread into droplets by gas or water, the material is molten and spread using a plasma torch. This process can be done in an inert gas chamber to manufacture oxide sensitive material. As gas atomized technique, plasma atomized process produces spherical morphology powder. An example of the results obtained with this process is shown in Figure 2.26.

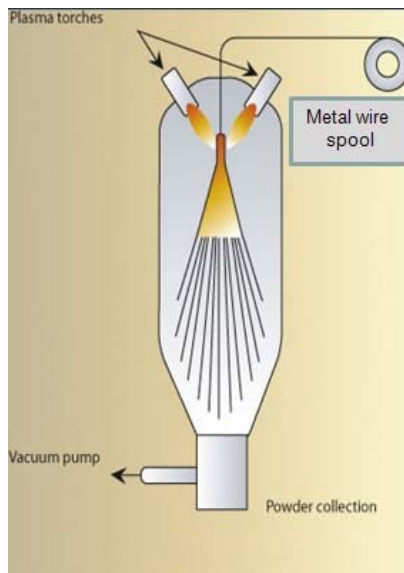


Figure 2.25 : Schematic of a plasma atomized system (from [79])

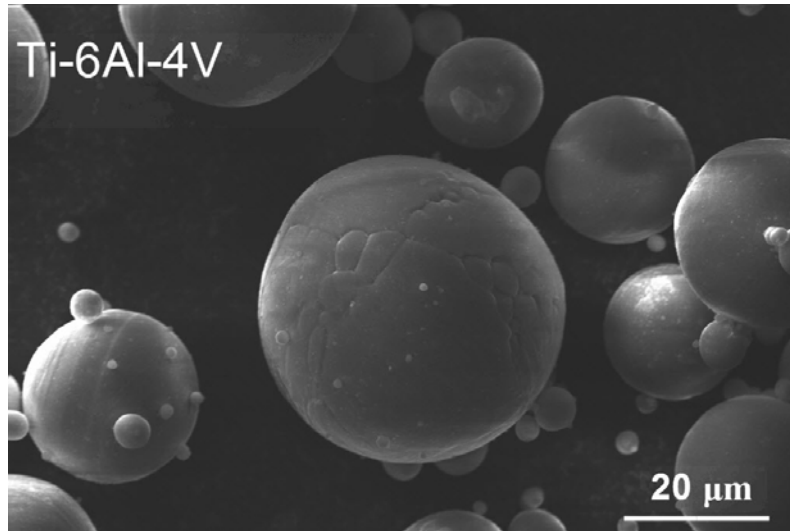


Figure 2.26 : Inert plasma atomized Ti-6Al-4V powder

2.9.3 Hydride-dehydride Powder

Hydride-dehydride (HDH) can only be used with transition metal such as Titanium, vanadium and tantalum. The reason is that transition metal can absorb low amount of hydrogen to become brittle [80]. This manufacturing process uses scrap parts, billets or machined turning as feedstock. They are heated in a hydrogen environment to produce the hydride form of the material which is brittle. The hydride material is then transferred in a vibrated ball mill to reduce the size of the particle from the milling. After some time, an inert gas is incorporated in the milling chamber to dehydride the particles and obtain the required material composition. As a final result, the particles' present irregular shapes and a rough surface morphology as seen in Figure 2.27. Since this process uses recycled by-products from other manufacturing, its cost is low compared to the other processes.

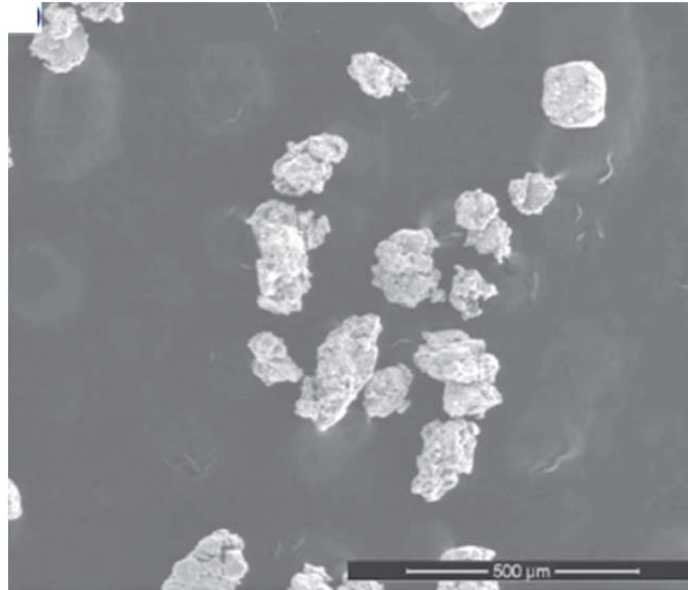


Figure 2.27 : HDH manufactured of Titanium grade 2 powder

The irregular shape of the powder produces a higher drag coefficient which is considered beneficial for the powder velocity. Drag coefficient is affected by particle orientation in the gas stream. Since the drag coefficient can vary, the particles might travel at different velocity [81].

2.10 Characteristics of Titanium Alloy Coatings

Ti-6Al-4V coatings characteristics obtained by other researchers will be discussed in this section. All the coatings mentioned in this section were produced with HPCS process using either helium or air as driving gas. Microstructure, hardness, bond-strength, deformation and, metallurgical bonding obtained will be reviewed.

2.10.1 Ti-6Al-4V Powder Sprayed on Pure Titanium Substrate

Blose [82] conducted experimental research covering spraying of Ti-6Al-4V powders manufactured with different techniques on a commercially pure Titanium (CP Ti) substrate. The different types of powders used in his studies and the properties of the coatings that he obtained are presented in Table 2.6.

Table 2.6 : Titanium powder manufacturing techniques and characteristics (from [82])

Powder Material	Manufacturing Technique	Powder Morphology	Particles Mean size (μm)	Powder Hardness (VHN)	Coating Porosity (%)	Coating Hardness (HVN)
Ti-6Al-4V	Gas Atomized	Spherical	29	291	18	215
Ti-6Al-4V	Plasma Atomized	Spherical	27	280	18	272
Ti-6Al-4V	Hybride-DeHydride	Irregular shape	30.7	351	4	258

Blose used a HPCS system at 350 psi and a gas temperature of 550°C to conduct the spraying work in his research. He explains the lower porosity for the irregular shaped powder material by their capability to better fill inter-particle voids. Since there were no deformations of the spherical powder, voids could not be filled. His analysis of the lower coating hardness compared to the feedstock indicates that it is the result of the coating high porosity.

2.10.2 Ti-6Al-4V Powder Sprayed on Ti-6Al-4V Substrate

Blose [83] presents another study where he incorporated a powder heater in his HPCS systems and spraying on Ti-6Al-4V substrate with helium as the driving gas . Using the plasma atomized powder mentioned in Table 2.6 with different powder temperatures; he observed that the porosity decreases as a function of the powder temperature increase, as shown in Table 2.7.

Table 2.7 : Coating characteristics as a function of the process parameters (from [83])

Powder temperature (°C)	Gas Pressure (MPa)	Gas Temperature (°C)	Powder Gas Pressure (MPa)	Coating Porosity (%)
300	3.1	500	3.8	8.8
400	3.1	500	3.8	5.2
500	3.1	500	3.8	4.6
700	3.1	500	3.8	1.5

A major conclusion from his research work is the important reduction effect on the porosity level in the resulting coating provided from the use of a powder heater in the spray system.

Li [84] used a HPCS system with air to spray spherical Ti-6Al-4V powder on Ti-6Al-4V substrate to conduct his research work. He used the following parameters with the system: a gas pressure of 2.8 MPa and gas temperature of 520°C. The feedstock that he used was spherical with an average

diameter of 47 μ m. The results of the properties of the coatings that he obtained are presented in Table 2.8.

Table 2.8 : Coating characteristics (from [84])

Powder	Powder oxide content (wt%)	Porosity (%)	Coating oxide content (% by weight)	Adhesion strength (MPa)
Ti-6Al-4V	0.42	22.3 $\pm$ 4.7	0.57	< 15

Li has been able to obtain Titanium alloy coating with air as the carrier gas. However, this choice of gas was detrimental to the final results as indicated by the elevated oxide content in the coating produced, as indicated in Table 2.8. It is interesting to note that even with above 20% of porosity (Figure 2.28a), a formation of metallurgical bonding between particles was obtained; as seen in Figure 2.28b. Adhesion tests gave a value of adhesion of less than 15 MPa but microscopic study of the fracture surface provides clear indications of the formation of metallurgical bonding in the coating (Figure 2.28c).

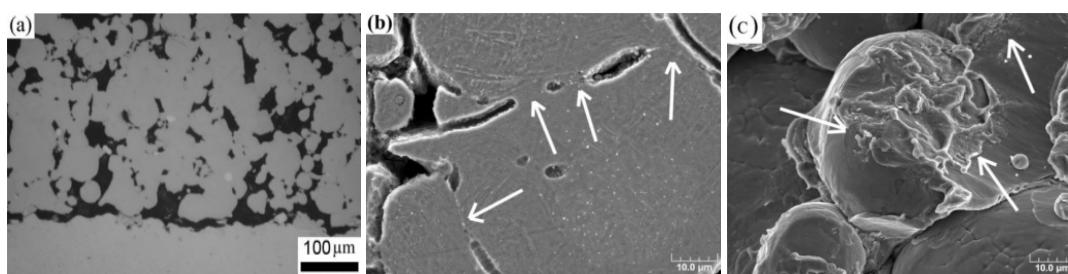


Figure 2.28 : Microstructure of the coating a) using optic microscope b) scanning electron microscope in the etched state c) fracture surface (from [84])

Chapter 3 – Description of the Research Objectives

The objective of this work is to develop a technique to repair Titanium parts since there is currently no repair technique commercially available. It is envisioned that commercial cold spray systems could be used to repair gashes in Titanium components. The specific objective of this work is this to perform experimental studies of the spray parameters for the production of Ti-6Al-4V repairs/coatings on Ti-6Al-4V substrates to understand their effects on the properties of the resulting coatings. An additional objective is related to attempts to verify the ability to obtain oxide and nitride free coatings with the methods and parameters values studied. Studies of properties, such as adhesion, microstructure and oxidation characteristic, will be used to evaluate the coatings obtained in an effort to obtain indications of the best values for the parameters in the range studied.

To achieve these goals, three phases were defined. The first one is the evaluation of the feasibility of the method to create a coating on the substrate. The following one involves the optimization of the spray parameters to maximise the coatings properties. Finally, qualification tests are performed to verify coating properties using the best parameter values obtained in the previous part.

3.1 Feasibility of Producing Ti-6Al-4V Alloy Coatings

Experiments described throughout this section were performed with two commercial cold spray systems. Both the LPCS and PGDS process systems were used to investigate the possibility to create a coating. Evaluation of the coating is performed using two properties: adherence and porosity.

3.2 Experimental Study of Parameters

The second part of the research deals with experimental study of the parameters for each system in an effort to understand their influence on the final properties and select the values providing the best results. The experimental plan used can be described as a screening Design of Experiment (DOE) aimed at studying only the individual effects of each parameters, therefore one parameter is changed at a time while the others are fixed. The general objective of this phase is to obtain the highest values of the result variable, in this case the density of the coating.

The parameters studied for LPCS process were: nozzle inlet pressure, nozzle inlet temperature, powder inlet temperature, substrate traverse speed, powder feed rate, substrate displacement pattern.

Along with the parameters mentioned above, additional ones were studied for the PGDS process because of the possibility to modify the barrel length, valve frequency and the valve opening time. Investigation of surface preparation, powder size and morphology were also considered with this system. At the end of this section, the values for each parameter providing better coating properties are presented. As indicated above, they were the basis for the remaining of the work performed in this research.

3.3 Qualification of Parameters

Qualification testing represents the last part of the research work. Each of the tests planned to be performed is a general thermal spray qualification test. This chapter includes investigation of the coating properties such as particle deformation, bonding, oxide and microstructure (porosity and micro-hardness). In this phase the manufacture of a coating on a damage substrate was also produced. Figure 3.1 and Figure 3.2 show a general overview of the planning of all the phases of this research

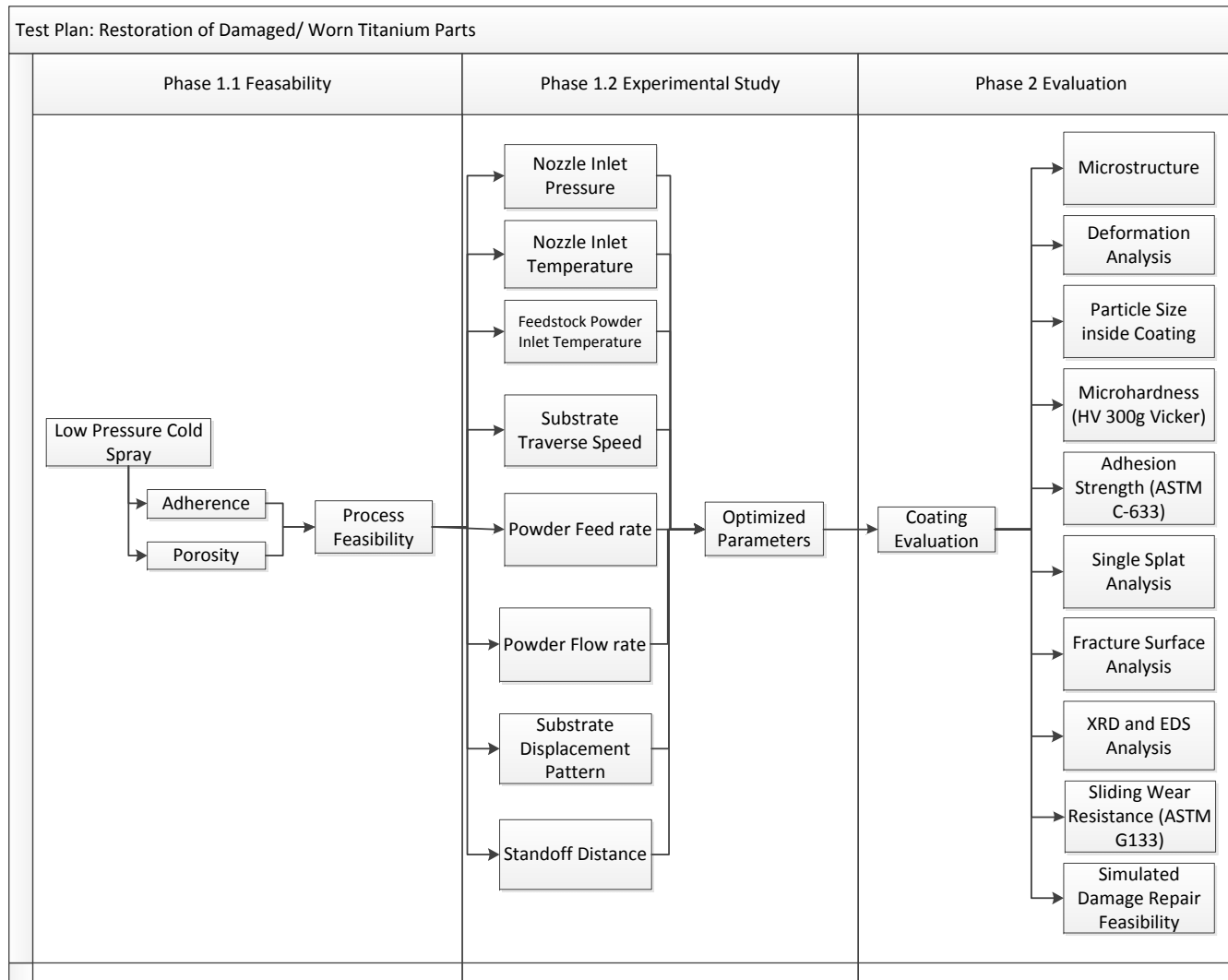


Figure 3.1 General Test Plan of LPCS research.

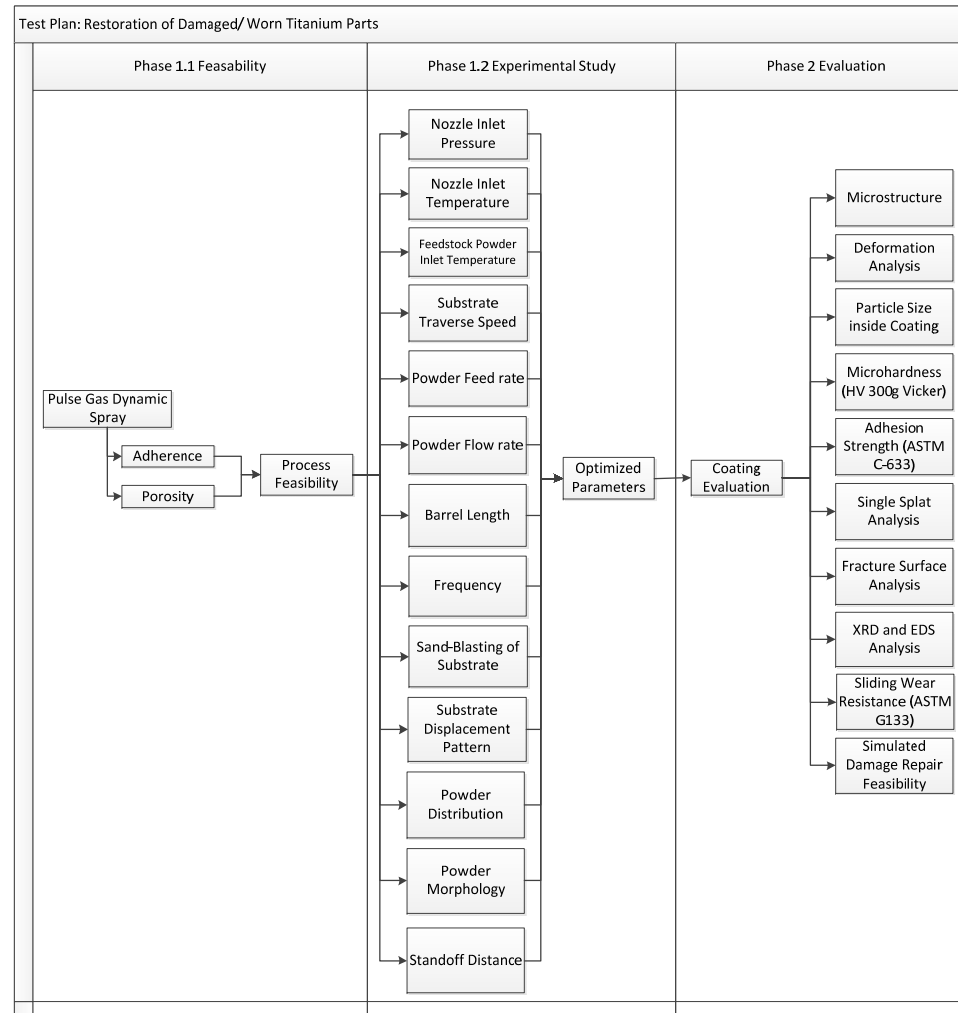


Figure 3.2 General Test Plan of PGDS research.

Chapter 4 –Equipment, Measurement Methods and Procedures

4.1 Introduction

This chapter outlines all the equipment used to spray with LPCS system. This is followed by the same type of information for the PGDS system. An overview of the coating preparation and evaluation equipment is then discussed in details. Finally feedstock as well as material storage and processing are presented.

4.2 Low Pressure Cold Spray (LPCS)

Low pressure cold spray technique encompasses six major components: driving gas, spraying chamber, LPCS nozzle, powder feeder, powder heater and gas heater. They will be further explained in this section. The spraying chamber, powder heater and gas heater have been built in-house for previous research studies.

4.2.1 Driving and Carrier Gas Supplies

The first component plays a major role for LPCS system because the driving gas accelerates the particle and carries the powder to the nozzle. In LPCS system, the driving gas is the flow accelerated by the nozzle and accelerating the particles until impact. Carrier gas passes into the powder feeder

and push the powder toward the nozzle. The nature of the gas used in this process has a major incident on the velocity obtained in nozzle. As mentioned in Chapter 2, Ti-6Al-4V having a high critical velocity dictates the requirement for a gas with high speed of sound. In addition, since titanium alloy can react with air to form nitrides and oxides, an inert gas should be used as the driving gas to prevent the formation of these phases. The combination of the requirement for a high speed of sound and inert gas led to the selection of helium for the purpose of this research. Six bottles of industrial helium (shown in Figure 4.1a) are used in the experimental setup to perform spraying and ensure a constant driving gas stagnation pressure.

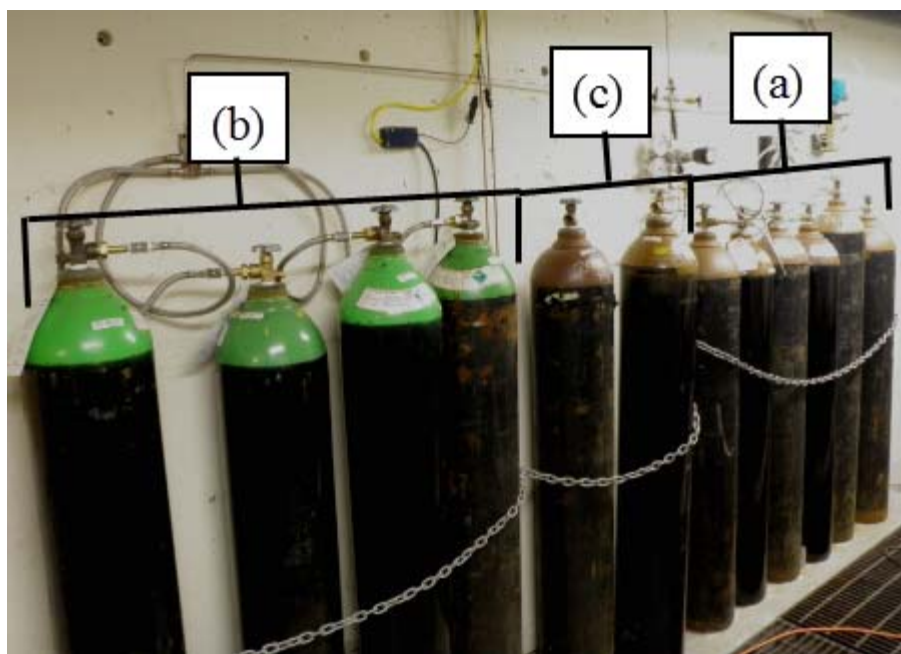


Figure 4.1 : View of the bottle arrangement a) driving helium bottles, b) driving nitrogen bottles and c) carrier helium bottle

Four bottles of nitrogen (shown in Figure 4.1b) are used to pre-heat the system since nitrogen is relatively inexpensive compared to helium. When the system reaches the desired temperature, nitrogen gas is switched to helium through a three-way valve.

One bottle of helium (Figure 4.1c) is also used as the carrier gas. This bottle is equipped with a pressure regulator (55850-277 model, VWR International) decreasing the pressure exiting from the bottle (Figure 4.2a) to the intermediate pressure required to produce the required carrier gas flow rate (7520 model, King instrument company). A flow meter, as shown in Figure 4.2b, is connected to the pressure regulator to ensure a constant flow; no matter the pressure in the nozzle.

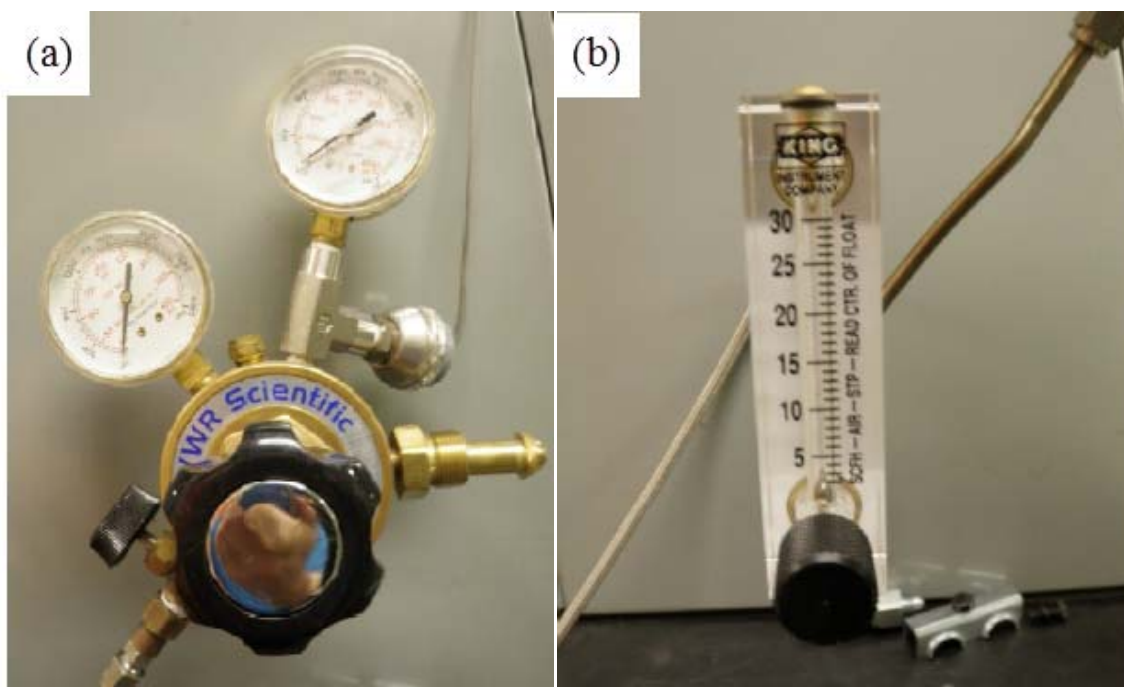


Figure 4.2 : View of a) pressure regulator, b) flow meter used in LPCS system

4.2.2 Spraying Chamber

The purpose of the spraying chamber is to contain the powder that was not successfully sprayed in a closed environment. It consists of an aluminum frame fitted with transparent acrylic windows, as shown in Figure 4.3. This chamber is equipped with a ventilation system using a 1.5HP fan and a filter with 0.4 μ m openings. This filtering system collects powder, which did not bond to the substrate via a metallic dust collector (Figure 4.3a). Inside the chamber, a two axis table consisting of two perpendicular lead screw tracks move a sample holder (Figure 4.3b) in the X and Y directions (Model A1 from Velmex, Bloomfield, NY). This system is activated by an electronic stepper motor linked to the COSMOS software interface. This program reads a text file which can be coded for multi-passes and overpass's displacement. The substrate is fixed to the sample holder with screws on each side. To adjust the nozzle standoff distance, a micrometer is fixed on a vertical linear stage (Figure 4.3c). The nozzle is maintained on the nozzle holder (Figure 4.3d) by two screws.

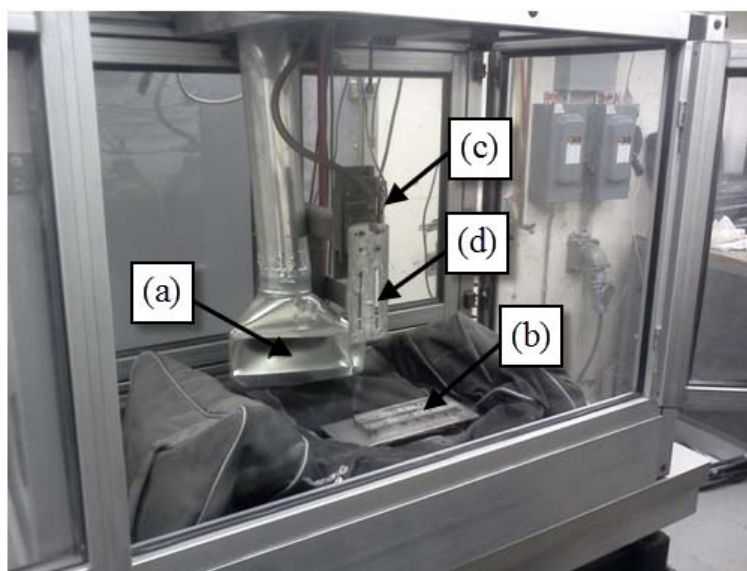


Figure 4.3 : Component of the spraying chamber a) metallic dust collector, b) X-Y axis table, c) micrometer, and d) nozzle holder

In this system, the driving gas pressure and temperature are recorded from different locations along the main gas line. All these sensors transmit a signal transferred to a Labview software interface shown in Figure 4.4. Using the recorded data, calculations are performed and the important results such as the pressure in the bottle, pressure just before the nozzle and temperature after the gas heater are then written in a Microsoft Excel™ spreadsheet at a rate of 10 samples per second.



Figure 4.4 : Screenshot of Labview interface computing pressure and temperature parameters

4.2.3 LPCS Nozzle

The LPCS nozzle is one of the most important parts of this spraying system. It is used to increase the velocity of the feedstock powder flow above the critical velocity. The nozzle used during this project was produced by Centerline Ltd. Supersonic Spray Division (Windsor, Canada). This nozzle is a four part assembly. The nozzle orifice (converging-diverging) is made of brass. The nozzle throat diameter is 2mm with an exit diameter of 6.5mm and an area ratio of 10. The propellant gas is injected into the inlet of the converging part. Powder is injected after the throat with a 45° powder injection tubing. A metal o-ring is used outside the nozzle to prevent leakage. A nut is used to tighten the orifice to the nozzle. A 12 mm long and smooth diverging hydroformed metallic nozzle is located at the front end of the orifice part. All these parts are shown in Figure 4.5.

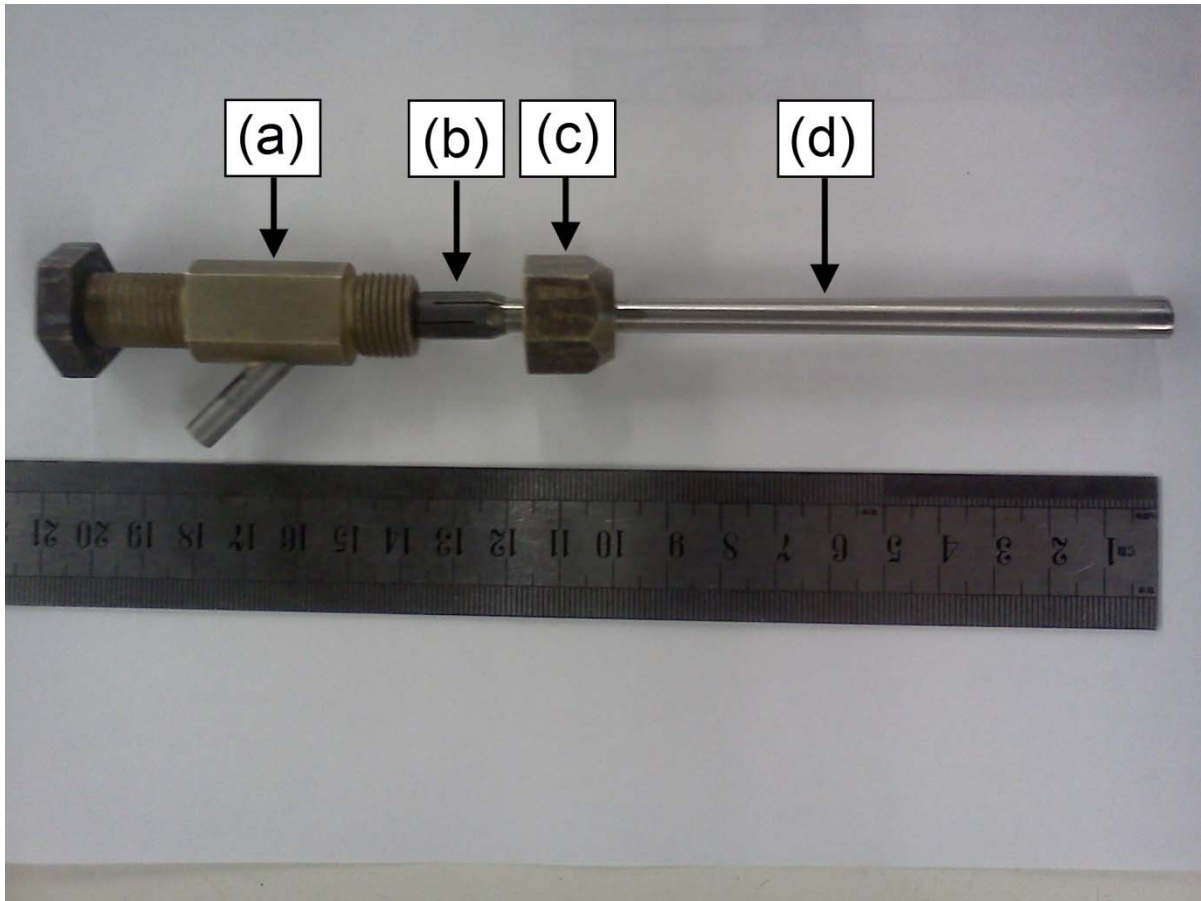


Figure 4.5 : Photograph showing a) the orifice, b) the metal o-ring, c) the nut and d) the nozzle

4.2.4 Powder Feeder

The commercial powder feeder (Praxair, model 1264) shown in Figure 4.6 is used to inject the feedstock powder in the powder line. The powder feeder is made of a cylindrical canister that holds the powder.

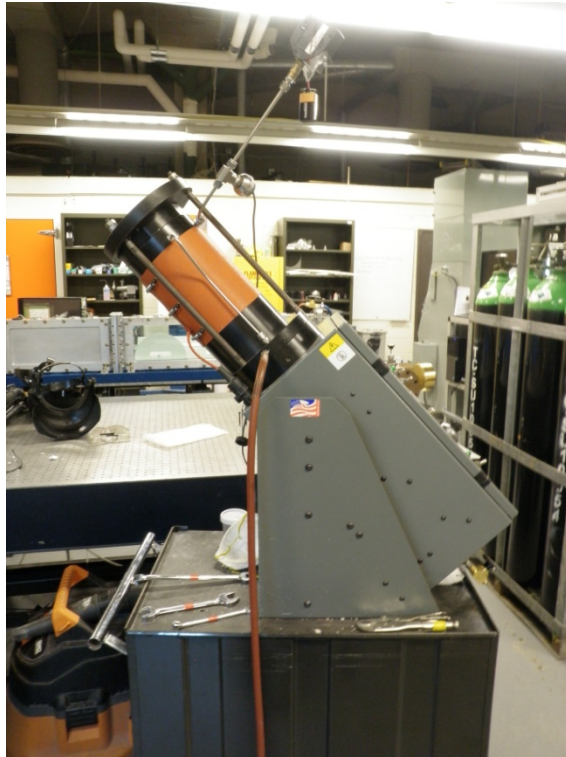


Figure 4.6 : General view of the powder feeder

A rotary wheel with small holes all around the edge rotates at the bottom of the canister (Figure 4.7a). Each hole takes a small amount of powder from the bottom of the canister. This powder is brought about an opening which leads it to the feeding tube. Inside the canister, there is also a hammer that taps the wheel and dislodges the powder to prevent clogging (Figure 4.7b). Changing the wheel rotational speed increases or decreases the amount of powder supplied by unit of time. A carrier gas flow is used to create a higher pressure in the canister to force the powder towards the nozzle.

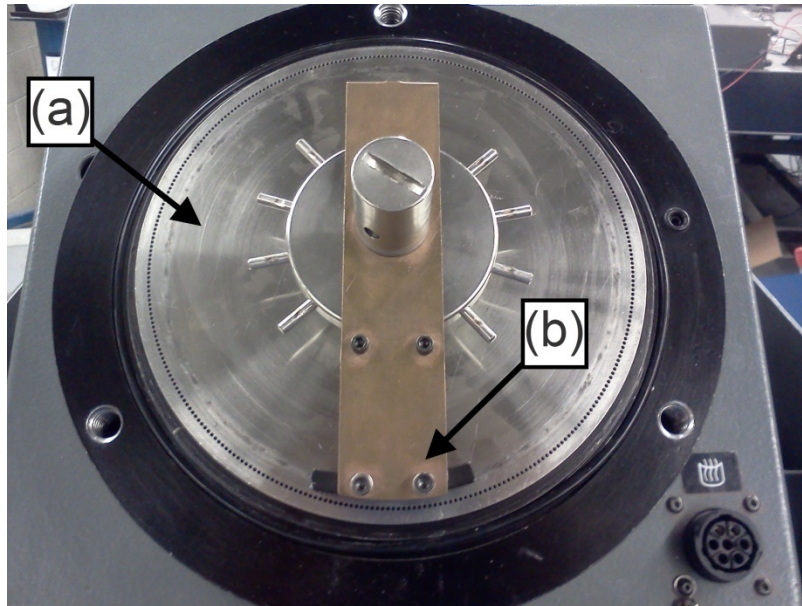


Figure 4.7 : Inside view of a) rotary wheel with small holes, and b) hammer preventing clogging

4.2.5 Powder Heater

A powder heater is used to increase the powder temperature in order to increase its ductility. This equipment is located between the powder feeder and the nozzle. It is designed from a two meters quarter inch metal tubing coil covered with a plasma coating of alumina on its surface (see Figure 4.8). A type K thermocouple is fitted on a small section of the tubing without coating located in the middle of the coil and connected to a Type K temperature controller.

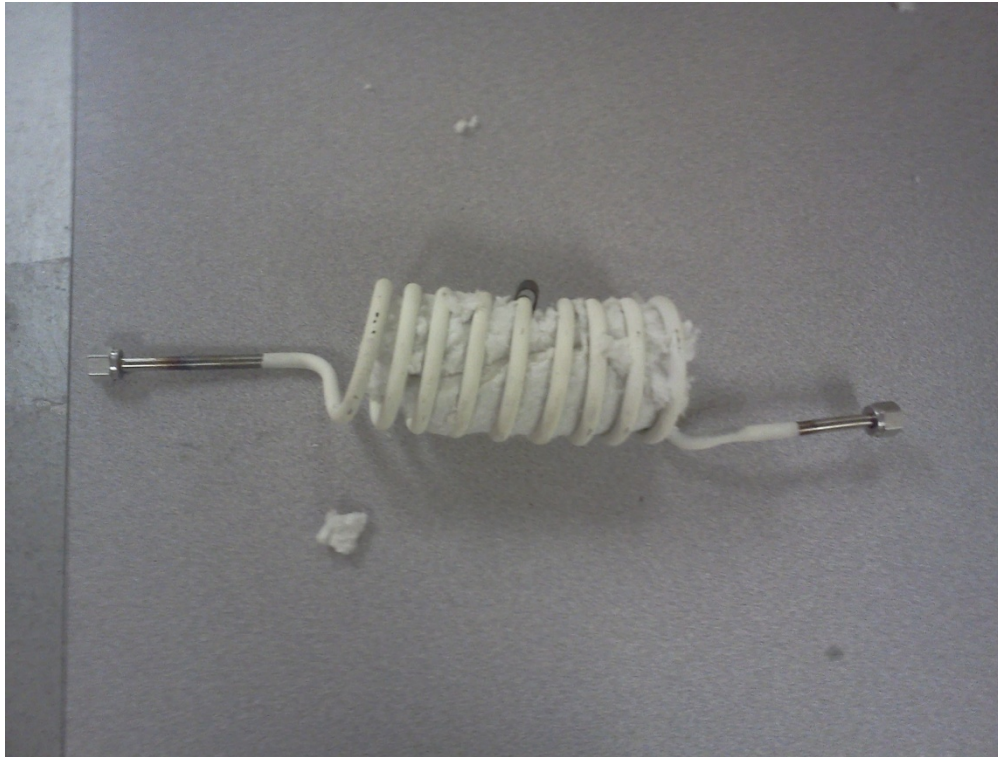


Figure 4.8: Powder heater coil coated with alumina.

A copper plate is set at each extremity of the coil and connected to 10KW powder supply shown in Figure 4.9. An electric current is applied between the copper plates, and the coil is heated up by its resistance. To ensure thermal homogeneity of the coil between the two copper plates, ceramic wool insulation is applied on the outside the coil.



Figure 4.9 : 10kW Powder supply to heat the coil

4.2.6 Gas Heater

The gas heater is used to heat the main gas flow before the throat. It is built with four meters long 5/8" outside diameter tubing. The pipe is coiled and is connected to a 30 kW power supply shown in Figure 4.10a. Heat is created using the Joule's effect on the coil and is transferred to the gas that flows in it. The temperature inside the coil is regulated by a variac controlling the voltage applied across the coil. Ceramic wool is used to insulate the heated coil from the outside environment as shown in Figure 4.10b.

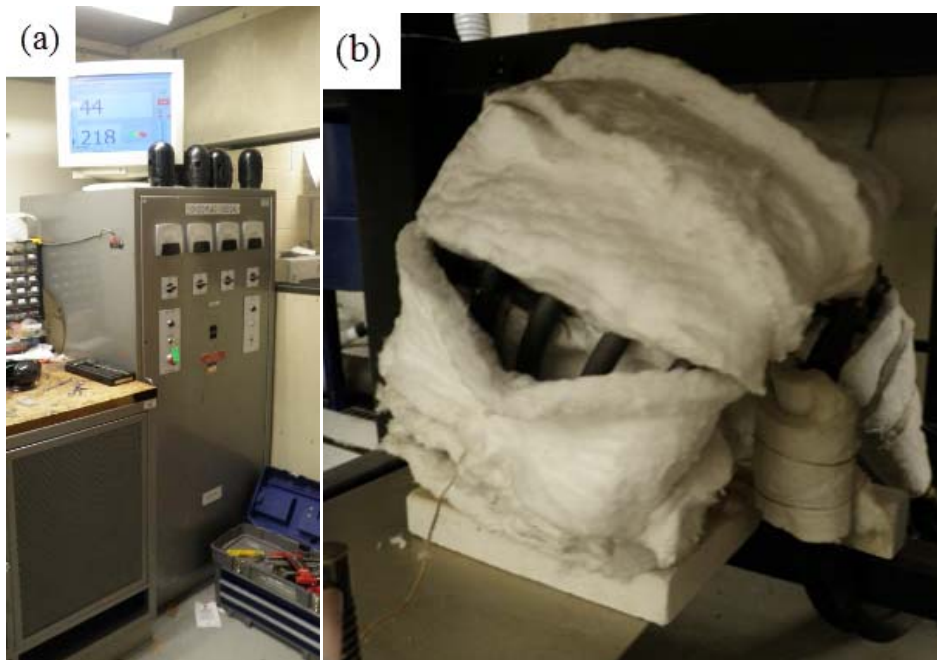


Figure 4.10 : View of a) 30kW system powder supply, b) gas heater with ceramic wool insulation

4.3 Pulse Gas Dynamic Spray (PGDS)

This section explains the equipment used in the pulse gas dynamic spray system often referred by the acronym "PGDS".

4.3.1 Driving and Feeding Gas Supplies

In this system, commercial helium gas bottles fitted with a regulator are connected to the control panel of the system. A second regulator maintains the inlet gas through the valve at a constant pressure.

The first step before spraying is to heat the system with pressurized air. When the system reaches the desired temperature, a three-way-valve is used to switch from air to helium. Compressed air is used to heat the system due to his low cost compared to helium. A bottle pack of helium (shown in Figure 4.11) is used to provide the gas for the system.



Figure 4.11 : Helium and nitrogen bottles packs

One bottle of helium is also used as carrier gas to develop a pressure above the main gas pressure in the powder feeder to carry powder to the nozzle. A flow meter is set installed on the bottle to regulate the gas to obtain a constant flow of powder in the nozzle without fluctuation due to pulses.

4.3.2 Spraying Chamber

The spraying chamber contains the nozzle and a displacement table to move the substrate. It is used to keep non-sticking powder in a closed environment. The chamber is made of an aluminum frame fitted with two windows to see the coating formation. Next to the chamber, there is a 10 HP down draft water filtration system used to filter powder coming from the chamber (see Figure 4.12).

An X-Y table is used to displace the substrate (Model A1 from Velmex, Bloomfield, NY). This unit is the same as the one used in the low pressure system and it is connected to COSMOS software. It is made of two perpendicular lead screws actuated by an electric motor. The Z adjustment is obtained with a laboratory jack. The substrate is fixed with a vise on the jack.



Figure 4.12 : Spraying chamber and water filtration unit

4.3.3 Spray Guns

Pulse gas dynamic spray gun is a process based on shock waves to accelerate particles. The shock wave is created by the quick opening of the system valve creating an overpressure. The valve tank is filled with gas coming from the gas bottle (Figure 4.13a). An electric motor activates the rotation of a three slotted disk (Figure 4.13b) over a fixed seat (Figure 4.13c) also presenting three openings.

Each third of a turn of the slotted disk creates a shock wave when the disk is aligned with the seat. The gas flows coming out of each opening are mixed together and exit the valve (Figure 4.13d). The gas then goes through a heater. The valve is not located after the gas heater because it would then require to be manufactured with high temperature resistant material (1000°C). The frequency of each shock is adjusted by the velocity of the electric motor.

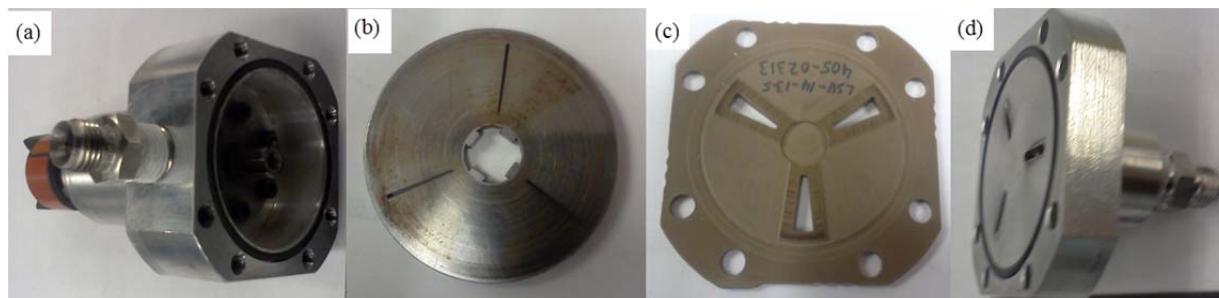


Figure 4.13 : Picture of the valve section a) the gas tank, b) the rotating slotted disk, c) the fixed seat and d) exit valve

The shock wave travels into the gas heating section where an electric coil hooked to a 14kW power supply is used to heat the gas. The wave then leaves the heating section and enters the powder injection unit. This section consists of a T joint where the heated powder from the powder heating section is inserted into the hot gas flow. This is followed by a straight tubing section reaching the end of the unit. Each part is shown in Figure 4.14.

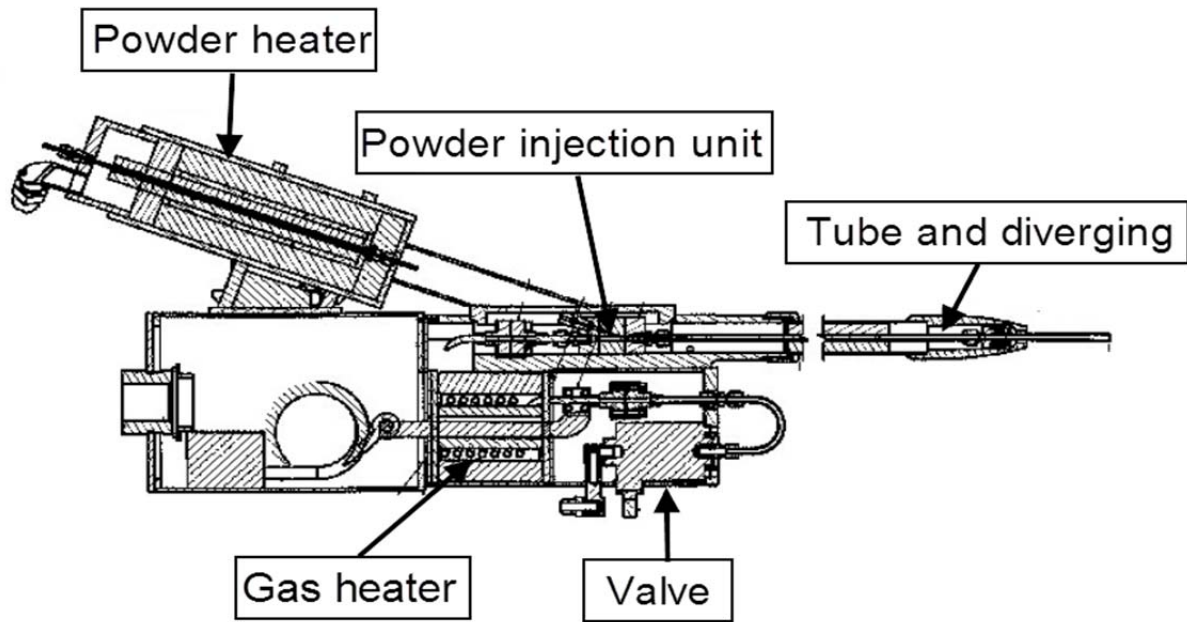


Figure 4.14 : Pulse gas dynamic spray schematic

4.3.4 Powder Feeder

The powder feeder unit is similar with the one described in section 4.2.4 for the low pressure cold spray system.

4.3.5 Powder Heater

The powder heating unit used in the pulse gas dynamic spray is similar to the one described in section 4.2.5 for the LPCS system.

4.4 Powder and Coating Characterization

4.4.1 Microscopic Observation

Microscopy observation was used to characterize the coating made by both systems. Using an abrasive saw (Secotom-10), cross-sections of the coating were prepared. The cut samples are mounted in a thermosetting epoxy resin using Struers LaboPress-3 equipment. The sample was then polished with Struers TegraPol, Tegraforce-5 and TegraDoser-5 using Struers polishing method for bulk Ti-6Al-4V. These equipments are shown in Figure 4.15. The samples structures were studied with an optical microscope (Kingdak NMM-800TRF) fitted with a camera and connected to computer to enable the analysis of the sample on the computer screen. The "Clemex Vision Lite" image analysis software was used to determine the porosity, thickness and particles size of the coating. Each evaluation was performed on multiple samples. Cross-sections of the coating from each sample were cut and, for each of these cross-sections, multiple regions inside the dense coating region were analyzed. The coating in each sample was etched with a solution of 15 mL of HNO_3 , 10 mL of HF and 70 mL of H_2O in order to perform particle size measurement.

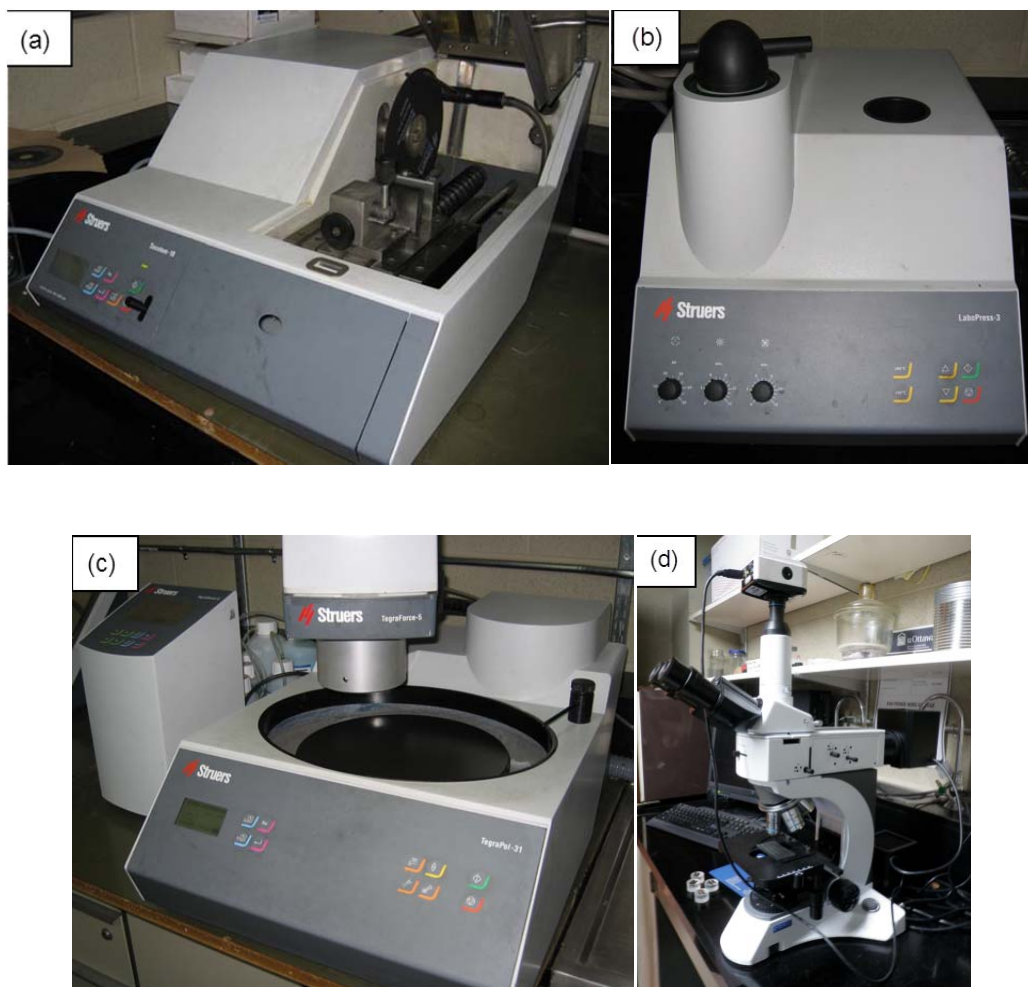


Figure 4.15 : Sample preparation equipment and analytical instruments used for sample investigation: a) Cut-off saw with silicon carbide blade (Struers Secotom-10); b) Thermosetting resin mounting chamber (Struers LaboPress-3); c) Sample polisher (StruersTegrapol, TegraForce-5 and TegraDoser-5); d) Optical microscope equipped with digital camera for image analysis (Kingdak NMM-800TRF and Clemex Vision Lite Software)

For the evaluation of the coatings with a scanning electron microscope (SEM), a cold plasma gold sputtering device DESK IV from Denton Vacuum (Moorestown, NJ, US) is first used to prepare the

samples. The purpose of this equipment is to create a thin conductive layer of gold on the coating. This gold sputtering device is shown in Figure 4.16.



Figure 4.16 :Cold plasma gold sputtering equipment

The samples are then beamed with electrons in the SEM equipment. A model Evo10 scanning electron microscope (SEM) from Carl Zeiss Microscopy GmbH (Jenna, Germany) was used for this research (see Figure 4.17). This system was equipped with secondary electron (SE), back-scattered (BSE), energy-dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD).

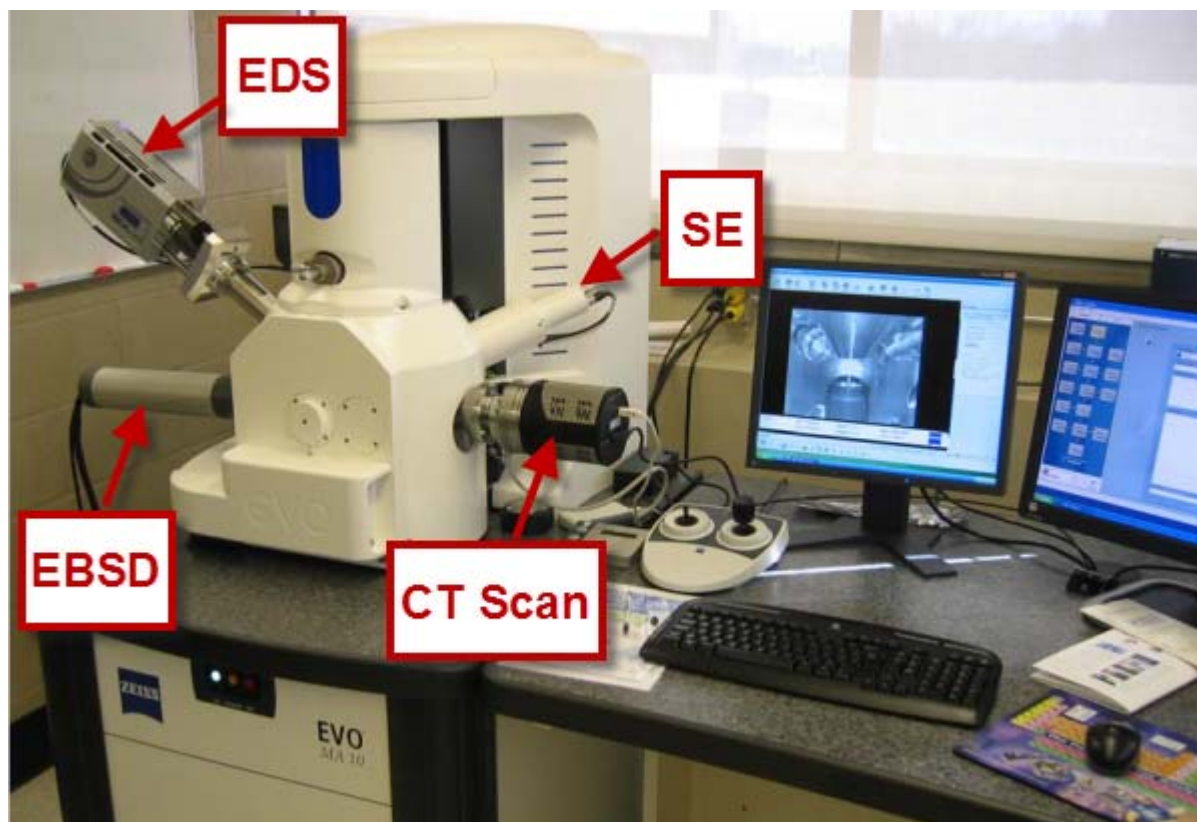


Figure 4.17: Scanning Electron Microscope (Zeiss Evo10) with SE, BSE, EDS, EBSD and CT Scan detectors

4.4.2 Particle Size Distribution

Particle size is used to characterize the dimension of particles. Using LS 200 equipment from Beckman Coulter (Brea, CA, US), powder distribution was achieved. This apparatus is shown in Figure 4.18. The powder is put in suspension in distilled water to produce a low concentration electrolyte solution to perform the analysis with this instrument. Fraunhofer theory is used to determine the diameter of the particle from the diffraction of the laser path through the powder solution. One assumption used in this theory is there are only spherical morphology particles in the solution. The tests are performed for 60 seconds duration to ensure repeatable results.



Figure 4.18 : LS 200 equipment from Beckman Coulter

4.4.3 Hardness

Hardness is evaluated on polished cross-section samples using a Struers Duramin-1 micro-hardness

Vicker micro-hardness tester shown in Figure 4.19.



Figure 4.19 : Struers Duramin-1 micro-hardness

Loads of 2.942N (HV₃₀₀) and 245 mN (HV₂₅) are applied on a diamond indenter and penetrates the coating for 10 sec. Following the indentation performance, two diagonal widths are measured under a microscope at 400 X. The equation to obtain Vickers's hardness determination is as follows:

$$HV = 1854.4 \frac{B}{w^2} \quad (\text{Eq. 4.1})$$

Where HV is the hardness value, B is the applied load on the indenter (in grams) and w is the width's length (in μm). The precision of this device allows evaluation of the hardness of small part and coating.

4.4.4 Wear test

Wear test evaluates the capacity to sustain the integrity of the coating when there is a sliding object on it. The test is based on ASTM Standard G133. The substrate sample is made of Ti-6Al-4V coated with Ti-6Al-4V powder material using the methods described above. The coating is machined to obtain a constant thickness and then ground and polished with 320, 500 and 1200 SiC papers. Prepared samples are fixed on a horizontal linear stage activated via a lead screw and an electric motor. A constant force load of 10 N is applied downward vertically with a 3/8" ball on the mounted flat specimen. This test does not use lubricant between ball and specimen to represent the general application of this sample. Each cycle is counted using Labview software and the test is stopped at a given cycle. Each specimen is then cleaned with acetone in an ultrasonic bath, air dried, cleaned with ethanol in ultrasonic bath and finally air dried. Equipment used to perform this test is shown in Figure 4.20. Mass loss is evaluated with Mettler Toledo AG285 analytical balance at a precision of 0.0001 grams.

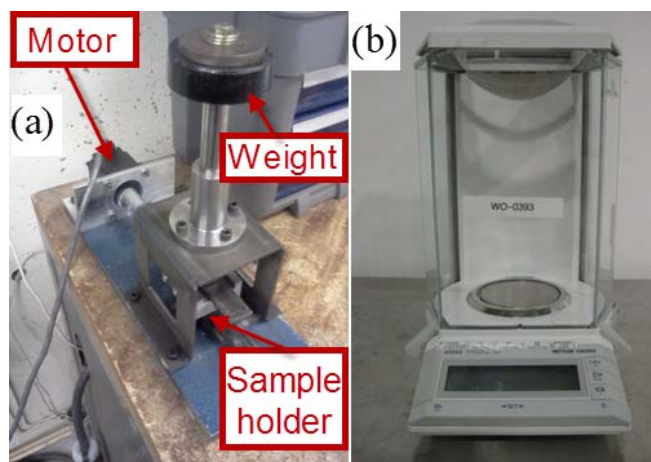


Figure 4.20 : a)Wear test equipment and b) Mettler Toledo AG285 analytical balance

4.4.5 X-Ray Diffraction Analysis

X-Ray Diffraction or XRD was used to identify the crystal structure and chemical composition of materials. The principle behind the XRD is the radiation of atoms with X-Rays. The X-Rays creates secondary waves when striking the electrons. The secondary wave is then collected and analysed. The output takes the form of peaks of different intensity and inter-atomic spacing related with the structure and composition of the material studied. The XRD used during this research was a Philip X-Pert model PW 1830 (Amsterdam, Netherland) generator diffractometer with Cu K α radiation at 50 steps per degree and count time of two seconds per steps and is shown in Figure 4.21.

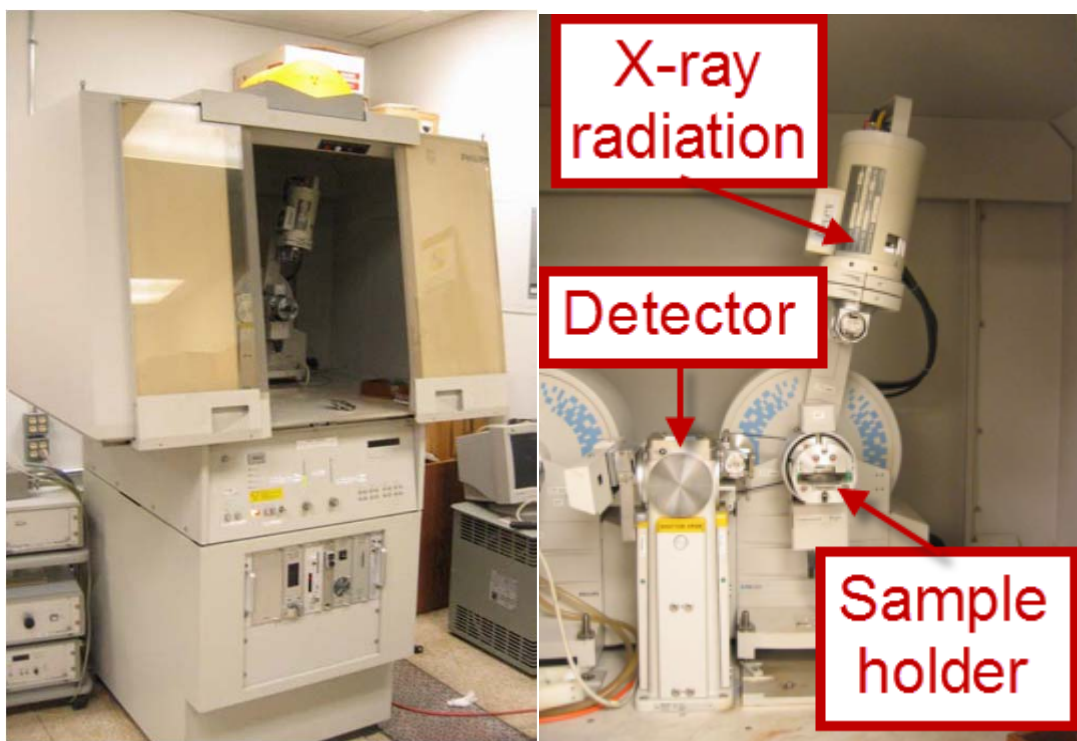


Figure 4.21: Philip X-Pert model PW 1830 XRD.

4.4.6 Adhesion Strength

Adhesion strength is performed according to ASTM Standard C 633-01. The substrates samples are made of Ti-6Al-4V machined in the shape of two cylinders of 25.4 mm diameter by 71.5 mm long. The end of one cylinder is covered with the coating and then machined to obtain a flat surface. One end of the other cylinder is sand-blasted with 80 alumina grit at an angle of 45° and a pressure of 55 psi with the nozzle of the gun located at about 76mm (3 inches) from the surface. A solid glue disc, commercial item FM1000 from Cytec Industries Inc, is dried in an oven at 50°C for one hour. The disk is inserted between the coated end of the first cylinder, and the sand-blasted end of the second one followed by the application of a torque of 4 N-m on the sample assembly (shown in Figure 4.22). The sample assembly is then put into an oven at 190°C for 2 hours to cure the adhesive.

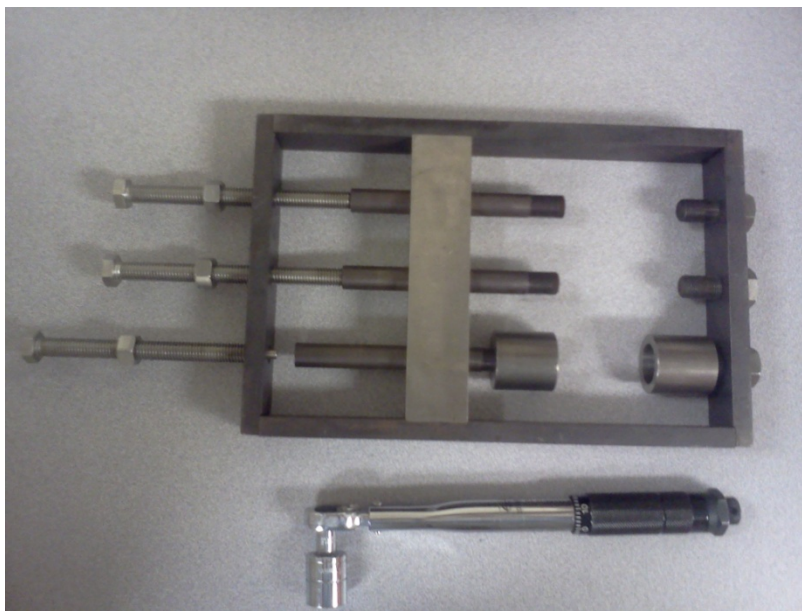


Figure 4.22 : Sample assembly

Following the preparation, the glued sample is installed in an Instron model 4482 tensile testing machine(Norwood, MA, US) equipped with a static load cell of 100 kN (see Figure 4.23). The tensile

load is increased at a constant rate of 0.021 mm/s (0.05 in/s) according to the ASTM standard mentioned above. The load is applied on the sample until rupture occurs and the value is recorded. A minimum of three samples was tested for each coating of interest for statistical and material reason.



Figure 4.23 : Instron model 4482 tensile testing machine

4.5 Feedstock material Storage and Processing

In this section, powder storage cabinet is presented followed by description of sieving and milling techniques.

4.5.1 Powder storage

In order to have a safe environment, a fireproof powder cabinet is used to contain all the powder in Cold Spray Laboratory at University of Ottawa. The cabinet contains an electric heater to heat the cabinet at a given temperature and maintain low humidity. Figure 4.24 shows the powder cabinet.



Figure 4.24 : View of a controlled humidity powder cabinet

4.5.2 Sieving of Ti-6Al-4V powder

A rotating sieve, Sieve VWR 8'' 20 μ m Test sieve CETYIER Incorporated shown in Figure 4.25, with a WST Ro-Tap R-30050 shown in Figure 4.26 was used to obtain powder with particle size between 0 and 20 μ m to be tested in this study.



Figure 4.25 : Sieves VWR 8" from CETYIER Incorporated



Figure 4.26 : WST Ro-Tap R-30050

4.5.3 Milling of Ti-6Al-4V powder

Milled Titanium alloy is not commercially available. The feedstock powder was mechanically milled for several hours to plastically deform the spherical powder into a flake shape. The ball mill system used was consisted of an impeller activating stainless steel balls (shown in Figure 4.27) to crush and deform the powder. The ball mill container is filled with ethanol during the milling. The added ethanol protects the powder from oxidation because this system is in an air environment. A water cooler is used to maintain a temperature below 50°C. The impeller is activated by an electric motor at a constant velocity of 260 RPM.



Figure 4.27 : Impeller and stainless steel balls

4.6 *Simulated Damage Processing*

The substrate machining process to produce gauge samples from a flat plate is explained in this section.

4.6.1 Computer Numerical Control Milling

Ti-6Al-4V samples used for simulated damaged repair are produced using a computer numerical control mill. V shape groove with an angle of 10° is milled with this equipment on a flat plate. It is then cut into small samples of 1" by 4" size. The mill and the machined plate are shown in the next figures.

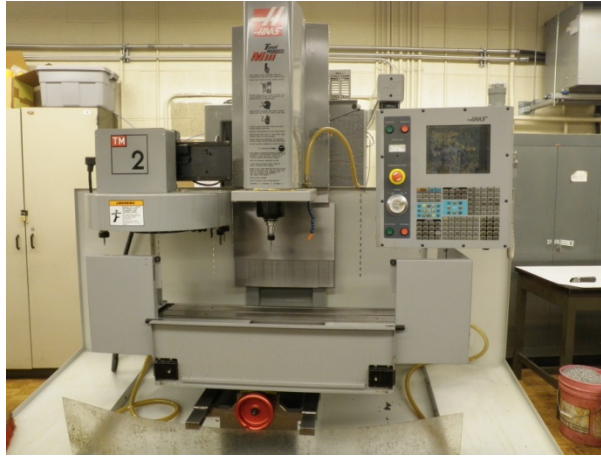


Figure 4.28 : Computer numerical control mill used to prepare the samples

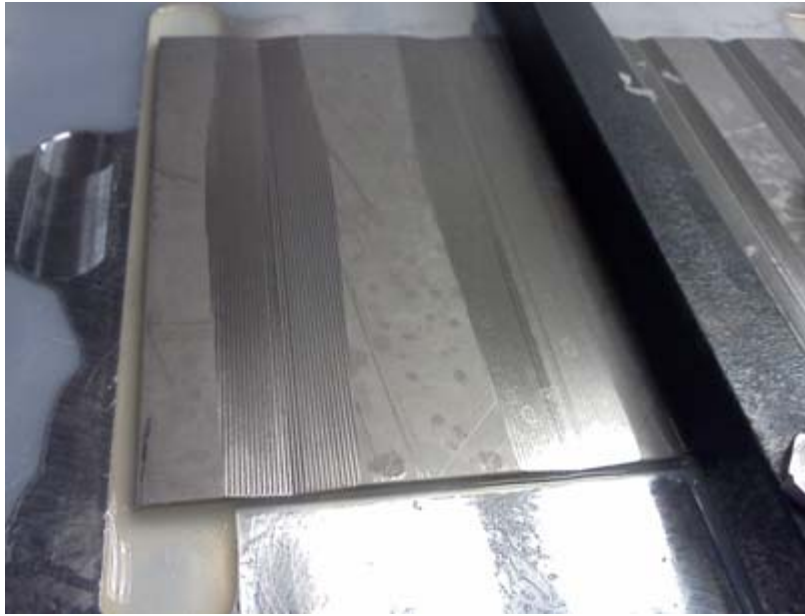


Figure 4.29 : Milled plate with a V shape groove at a 10° angle

Chapter 5 –Characterization of Feedstock Powder

5.1 Introduction

A definition of the feedstock powder chemical components is presented in this chapter. Powder morphology is defined using SEM and particle size distribution is determined with the LS 200. The two different powder morphologies used in this study are described here.

5.2 Feedstock (conventional) Powder

The powder use for this work is Ti-6Al-4V alloy grade 5 manufactured by Raymor Industries (Montréal, QC, Canada). The powder chemical composition provided by the manufacturer is presented in Table 5.1.

Table 5.1 : Chemical composition of Titanium alloy powder

Element (wt.%)								
O	N	C	H	Fe	Al	V	Others	Ti
0.15	0.1	0.02	0.001	0.2	6.0-6.5	3.5-4.5	< 0.1	Balance

During plasma atomization process, Ti-6Al-4V ingots are melted in an inert environment. Nevertheless, Table 5.1 shows added elements such as hydrogen, nitrogen, carbon, oxygen and iron, etc., into the powder. Even in optimal conditions, it is nearly impossible to have a complete inert environment due to contaminant in the inert gas such as hydrogen, nitrogen and oxygen. Iron and carbon impurities are coming from equipment erosion during the process.

XRD evaluation of the feedstock powder was undertaken to determine the structure and the orientation of Ti-6Al-4V crystal. XRD results are presented in Figure 5.1

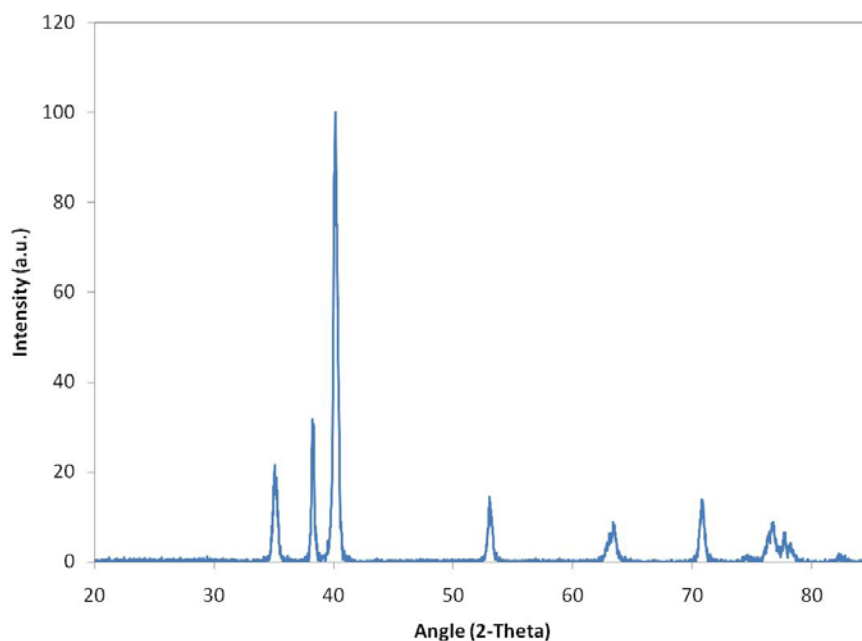


Figure 5.1 : XRD analysis of as received Ti-6Al-4V powder

This figure shows Titanium hexagonal close pack as the only element of the powder. No added elements are present as a crystal structure.

Using a scanning electron microscope, powder morphology was observed and a picture is presented in Figure 5.2.

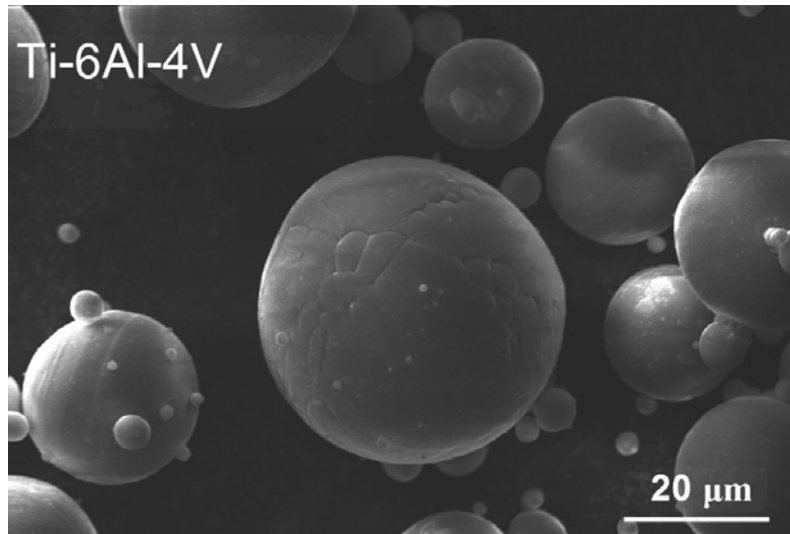


Figure 5.2 : SEM image of Titanium alloy powder

Spherical morphology of the powder is observed with SEM as mentioned above. In addition, the surface of the powder is observed and shown to be smooth in this case. Powders with spherical morphologies are more difficult to accelerate due to their lower drag coefficient compared to irregular shaped powder [81] as indicated previously in Chapter 2.

The feedstock powder size distribution obtained the LS 200 is presented in Figure 5.3 and

Table 5.2.

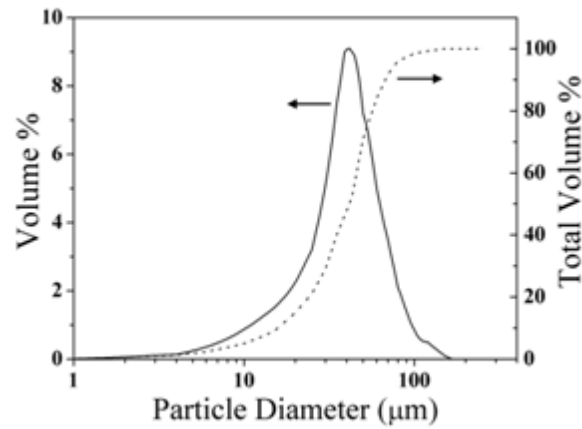


Figure 5.3 : As received Ti-6Al-4V particle distribution

Table 5.2 : Particle size in function of the remaining volume percentage

μm	20	30	44	74	105
% <	15.2	30.3	63.0	92.9	98.5

Figure 5.3 shows the particle mean diameter is 40.3μm. From this table, it can be observed that 63% of the powder has a mean diameter lower than 44 μm and that the powder presents a wide range of particle size. After using the hardness tester, Ti-6Al-4V powder hardness was evaluated at 350±12 HV₂₅.

5.3 Milled Powder

In order to determine the impact of powder morphology on the resulting coating, irregular shaped Ti-6Al-4V powder was studied. Since this morphology is not commercially available, as received Titanium alloy powder was mechanically milled for three hours with the equipment described above. The powder chemical composition was not affected because this process only deforms the feedstock particles without adding other elements. Using an XRD, crystal structure and orientation could be determined for milled powder and the result is seen in Figure 5.4.

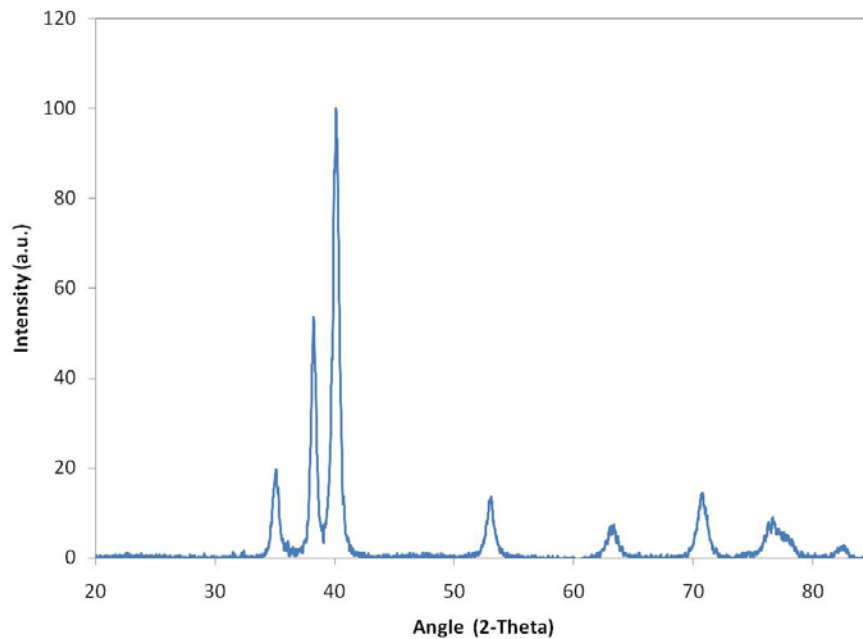


Figure 5.4 :XRD analysis of milled Ti-6Al-4V powder

The XRD of this powder has no new peak and the crystal structure remains hexagonal close pack. This result confirms that the milling process does not change the crystal structure of the powder. An observation of the milled powder morphology was performed with SEM. (see Figure 5.4),

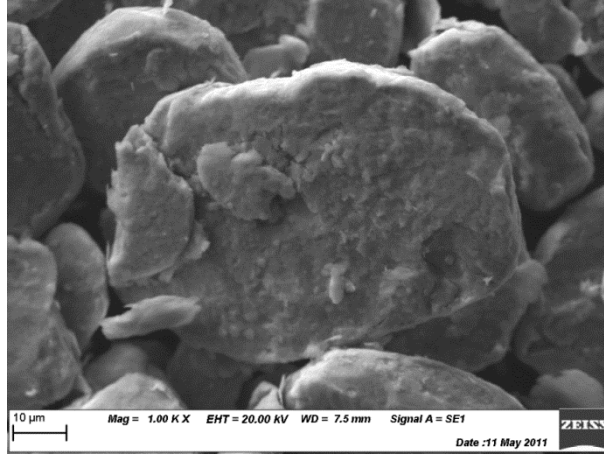


Figure 5.5 : Titanium alloy powder after three hours of milling

In Figure 5.5, milled powder has a different morphology relative to the initial powder. Instead of the spherical morphology with smooth surface, milled powder presents an irregular shape with rough surface. One side of the powder presents a near disc form and an elongate oval on the other side as illustrated in Figure 5.5.

Using LS 200 equipment, the milled powder size distribution was obtained to determine the size change after milling. The results are shown in Figure 5.6.and Table 5.3.

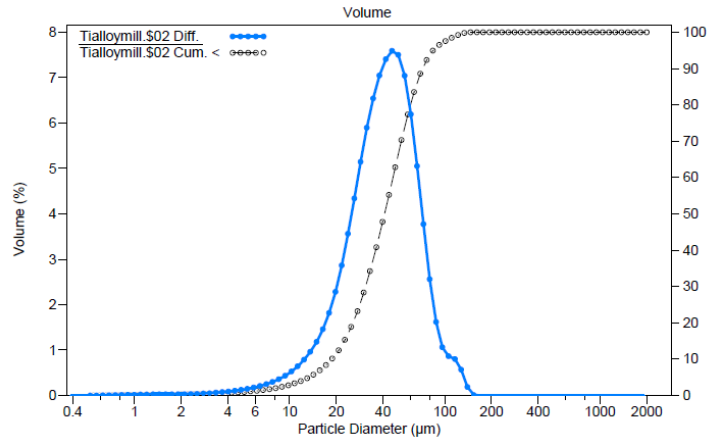


Figure 5.6 : Milled Titanium alloy particle distribution

Table 5.3 : Milled particle size in function of the remaining volume percentage

μm	44	74	105	149	177
% <	55.8	91.0	97.9	99.9	100

Using Figure 5.6, the mean diameter of Ti-6Al-4V milled powder was determined to be 43.8 μm. This represents a slight increase of the particle diameter from his initial dimension of 40 μm meaning there is an only small increase of the diameter of particles. This slight increase can be explained from the assumption used in the calculation performed by the LS 200 equipment that all the particles need to be spherical in order obtain low result deviation. The elongated oval side is not adequately computed by the instrument hence the decrease of the mean diameter due to it smaller area. An important consequence from the deformation obtained by the milling process is the hardness increase of 38 HV₂₅ to reach 388 HV₂₅ compared the feedstock powder value.

Chapter 6 – Feasibility and Experimental Studies of Spray Parameters for LPCS and PGDS Processes

6.1 Introduction

The objective of this chapter is to demonstrate the feasibility of the experimental approach adopted to demonstrate the feasibility. In addition, we show the experimental parametric studies carried out with the LPCS Ti-6Al-4V and PGDS Ti-6Al-4V alloy coating processes. The first section of the chapter covers the spray trials used to prove the capability to obtain LPCS coating deposition on Ti-6Al-4V. Following these reference experimental trials, experimental studies on the spray parameters are then presented. Similar information is then presented for PGDS coatings.

6.2 LPCS Ti-6Al-4V Alloy Coatings Feasibility Study

6.2.1 Preliminary Trials: Baseline Spray Conditions

The following conditions were selected to conduct preliminary tests in order to show the feasibility of the LPCS coating process with Ti-6Al-4V alloy and to obtain baseline results prior to additional studies. These original parameters came from the CP Ti spray parameters used by the University of Ottawa cold spray laboratory. The detailed parameters and baseline values are presented in Table 6.1.

Table 6.1 : LPCS parameters for feasibility testing

Parameters	Value
Substrate	Ti-6Al-4V; Acetone cleaned
Powder	Ti-6Al-4V
Propellant Gas	Helium
Gas Inlet Pressure	1.5MPa
Gas Inlet Temperature	625°C
Powder Inlet Temperature	Room Temperature
Powder Feed Rate	3.2 g/min
Carrier Gas Flow Rate	12.5 SCFH
Standoff Distance	10 mm
Nozzle Length	120 mm
Orifice Diameter	2 mm
Traverse Speed	1 mm/s

SCFH : standard cubic feet per hour

6.2.2 Preliminary Trials: Results

Ti-6Al-4V coatings were successfully produced using the parameters presented in the Table 6.1. Representative SEM images of the coatings cross sections are presented in Figure 6.1. However, although the production of coatings with adequate adherence to the substrate was obtained, the analysis of the coating material has revealed porosity levels up to $11.2 \pm 2.3\%$. Consequently, it appeared necessary to improve the quality of the coating.

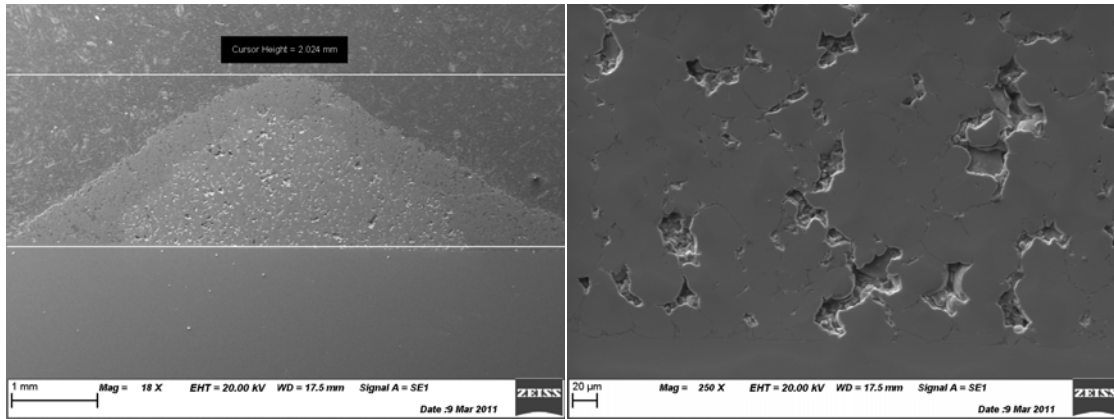


Figure 6.1 : Overview and magnification at 250X of preliminary of Ti-6Al-4V coating tests with LPCS

Starting with the spray parameters used in the baseline trial, a series of experimental tests were defined to study the effects of variation of the LPCS parameters in order to reduce the coatings' porosity level while ensuring to keep good bonding with the substrate. This will be described in details in the next section.

6.3 LPCS Spray Parameters Experimental studies

6.3.1 Strategy for the Study of the Influence of Various Spray Parameters

The effects on the coating quality obtained by varying of the major LPCS spray parameters mentioned above for the baseline tests were studied. These were tested in the following order: nozzle inlet pressure and temperature, powder injection temperature, substrate traverse speed, powder feed rate, powder flow rate, substrate displacement pattern and standoff distance. The optimized values of the parameters were obtained sequentially using the order mentioned. The testing strategy was to select the optimized value based on the best coating obtained for the parameter studied and then to use it, along with those obtained from the previous parameters, in the performance of the testing of the subsequent parameter, until they were all tested. The values for the parameters used to conduct the baseline test were used for the parameters until they were

tested and their best value was determined. The LPCS parameters mentioned above were studied during a series of experimental tests aiming at improving the coating.

It should be noted that while nozzle inlet pressure and temperature affect the particle velocity, the other spray parameters affect the deformation of the particle upon impact.

6.3.1.1 Nozzle Inlet Pressure

This spray parameter controls the particle acceleration because it governs the driving gas flow and density in the nozzle according to the perfect gas law. The particles' velocity is directly related to this flow. Therefore, the nozzle inlet pressure is considered a major parameter in cold spray techniques [32,85,86]. Experiments were conducted using two values of pressure while using the baseline values for the other parameters as discussed in the strategy. Those parameter values are the listed in Table 6.1. The first value selected for nozzle inlet pressure was 225 psi or 1.5 MPa which was used during the feasibility tests. Since the maximum pressure in the commercially available system is limited to 250 psi (1.7 MPa), the second series of tests carried out at this pressure.

Table 6.2 : Coatings' microstructure of the nozzle inlet pressures optimization.

Nozzle inlet Pressure (Psi)	Porosity Level (%)
225 (1.5 MPa)	11.2 ± 2.3
250 (1.7 MPa)	5.9 ± 3.4

Even if the difference is only 25 psi (0.2 MPa) between the two values tested, the porosity in the microstructure presented a major decrease from 11.2%to 5.9%, as indicated in Table 6.2. The increase of pressure affects the velocity by accelerating the flow as indicated by Eq. 2.8 in chapter 2. By accelerating the flow, there is thus a decrease of the coating porosity because the particles' velocity is increased. It was therefore concluded that the maximum pressure achievable by the

commercial system (250 psi or 1.7 MPa) is the best inlet pressure to use. This should not vary according to the combination of other parameters, although the actual level of improvement may likely depend on the interactions with the other variables.

6.3.1.2 Nozzle Inlet Temperature

Higher gas inlet temperature yields greater acceleration of the gas stream. Therefore, this produces greater particle velocity and powder deformation. Two nozzle inlet gas temperatures were evaluated. During the preliminary test, coatings were achieved with a nozzle inlet temperature of 625°C. This temperature was used during parameters study since decreasing this temperature would have decreased the gas stream as reported from Eq. 2.4. Consequently, the powder velocity would have decreased and since preliminary test had shown high level of porosity, it was concluded that a higher temperature should lead to improved results. The second value of temperature tested was 650°C due to the limitation of the equipment related to the gas heating tubing. The nozzle inlet pressure providing better results (250 psi or 1.7 MPa) as shown in the previous section and other parameters values from Table 6.1 were used to conduct the tests. The porosity results are presented in Table 6.3.

Table 6.3 : Coatings' microstructure of nozzle inlet temperatures optimization

Nozzle inlet temperature (°C)	Porosity (%)
625	1.1 ± 0.3
650	0.2 ± 0.2

A decrease of the porosity with the increase of temperature was observed from cross-section evaluations using the two nozzle temperature values. This porosity diminution was also mentioned

by Schmidt [86] and Wong [87]. Since the temperature of 650°C produced the lowest value of porosity, this temperature was determined to provide the best results in the conditions tested.

6.3.1.3 Feedstock Powder Inlet Temperature

The feedstock powder is preheated prior to injection in the nozzle by the transfer of the gas flow high temperature to the particles. The gas is heated by the coil hot surface and then the heat transferred to the powder. Using higher particle temperature should theoretically reduce their critical velocity, thus potentially resulting in a denser coating [83]. Previous test made using the same powder heater with commercially pure Titanium resulted in best results obtained at a powder inlet temperature of 700°C. Using this knowledge, a test plan to study temperatures near this value using the values of gas pressure and temperature providing the best results presented in the last two sections along with Table 6.1 values for the other parameters was achieved. Powder heater was incorporated into the system to further decrease the porosity. An original temperature of 550°C was used to define the initial porosity value. A range of powder inlet temperatures varying from 650°C to 850°C with increments of 50°C was used to determine which value was providing coating with the highest quality. Coatings evaluation based on three output variables (porosity, micro-hardness and thickness) are presented in Figure 6.2 and Table 6.4. A sample was cut in different sections of the coatings obtained for each temperature tested and the following properties were measured inside of them: multiple porosity, micro-hardness and thickness.

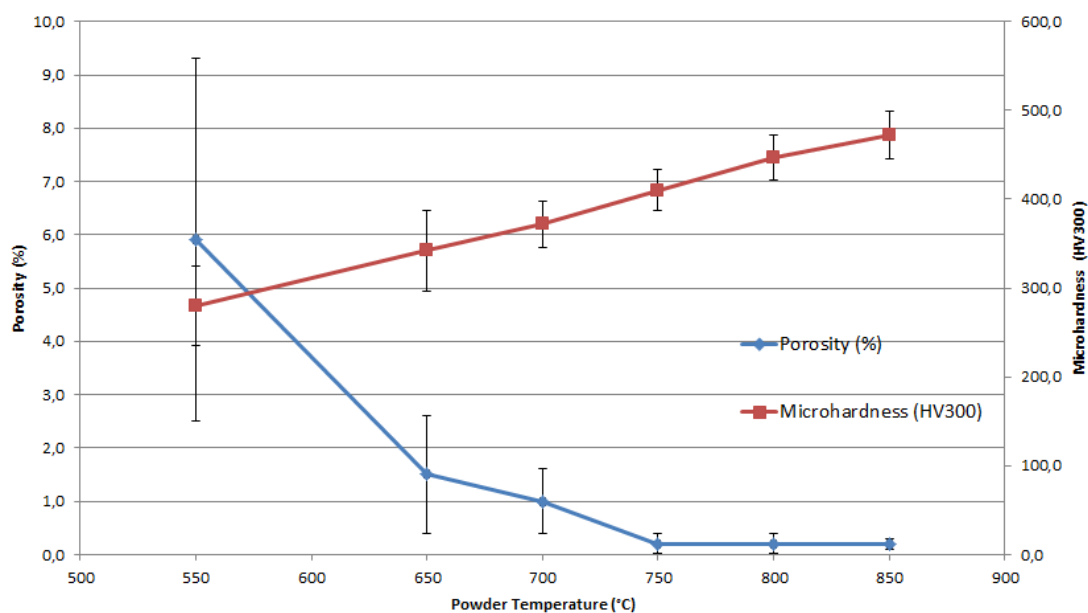


Figure 6.2 : Evolution of the porosity and micro-hardness as a function of powder inlet temperature for the LPCS system

Table 6.4 : Coatings' microstructure properties for a range of powder inlet temperature

Powder inlet temperature (°C)	Porosity (%)	Micro-hardness (HV ₃₀₀)	Thickness (mm)
550	5.9 ± 3.4	280 ± 45	2.5
650	1.5 ± 1.1	342 ± 45	1.9
700	1.0 ± 0.6	372 ± 30	1.6
750	0.2 ± 0.2	400 ± 20	1.1
800	0.2 ± 0.2	450 ± 25	0.8

850	0.2 ± 0.1	470 ± 25	0.7
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These results indicate that an increase of feedstock powder preheating temperature leads to a decrease in porosity, an increase in hardness, and a decrease in the coating thickness. The preheating of the powder softens particles before the injection in the high-velocity carrier gas. This allows better deformation upon impact and reduces the porosity level. However, oxide and nitride formation becomes more important as the powder temperature is increased as reported in other studies [43]. Higher content of oxide and nitride leads to an increase of hardness since these particles present higher hardness than the pure alloy. This hardness increase produces a decrease of particle deposition which influences the coating thickness. From 550°C to 750°C the porosity is mostly affected by the ductility of the particle. Temperatures above 750°C lead to the occurrence of oxides and nitrides inside the coating. Figure 6.2 shows that for temperatures above 750°C, a plateau is reached for the porosity while the coating thickness is still decreasing. The optimum powder inlet temperature was therefore considered to be 750°C since no oxide or nitride would occur, and it was the lowest temperature with the best compromise between porosity, hardness and thickness.

6.3.1.4 Substrate Traverse Speed

In this study, the substrate was fixed on a sample holder moving by and X-Y table. Two substrates velocities were evaluated. At 1mm/s, the substrate was at the X-Y table slowest speed. The second velocity tested 5 mm/s and the results are shown in Table 6.5. During this test, the sprays' parameters were from Table 6.1.

Table 6.5 : Coatings' microstructure optimization using traverse speeds parameter.

Traverse speed (mm/s)	Porosity (%)
1	11.2 ± 2.3
5	> 15

Observation of the coatings' microstructure shows that higher traverse speed produces an increase of the porosity level in the coating as indicated in Table 6.5. Based on this observation, additional higher velocities were not tested since there was no advantage to do so. Substrate traverse speed can affect the coating porosity level due to the impingement effect. This is created by the impacting particles and the deformation of those already on the substrate. A traverse speed of 1 mm/s was selected for the remainder of the experiments.

6.3.1.5 Powder Feed rate

Powder feed rate is the amount of powder injected into the nozzle per minute. This parameter influences the porosity and coating thickness. Titanium Alloys particles are easy to deposit and tend to bond against each other without deformation due to the active surface and high-temperature surface as mentioned by Li [84,88]. For this study aimed at obtaining improved coating, three values were tested. At 3.2 g/min the powder was at the minimal rate of the powder feeder. The two other values were chosen to view the influence of a higher feed rate on the microstructure. During this test, the sprays' parameters were those giving the best results for those already tested and discussed above while the values for the remaining parameters were those presented in Table 6.1. The coating results are presented in Table 6.6.

Table 6.6 : Coatings' microstructure optimization for powder feed rate parameter.

Powder feed rate (g/min)	Porosity (%)	Thickness (mm)
3.2	0.2 ± 0.2	1.1
7.7	4.7 ± 3.0	1.6
12.1	> 10	2.3

The lowest porosity and higher thickness values were achieved with the lower feed rate, as shown in Table 6.6. This can be explained by the low powder injected in the nozzle creating thin coating at lower feed rate. At low feed rate, the angle of impact for a second pass is higher (Figure 6.3 left side) compared to a coating formed at higher feed rate (Figure 6.3 right side). This has an incidence on the particle force impacting the coating since the coating is not perpendicular.

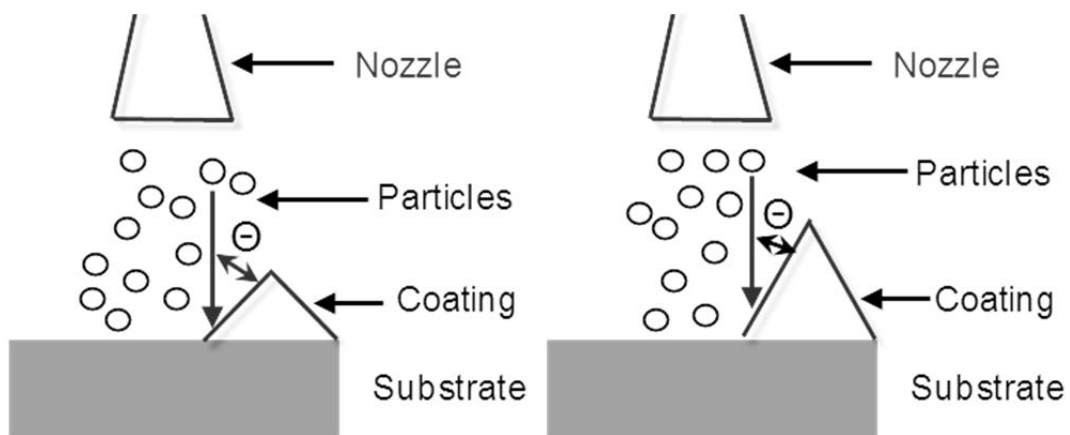


Figure 6.3 : Low feed rate coating (Left) vs high feed rate coating (Right)

A feed rate of 3.2 g/min was selected for the remainder of the experiments since the porosity was the lowest at this value of the parameter.

6.3.1.6 Powder Flow rate

This parameter affects the amount of gas injected into the powder feeder to move the powder toward the nozzle. Three values were tested for this parameter. Along with the initial 12.5 SCFH used in the preliminary test, flow rates of 10 and 15 were tested. During this test, the sprays' parameters used were those providing the best results in the previous sections and the remaining ones taken from Table 6.1. The results are shown in Table 6.7.

Table 6.7 : Coatings' microstructure optimization for powder flow rate parameter.

Powder flow rate (SCFH)	Porosity (%)	Thickness (mm)
10	0.5 ± 0.3	0.6
12.5	0.2 ± 0.2	1.1
15	1.3 ± 0.5	1.5

Cross-section evaluations of the three values show that the flow rate would affect the amount of particles projected on the coating. At 10 SCFH, there are not enough particles resulting in a decrease of impingement effect leading to an increase of porosity and a small thickness. At 15 SCFH, the flow rate is too high thus affecting the gas stream in nozzle and increasing the porosity. During these tests the thickness of the coating increased with the powder flow rate since there is more powder

carried in the nozzle. The best value for the powder feed rate was concluded to be 12.5 SCFH since the porosity was at its lowest point for this value.

6.3.1.7 Substrate Displacement Pattern

The study of the substrate displacement pattern aimed at testing the influence of the substrate displacement in function of the system nozzle. This parameter influences the temperature of the substrate because the nozzle heats the substrate with the gas.

There are two patterns to spray a substrate when its length is not equal to its width. The first method consists in spraying the longer side first with a small increment parallel to the shorter side then coming back. The second method is to spray parallel to the shorter side with a small increment on the longer side. These two methods are illustrated in Figure 6.4 where the two circles represent two substrates needing to be coated positioned side by side. The blue line represents the substrate displacement over the fixed nozzle. In Figure 6.4, green lines represent cold substrate regions while red lines show hot areas. On the left side of Figure 6.4, the substrates' temperature is fluctuating due to the movement of the nozzle because the substrate does not have time to be reheated by the gas. This phenomenon is happening using the first method labelled long side pattern in this study. However, in the short-side spray pattern (right side), samples are sprayed one by one decreasing the drop of substrate temperature. Table 6.8 shows adhesion results using the long-side and short-side spray pattern. This test was conducted with the values providing the best values for the parameters tested previously and values from Table 6.1 for the remaining parameters.

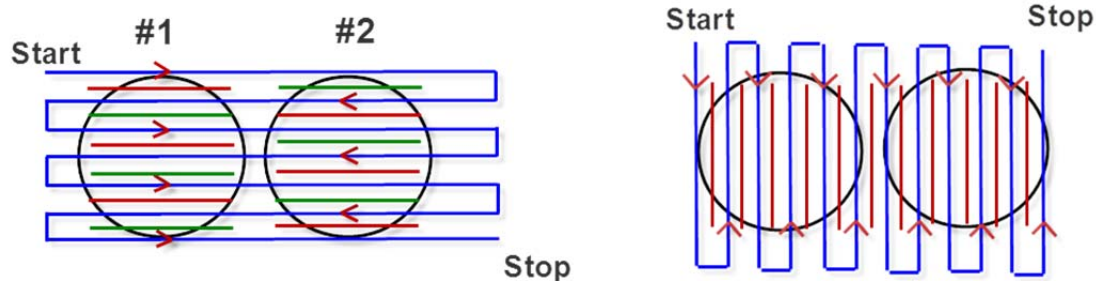


Figure 6.4 : Long-side spray pattern (Left) vs short-side spray pattern (Right)

Table 6.8 : Adhesion strength results of long-side spray pattern and short-side spray pattern

Spray Pattern	Spray Pattern [Psi (MPa)]	Type of Failure
Long-Side	4100 ± 650 (28.2 ± 4.5)	Adhesive/Cohesive
Short-Side	5900 ± 600 (40.7 ± 4.1)	Adhesive/Cohesive

A 30% increase of adhesion strength was achieved with the short-side pattern using this process in comparison to the long-side pattern. This is explained by a constant high temperature of the substrate temperature during a short-side spray pattern compare to a fluctuating temperature during the other pattern. Both patterns have the same failure type; between the particles and between the particles and the substrate. Based on these results, the second way of spraying (short-side) was selected for the remaining studies.

6.3.1.8 Standoff Distance

Standoff distance is the distance between the exit of the nozzle and the substrate. It influences the time required between the end of the accelerating phase and the impact on the substrate. This time affects the particle velocity and the position efficiency as mentioned by Li [89]. From his study, the standoff value originally selected for the baseline was at 10 mm. This value was not further tested in

this study because a shorter distance would have brought interference with the coating while longer one would have produced deceleration of the particles.

6.3.2 Optimized Spray Parameters Summary

The effects of the spray parameters have determined experimentally as discussed in the different sub-sections of section 6.3.1 aiming at finding the best results. The important parameters are summarized in the following table. Different fonts are used in the table to recognize the three following situations: parameters values tested to provide the best results in bold, those limited by the system in which are underlined and finally those which were not tested to bring improvement in italic. The evaluation of the coating obtained using the LPCS process with the spray parameter values providing the best results is discussed in more details in Chapter 7.

Table 6.9 : Optimized LPCS parameters

Parameters	Value
Substrate	Ti-6Al-4V; Acetone cleaned
Powder	Ti-6Al-4V
<i>Propellant Gas</i>	Helium
<u>Gas Inlet Temperature</u>	650°C
<u>Gas Inlet Pressure</u>	1.7 MPa
Powder Inlet Temperature	750°C
Powder Feed Rate	3.2 g/min
Carrier Gas Flow Rate	12.5 SCFH

<i>Sand-Blasting of Substrate</i>	n/a
Traverse Speed	1 mm/s
<i>Powder Distribution</i>	0-70 μm (as received)
<i>Powder Morphology</i>	Spherical Powder (as received)
Spray Pattern	Short-side
<i>Nozzle Length</i>	120 mm
<i>Orifice Diameter</i>	2 mm
<i>Expansion/Aera Ratio</i>	10
<i>Standoff Distance</i>	10 mm

SCFH : standard cubic feet per hour

6.4 PGDS Coatings Feasibility Study

6.4.1 Preliminary Trials: Spray Conditions

Preliminary spray trials were carried out using PGDS with helium as propulsion gas. No powder heater was used in these tests. The powder used was the conventional Ti-6Al-4V sprayed on Ti-6Al-4V substrate following acetone degreasing. These tests were performed to confirm the general feasibility of the technique using the following parameters in Table 6.10 and provide a baseline for the studies aimed at further improving the results.

Table 6.10 : PGDS parameters for feasibility testing

Parameters	Ti-6Al-4V
Substrate	Ti-6Al-4V; Acetone cleaned
Powder	As received Ti-6Al-4V
Propellant Gas	Helium
Gas Inlet Temperature	550°C
Gas Inlet Pressure	4.5MPa
Powder Feed Rate	9.8 g/min
Carrier Gas Flow Rate	20 SCFH
Standoff Distance	10 mm
Valve Frequency	10 Hz
Valve opening time	10 ms
Barrel Length	75 cm
Traverse Speed	1 mm/s

6.4.2 Preliminary Trials: Results

A coating was successfully produced using the parameters presented in the previous section, hence proving the feasibility of the method. The porosity level obtained was above 15%, as shown in Figure 6.5, therefore, further studies were required before the characterization of Ti-6Al-4V coating could be completed.

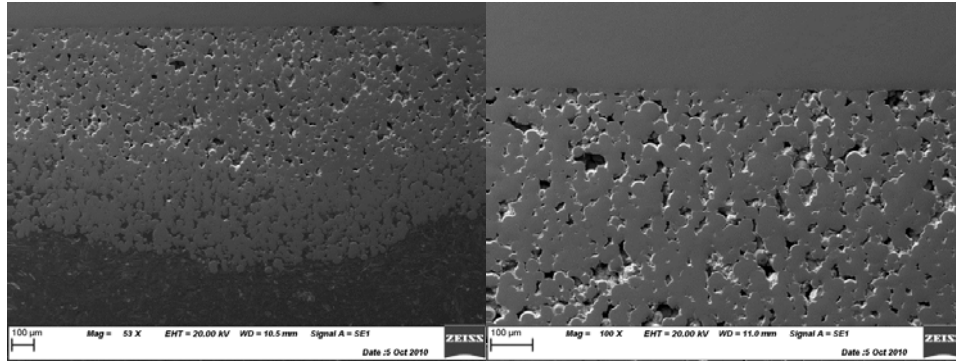


Figure 6.5 : Overview and magnification at 100X of Ti-6Al-4Vcoating obtained during feasibility tests using PGDS

6.5 PGDS Spray Parameters – Experimental Studies

6.5.1 Strategy for the Study of the Influence of Various Spray Parameters

As indicated in section 6.4.1, many parameters can influence the coating microstructure. The number of parameters could be further increased with the PGDS process compared to the LPCS process studied in section 6.3 because of the possibility to change the barrel length, valve frequency and the valve opening time. In addition, these studies included the investigation of surface preparation, powder size and morphology in the list of parameters tested to improve results. The same strategy used before for the LPCS process was also used to study the parameters yielding the best results for the coating properties. Thus, parameters were tested individually in a successive fashion so the best value for a tested parameter was carried out when testing the next parameters. The parameter values found in Table 6.10 for the baseline tests were used until the parameter was tested.

6.5.1.1 Nozzle Inlet Pressure

As in the case of LPCS, pressure affects the particle velocity because the acceleration of particles after their injection in the barrel is influenced by the main gas stream. Eq. 2.8 in Chapter 2 shows that an increase of inlet pressure increases the Mach number of the gas stream. In this experiment, three pressures were selected to select the best results obtained. The maximum pressure used was 4.5 MPa due to physical and economic constraint in the process. The two other tested pressures were defined to be decrements of 1 MPa from that maximum pressure. The test results obtained from those nozzle inlet pressure values with other parameter values being those found in Table 6.10 are presented in Table 6.11.

Table 6.11 : Resulting coatings properties obtained during nozzle inlet pressure optimization.

Nozzle inlet Pressure (MPa)	Adherence (Y/N)	Porosity (%)
2.5	N	n/a
3.5	Y	> 15
4.5	Y	> 10

The microstructure examination showed that the coating obtained with 4.5 MPa produced the lowest level of porosity, which can be explained by a higher deformation thus reduction of the voids. This pressure was therefore chosen for the remaining tests. It is interesting to note the limiting pressure required to obtain adherence which is between 2.5 and 3.5 MPa although it was not defined precisely.

6.5.1.2 Nozzle Inlet Temperature

Four nozzle inlet gas temperatures were evaluated. The first temperature evaluated was 350°C to determine the effects on the porosity when the gas temperature was lower compared to the

preliminary test. From the temperature used during feasibility test (550°C) incremental increases of 100°C until 750°C was tested. The optimized parameter value from the previous section and the remaining ones from Table 6.10 were used in the tests. The results are presented in Figure 6.6 and Table 6.12. A sample was sectioned at different sections from the coatings obtained at each temperature and multiple porosity and micro-hardness were measured inside of them.

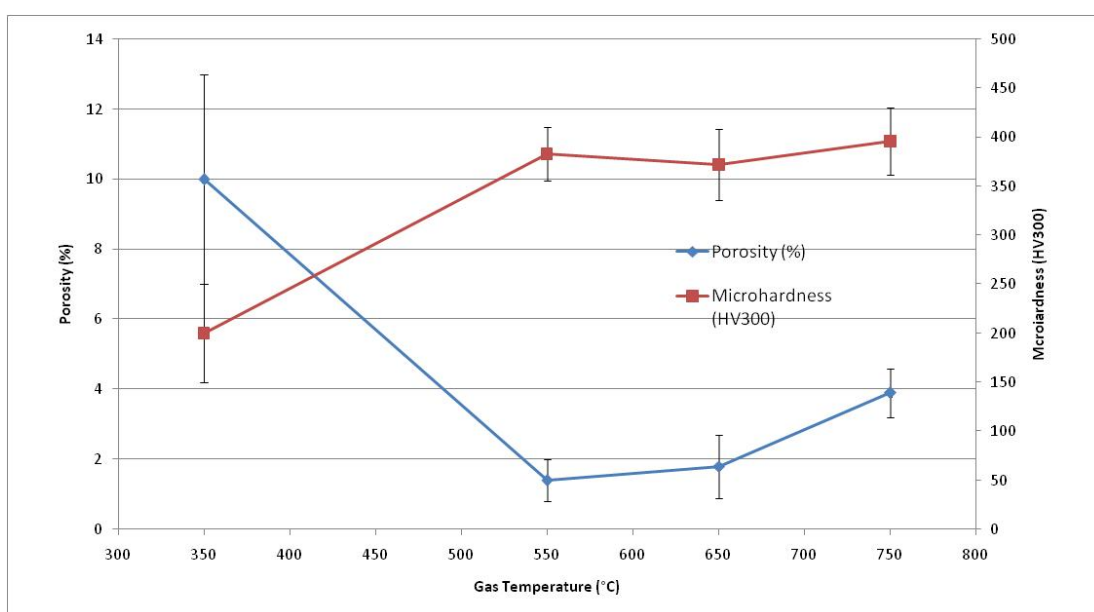


Figure 6.6 : Evolution of the porosity and micro-hardness as a function of the nozzle inlet temperature for the PGDS system

Table 6.12 : Coatings' microstructure of nozzle inlet temperature optimization

Nozzle inlet temperature (°C)	Porosity (%)	Micro-hardness (HV ₃₀₀)
350	> 10	n/a
550	1,4± 0.6	383± 30

650	1,8± 0.9	375± 40
750	3,9± 0.7	396± 30

There was a decrease of porosity as the temperature was increased from 350°C to 550°C because higher particle temperature produces higher deformation at impact. The porosity increased with temperature for temperatures above 550°C. This is explained by an increase of particle temperature resulting from the increase of in-flight oxidation of the particles. The increase of hardness affects the ductility of the impacting particles and increases the porosity in the coating at high temperatures. There was also an increase of micro-hardness as a function of the gas temperature up to 550°C and then a plateau between 550°C and 750°C. This is due to oxidize and nitrides particles inside the coating above 550°C. It was concluded that the best results were obtained with a nozzle inlet temperature of 550°C because oxidation is not allowed and the porosity is at its lowest point.

6.5.1.3 Feedstock Powder Inlet Temperature

The feedstock powder was preheated prior to injection in the nozzle by the transfer of the flow high temperature to the particles. Powder heater was first tested at 450°C to define a baseline porosity value. Temperatures from 450°C to 950°C in 100°C increments were tested to determine the powder temperature providing the best results. As mentioned previously, the spraying parameter values were either those determined in the previous sections or values from Table 6.10 for the parameters that not been tested prior to this one. The evolution of the porosity and micro-hardness as a function of temperature for the PGDS system are shown in Figure 6.7 and Table 6.13.

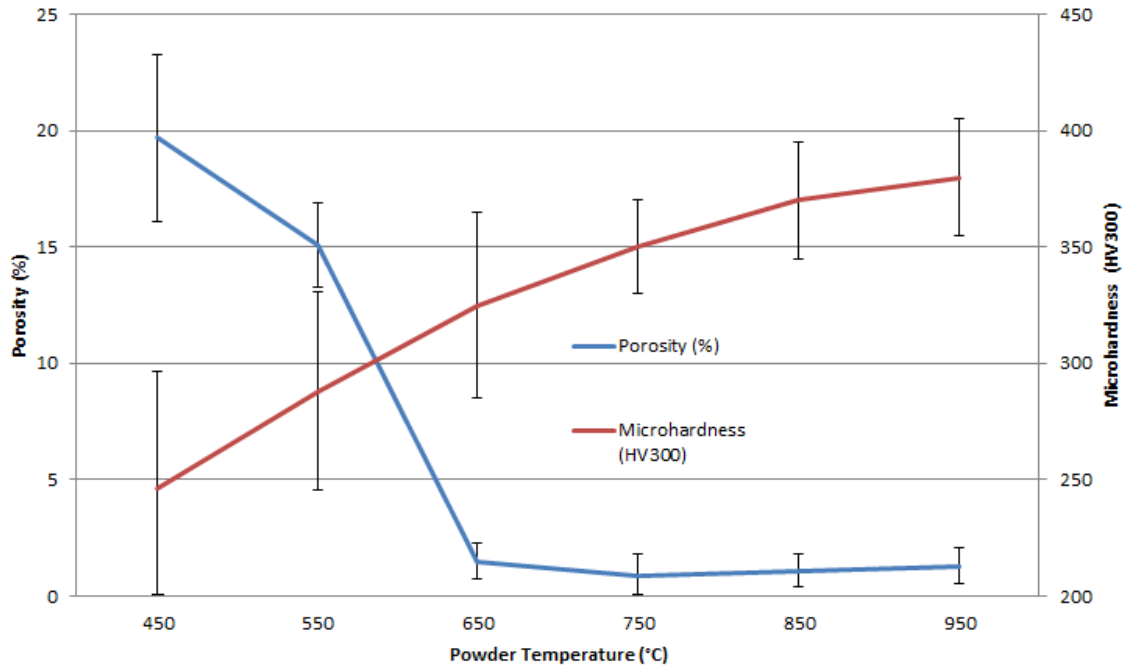


Figure 6.7: Evolution of the porosity and micro-hardness as a function of the powder inlet temperature for the PGDS system

Table 6.13 : Coatings' properties for powder inlet temperature optimization tests

Powder inlet temperature (°C)	Porosity (%)	Micro-hardness (HV ₃₀₀)	Thickness (mm)
450	19.7 ± 3.6	246 ± 50	2.2
550	15.1 ± 1.8	288 ± 40	2.3
650	1.5 ± 0.8	325 ± 40	1.7
750	0.9 ± 0.9	350 ± 20	1.3
850	1.1 ± 0.7	370 ± 25	0.9
950	1.3 ± 0.8	380 ± 25	0.8

Powder temperature variation produces major effects upon the microstructure, hardness and thickness. Between 450°C and 650°C, a decrease of porosity is observed. A plateau occurs for temperatures between 750°C and 950°C. The micro-hardness of the samples increases while the powder inlet temperature increases. This may result from oxide and nitride formation on the deformed powder. Review of the results presented in Table 6.13 shows that the thickness is about the same at 450 and 550°C and then drops until 850 °C is reached. The analysis for the behaviour of the three properties led to the selection of 750°C as the optimal temperature of the powder for the remainder of the tests because it was providing the best compromise between the coating properties.

6.5.1.4 Substrate Traverse Speed

Two substrates velocities were evaluated. At 1mm/s, the substrate was at the X-Y table slowest speed. The second velocity was at 8 mm/s and the results are shown in Table 6.14. During this test, the values for the parameters were those defined in sections 6.4.1.1 to 6.4.1.3 as those providing the best results and values taken from Table 6.10 from the remaining parameters.

Table 6.14 : Properties of the coatings obtained for traverse speed study.

Traverse speed (mm/s)	Porosity (%)
1	>10
8	>20

The coatings obtained with PGDS have porosities above 10% and above 20% while still providing adherence for the two traverse substrate speeds (1 mm/s and 8 mm/s) studied as presented in Table 6.14. A larger impingement effect was obtained with the lower travel speed. At that velocity, there is a lower porosity because the bigger particle hits those already in the coating. Additional speeds were not tested since the porosity increased as the velocity increases. The travel speed of 1mm/s was therefore chosen as the best value for this parameter because it was not possible to test a lower value.

6.5.1.5 Powder Feed rate

In this system, the feed rate regulates the amount of powder injected in the barrel. For this part of the study, four values were used. During the feasibility test, the powder feed rate had been set at 9.8 g/min as the baseline value. One value was selected to view the influence of lower feed rate on the microstructure and two values higher than the baseline value were studied. As done before, the values providing the best results for the parameters already tested and values from Table 6.10 for parameters which had not been already tested were used. The coating properties results are presented in Figure 6.8 and Table 6.15.

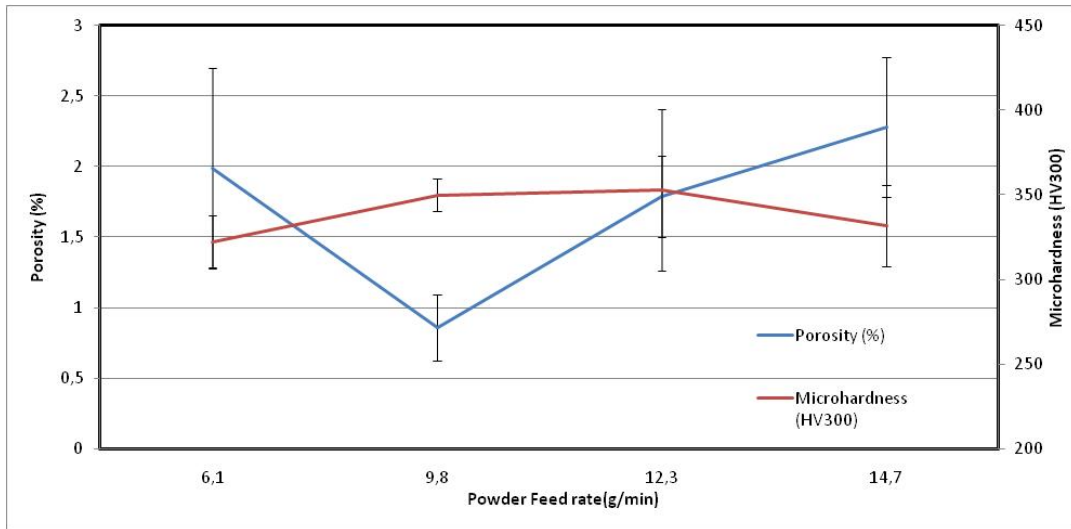


Figure 6.8: Evolution of porosity and hardness as a function of the powder feed rate for the PGDS system

Table 6.15 : Coatings' properties obtained for different powder feed rate

Powder feed rate (g/min)	Porosity (%)	Micro-hardness (HV ₃₀₀)
6.1	2.0 ± 0.7	322 ± 20
9.8	0.9 ± 0.2	350 ± 20
12.3	1.8 ± 0.3	350 ± 50
14.7	2.3 ± 0.5	330 ± 25

The low porosity at 9.8 g/min can be explained by the increase of the quantity of particles impacting the coating compared to what is obtained at a rate of 6.1g/min. At 12.3 g/min and above, the angle of impact for a second pass is lower (Figure 6.3 right side) compared to a coating formed at lower feed rate (Figure 6.3 left side). This has an incidence on the particle force impacting the coating

since the coating is not perpendicular. A feed rate of 9.8 g/min was therefore chosen as the best value for the powder feed rate parameter due to low porosity and high hardness obtained.

6.5.1.6 Powder Flow

Another important parameter regulating the amount of powder in the barrel is the flow of gas used to carry the powder to the barrel. This parameter affects the amount of gas injected into the powder feeder in order to move the powder towards the nozzle. Three values were tested to find the optimal conditions. Along with the initial 20 SCFH used in the preliminary test as the baseline value, flow rates of 10 and 30 were tested. During this series of tests, the value of the already tested parameters providing the best results as discussed in the previous sections along with values from Table 6.10 for the remaining parameters were used for Figure 6.9 and Table 6.16. This graph and table show the effect of the tested powder flows on porosity and micro-hardness.

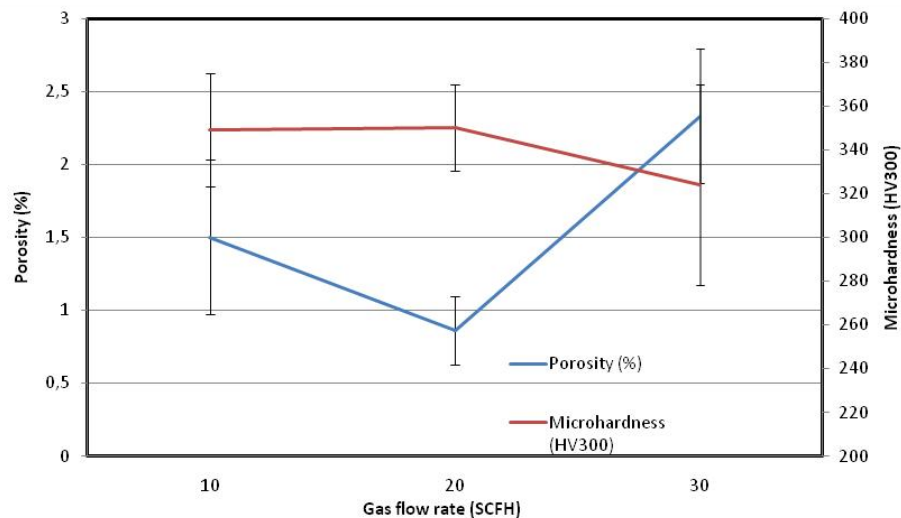


Figure 6.9: Evolution of the porosity and micro-hardness obtained for different gas flow rates for the PGDS system

Table 6.16 : Properties of the coatings for different powder flow rate

Powder flow rate (SCFH)	Porosity (%)	Micro-hardness (HV₃₀₀)
10	1.5 ± 0.5	350 ± 25
20	0.9 ± 0.2	350 ± 20
30	2.3 ± 0.5	324 ± 50

It can be observed in Figure 6.8 that the lowest value of porosity was obtained for 20 standard cubic feet per hour (SCFH) powder flow rate. This is explained by an increased amount of powder which contributes to the impingement effect. Since a larger amount of bigger particles impact those already in the coating, the porosity is decreased. At the same time, smaller particles are deformed between the bigger ones. At 30 SCFH, the flow is possibly disturbing the shock wave formation and quality. Micro-hardness remains constant between 10 and 20 SCFH then decreases at 30 SCFH. This can be explained by the fact that at powder flow rates below 20 SCFH, there is not enough voids in the coating to affect the micro-hardness. Based on this reason, 20 SCFH was chosen as the tested flow rate providing the best results.

6.5.1.7 Barrel Length

Barrel length affects the distance between the powder injection point and the coating. This parameter affects the amount of time the shockwave remains in the barrel. Three lengths were used to try to determine the best value. Along with the baseline 75 cm length used in the

preliminary test, barrel lengths of 50 and 100 cm were tested. During this test, the optimal value for the parameters already tested and those from table 6.10 for the other parameters were used during the tests. Table 6.17 shows the results obtained for each barrel length.

Table 6.17 : Properties of the coatings for different barrel lengths

Barrel length (cm)	Porosity (%)
50	9.5± 3.9
75	7.2± 1.2
100	8.3 ± 1.7

The three barrel lengths produced good adherence, but the lowest porosity was obtained with a barrel of 75 cm so this value was selected for the next for the next series of tests. This result is explained by the fact that heat was not completely transferred to the particles in a short barrel. In the case of the 100 cm long barrel, the heat is fully transferred but there could also be a formation of oxidation increasing the critical velocity of the particles.

6.5.1.8 Frequency

The frequency is regulated by the velocity of the electric motor activating the valve. The valve affects the amount of shockwaves created into the system per unit of time. Two frequencies were evaluated during the optimization step. The selected parameter values from the previous sections and the remaining one from Table 6.10 were used.

Table 6.18 shows the results obtained at each frequency.

Table 6.18 : Coatings' properties for different valve frequencies

Valve frequency (Hz)	Porosity (%)
5	9.8 ± 3.6
10	7.2 ± 1.2

Good adherence was obtained with both frequencies studied. Subsequent experimental work was performed at 10 Hz since it produced the best microstructure, i.e. lowest level of porosity, in order to confirm the results. This result can be explained by the increase of impingement effect at higher frequency since there were more high energy particles impacting the coating. No experiments were tried with a higher frequency due to economic constraint in the process.

6.5.1.9 Sand-Blasting of Substrate

Sand-blasting of the substrate is a common procedure used for thermal spray. In order to study the effect of the microstructure change of the coating, two samples: a sand-blasted and one without sand-blast, were tested. The optimized parameter from the previous section and the remaining one from Table 6.10 were used. The results are provided in Figure 6.10 and Table 6.19.

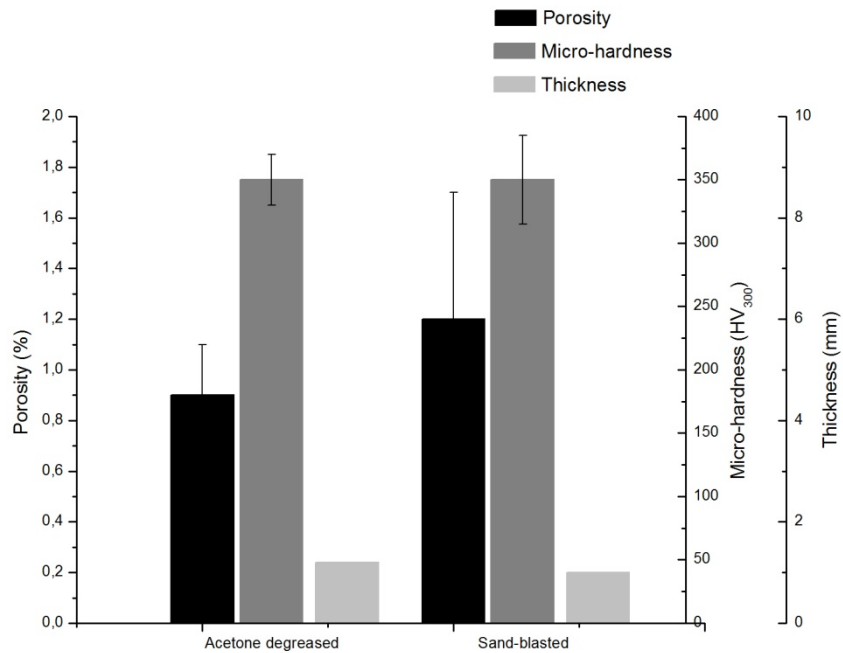


Figure 6.10 : Evolution of the porosity, micro-hardness and coating thickness as a function of the substrate preparation for PGDS system

Table 6.19 : Coatings' properties for different substrate preparation

Substrate preparation	Porosity (%)	Micro-hardness(HV ₃₀₀)	Thickness (mm)
Acetone degreased only	0.9± 0.2	350± 20	1.2
Sand-blasted	1.2 ± 0.5	350 ± 35	1.0

The previous figure and table show that there is only minor difference to the quality of Titanium alloy coating performed on a substrate as received or on a sand-blasted one. The sand-blasted substrate is only affecting the first layer of powder since the next layer will impact the first one. This result was also obtained by Richer [90]. Since it is more economical not to sand-blast the substrate, this option was selected as the optimal parameter.

6.5.1.10 Substrate Displacement Pattern

This parameter was studied using the methods discussed in LPCS process (Section 6.3.1.7). The optimized parameters from the previous sections and the remaining one from Table 6.10 were used. Table 6.20 presents the results obtained for both patterns.

Table 6.20 : Adhesion strength results of standard and modified patterns.

Spray Pattern	Adhesion strength [Psi (MPa)]	Type of Failure
Long-Side	8700 ± 400 (60.0 ± 2.8)	Adhesive/Cohesive
Short-Side	9100 ± 1450 (62.7 ± 9.7)	Adhesive/Cohesive

Since there was an increase of 5% of the adhesion strength for the short-side spray pattern for the same reason found for the LPCS process, it was decided to use it for all the spray work performed in the remainder of the project.

6.5.1.11 Powder distribution

Sieving of the powder was also studied to investigate his effect on the microstructure change. Three powders distributions were investigated. As received feedstock powder was sprayed first followed by 0-20 μm and 20-70 μm size powder. The optimized parameter from the previous sections and the remaining one from Table 6.10 were used. The results of the three powders are shown in Figure 6.11 and Table 6.21

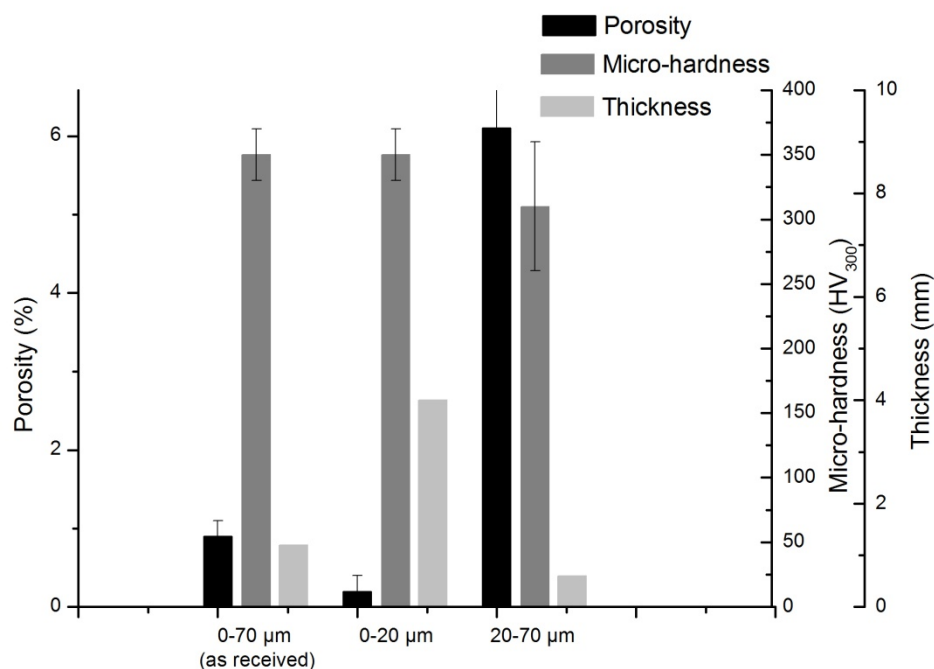


Figure 6.11 :Porosity, micro-hardness and thickness of the coating for different powder distribution used with the PGDS system

Table 6.21 : Coatings' properties obtained for different powder distribution

Powder distribution	Porosity (%)	Micro-hardness(HV ₃₀₀)	Thickness (mm)

0-70 μm (as received)	0.9 ± 0.2	350 ± 20	1.2
0-20 μm	< 0.5	350 ± 20	4.0
20-70 μm	6.1 ± 1.1	310 ± 50	0.6

Smaller particles produced a lower porosity, and same micro-hardness compared to feedstock powder. This is explained by smaller particles tend to have a higher velocity due to their lower inertia as mentioned in Chapter 2. There is an increase of particle deformation inside the coating because they impact the substrate at higher speed. However, the coating is thinner due to the small particle diameter. 0-70 μm powder has a higher porosity due to the slower bigger particles. In spite of that, they contribute to the impingement effect of small particle. Compare to bigger particle, the feedstock powder is better since the porosity is lower and hardness higher. There are a lot of voids when the PGDS is fed with 20-70 μm particles because they are more difficult to deform and there are no small particles between bigger one. The thickness is lower compare to the 0-70 μm coating since bigger particles don't go above their critical velocity. The particles with size lower than 20 microns represent 15% of the feedstock powder as seen in Chapter 5. Considering the limited improvement from the use of only smaller particles, it is not considered economical to perform the sieving operation due to the high wastage of powder material. Therefore, as received feedstock powder was selected as the optimal.

6.5.1.12 Powder morphology

Milled feedstock powder was sprayed to see the effect in the microstructure. This irregular shape could help the acceleration of the particle and increase the deformation inside the coating. The optimized parameter from the previous section and the remaining one from Table 6.10 were used.

Coating properties' results for the feedstock and milled powder are shown in Figure 6.12 and Table 6.22.

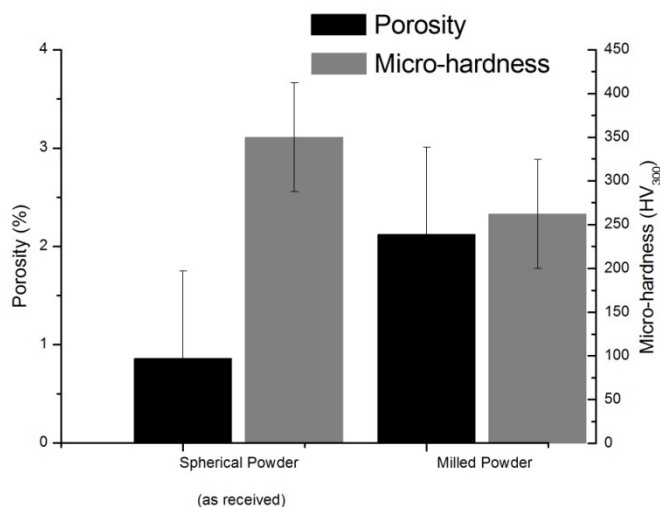


Figure 6.12 : Porosity and micro-hardness as a function of the powder morphology in the PGDS system

Table 6.22 : Coating' properties for different powder morphology

Powder morphology	Porosity (%)	Micro-hardness(HV ₃₀₀)	Thickness (mm)
Spherical Powder (as received)	0.9 ± 0.2	350 ± 20	1.2
Milled Powder	2.1 ± 1.6	260 ± 30	1.6

Even if the milled powder has an irregular shape and is already deformed, the as-received feedstock produced better microstructure properties. In milled coating, the particles tend to adhere in all directions creating a void when two particles are not paralleled. This has the consequence of

decreasing the coating hardness. Feedstock powder was selected instead of milled powder based on these reasons.

6.5.1.13 Standoff Distance

Standoff distance is the length between the exit of the nozzle and the substrate. It influences the time required between the end of the accelerating phase and the impact on the substrate. This time affects the particle velocity and the position efficiency as mentioned by Li [89]. From his study, the optimized standoff was at 10 mm. This value was not further optimized in this study because at a nearer distance, there would have been interference with the coating. Furthermore, at a longer distance the particles would have decelerated.

6.5.2 Optimized Spray Parameters Summary

Spray parameters were found experimentally as described in details in section 6.4.1. All the important parameters are summarized in Table 6.23 below. Parameters are presented with different fonts in order to define three cases: optimized parameters in bold font, those limited by the system are in regular underlined font and those non-optimized in italic font. The evaluation of the coating produced using PGDS process is presented in Chapter 7.

Table 6.23 : Optimized PGDS parameters

Parameters	Ti-6Al-4V
Substrate	Ti-6Al-4V; Acetone cleaned

Powder	As received Ti-6Al-4V
Propellant Gas	Helium
<u>Gas Inlet Temperature</u>	550°C
Gas Inlet Pressure	4.5MPa
Powder Inlet Temperature	750°C
Powder Feed Rate	9.8 g/min
Carrier Gas Flow Rate	20 SCFH
Sand-Blasting of Substrate	No
Valve Frequency	10 Hz
<i>Valve Opening time</i>	13ms
<i># Slots in disk</i>	3
Barrel Length	75 cm
Traverse Speed	1 mm/s
Powder Distribution	0-70 µm (as received)
Powder Morphology	Spherical Powder (as received)
Spray Pattern	Short-side
<i>Standoff Distance</i>	10 mm

Chapter 7 – Characterisation of Ti-6Al-4V coatings produced using LPCS and PGDS

7.1 Introduction

The purpose of this chapter is to review and analyze the CGDS Ti-6Al-4V coatings sprayed with both LPCS and PGDS methods on Ti-6Al-4V substrates. These coatings have been produced using the parameters defined in the previous chapter. This chapter includes detailed coating investigations such as microstructure (porosity), particle deformation level, micro-hardness, bond/adhesion strength, oxide level and simulated damage repairs

7.2 LPCS and PGDS Coatings

The CGDS coating results obtained with the LPCS and PGDS processes are discussed throughout this section.

7.2.1 Coating Microstructure

Back-scattered micrographs of the Ti-6Al-4V coating cross-sections using the selected spray parameters from the previous experimental studies for both processes are shown in Figure 7.1. The porosity levels of the coatings are presented in Table 7.1. It can be observed that nearly the same porosity level is obtained for both cases. Ti alloy coatings, regardless of the spraying method, are almost free of porosity. It can be observed from Figure 7.1 that the feedstock powders have been sufficiently deformed upon impact with the substrate to exhibit a non-spherical morphology in the coatings, thus suggesting that the impact velocity was greater than the critical velocity of this alloy.

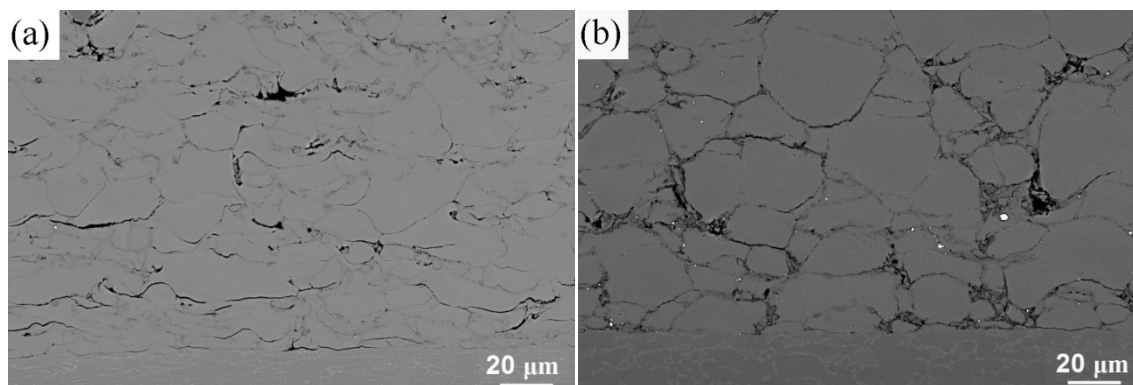


Figure 7.1 : Back-scattered(BS) micrographs (a) Ti-6Al-4V coating at using LPCS and (b) Ti-6Al-4V coating using PGDS.

Table 7.1 : Coatings' microstructure in function of the process

Process	Porosity (%)
LPCS	< 0.5
PGDS	<1

LPCS coatings show indications of smaller particles in the coating compared to particles in PGDS coating. Coatings produced by the latter process also exhibit more clear and well defined interfaces. The low porosity level and absence of cracks inside the coating obtained from a single spray pass demonstrate that the particle impact velocity was sufficient to efficiently deform the particles.

The PGDS coating shown on Figure 7.1 shows irregular and broader contours for each particle compared to LPCS. Agglomerations of smaller particle (below 3 μm) in areas between the larger particles, as shown in Figure 7.2 (areas inside the circles), were also observed. The presence of small particles in coatings was also observed in studies involving the HPCS process [91,92]. In these

studies, the possible explanation for the presence of those small particles was related to the development of high temperature areas in the jetting region during particle impact due to adiabatic shear instabilities leading to local melting. The high temperature area created would thereby be higher than the melting point for the bulk material. Nano-sized particle could be formed from the combination of high velocity and molten material after the splash and subsequent solidification. In the case of PGDS coating, the particles embedded at the grain boundaries are much larger, thus suggesting a different formation mechanism. Furthermore, these small particles are irregular, which is in contradiction with the observations made for the HPCS process. Consequently, further studies were undertaken in an effort to understand this phenomenon.

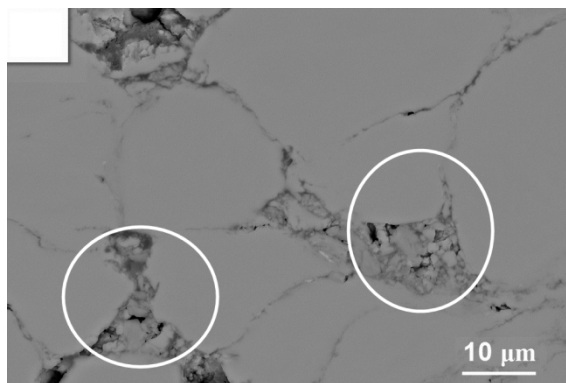


Figure 7.2 : Back-scattered(BS) micrographs Ti-6Al-4V coating using PGDS.

7.2.2 Deformation analysis

In order to study more closely the differences between each spray process, cross-sections were analyzed to investigate the particle deformation in each coating. In particular, the flattening ratio (Fr), representing the ratio between the average final length (L) of the deformed particle divided by the original diameter of the particles (D_0), was computed and the results are presented in Table 7.2 encompassing more than 1500 particles in each spray process.

Table 7.2 : Flattening ratio for both processes studied for more than 1500 particles.

Process	Flattening ratio ($Fr = L/D_0$)
LPCS	1.4 ± 0.2
PGDS	1.4 ± 0.2

It can be inferred that both processes have produced similar flattening ratios of 1.4. Both processes show a constant/uniform particle deformation level throughout the coating thickness at the exception of a thin layer near the coating surface, as shown between the arrows in Figure 7.3. This layer is also characterised by a larger porosity level. It is hypothesized that this layer did not receive enough particles for the impingement to take place. This is caused by the few incoming particles that would further deform this layer.

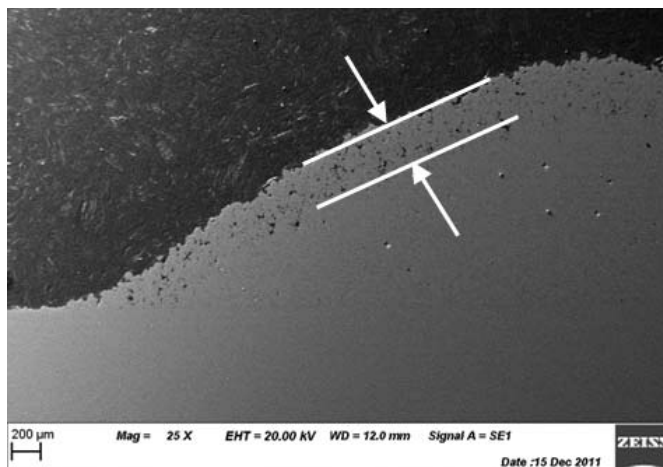


Figure 7.3 Example of the porous region at the surface of the coatings represented between the arrows

Similar observation regarding this area in Titanium coatings have been made in other researches [87,93–95]. This phenomenon was also observed with other powders such as copper [96]. It is possible to conclude that the particles deformations do not change in function of the system. During the studies of the deformation evaluation, particle size was measured and the results are presented in the next section.

7.2.3 Particle size distribution inside the coating

Particle size distribution measurements inside the coating have been performed using the cross-sections images obtained with each spraying process. The detailed Ti-6Al-4V particle size distributions for the coatings obtained by both systems are presented in Figure 7.4 along with the feedstock powder distribution.

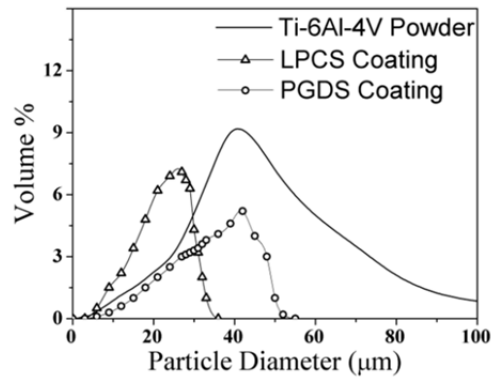


Figure 7.4 : Particle size distribution of Ti-6Al-4V in the powder and in the coatings

Figure 7.4 shows a shift of the average particle diameter toward smaller diameters especially for LPCS for both processes compared to the feedstock powders. This suggests that LPCS coatings may only contain smaller particles because these can reach the critical velocity to adhere to the substrate as opposed to the larger ones [32]. The larger particles contribute to the impingement effect providing increased deformation. Using only large particles does not lead to dense coating (see Chapter 6). Studies supporting this idea reported an increase in porosity for higher nozzle traverse speeds where less impingement effect is obtained [91]. In the case of PGDS coatings, larger particles adhered to the substrate because the higher temperature obtained with this process favours adhesion. This is caused by a constant high temperature process since there is no nozzle to decrease the gas temperature. High velocity process (LPCS) in comparison to high temperature process (PGDS) influences the particle size in the coating and could therefore affect the hardness which will be discussed for both systems in the next section.

7.2.4 Micro-hardness

The coating's micro-hardness measurement results along with those of the substrate and feedstock powder material are presented in Table 7.3

Table 7.3 : Coatings' micro-hardness in function of the process

Process	Micro-hardness (HV ₃₀₀)
Feedstock Powder	325 ± 5
Substrate	355 ± 17
LPCS	400 ± 20
PGDS	350 ± 20

As seen in Table 7.33, the feedstock particle micro-hardness was evaluated at 325 HV₃₀₀. After the spray process, the same particles show an increase of micro-hardness because of severe deformation produced during impact of the particles. This is also known as cold work and this creates strain-hardening. This phenomenon associated to the high-velocity of the particles hitting the substrate and the non-recovery of the dislocations. Such strain hardening increases with the degree of particle deformation. In addition to strain-hardening, impingement effect increases particle deformation when larger particles impact a coating layer thus plastically deforming the particles. This is causing voids reduction leading to an increase of hardness. Since the deformation is similar for both processes, the difference in micro-hardness between the systems is caused by a difference in the velocity and the temperature at impact as introduced in the last section. With LPCS system, the particles are colder in comparison with to PGDS particles. This causes an increase of cold work and strain hardening which is associated to a higher micro-hardness. PGDS particles reach a higher temperature so the strain hardening is released which explains the lower hardness. A

difference between the processes results was also observed in the adhesion strength property discussed in the next section.

7.2.5 Adhesion Strength

This mechanical test was performed to compare the coating/substrate and particle/particle adhesion for both processes. The results are presented in Figure 7.5 and listed in Table 7.4 below.

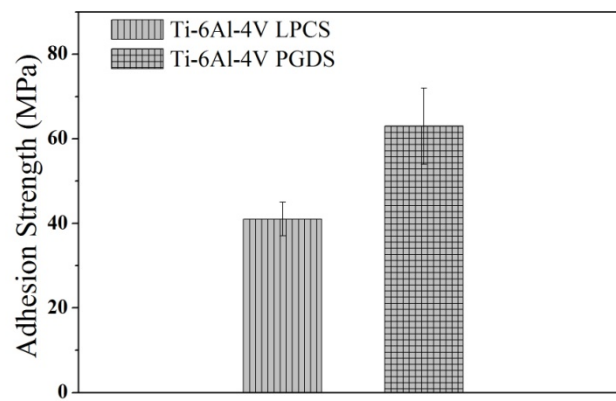


Figure 7.5 : Adhesion tests results

Table 7.4 : Coatings' adhesion strength in function of the process

Process	Adhesion Strength (MPa)
LPCS	41 ± 4
PGDS	63 ± 9

The adhesion strength for the PGDS process is considerably higher than the value obtained with the LPCS samples, even though both processes have produced similar microstructures and particle deformation level. These results are higher in comparison with the 15 MPa obtained by Li [84]. This is explained by the coating porosity of $22.3 \pm 4.7 \%$.

Increase of 35% seems to indicate the absence of relationship between porosity, deformation level or micro-hardness and the adhesion results. This conclusion is based on the fact that there is no major difference in porosity and in the particle deformation level between both processes. Therefore, another phenomenon must be inducing the higher adhesion strength in the PGDS coatings.

One side of the pulled samples was evaluated to see the amount of adhesive versus cohesive failure for each process using Clemex software. It was observed that the failure mode of the LPCS coatings was different from the PGDS coatings. Adhesion failure occurred for LPCS coatings while the failure mode of coatings produced with PGDS system was mainly cohesive. The quantification of the amount of cohesive failure for the LPCS was at $5 \pm 3\%$. An example of this coating is shown in Figure 7.6a. As for the PGDS process, the percentage of cohesive failure was $90 \pm 10\%$ and the samples are shown in Figure 7.6b.

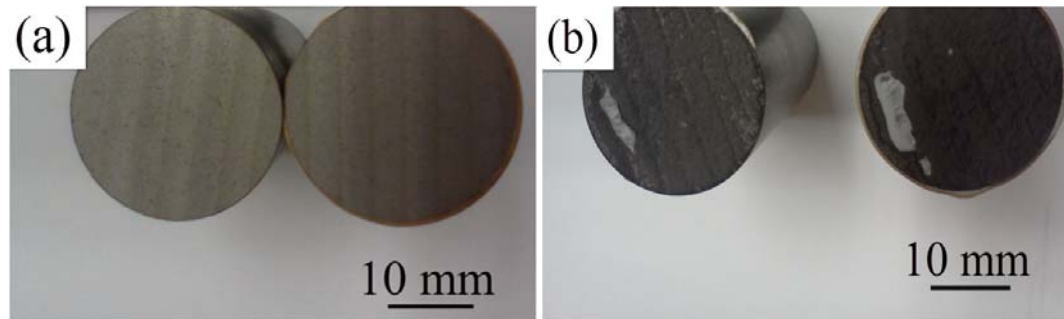


Figure 7.6 : Adhesion tests samples of (a) Ti-6Al-4V coating using LPCS and (b) Ti-6Al-4V coating using PGDS.

In order to determine the origin of the increased bond strength using the PGDS process and the difference of adhesion failure, single splat analysis was done to evaluate how particles deform on the substrate upon impact for each spraying system.

7.2.6 Single Splat Analysis

The purpose of analyzing single splats was to investigate the reason behind the considerably different adhesion strength values. Top-view pictures of splats for each spray process were taken by SEM, and they are shown in Figure 7.7a and c. SEM pictures of etched cross-sections were presented in Figure 7.7b and d.

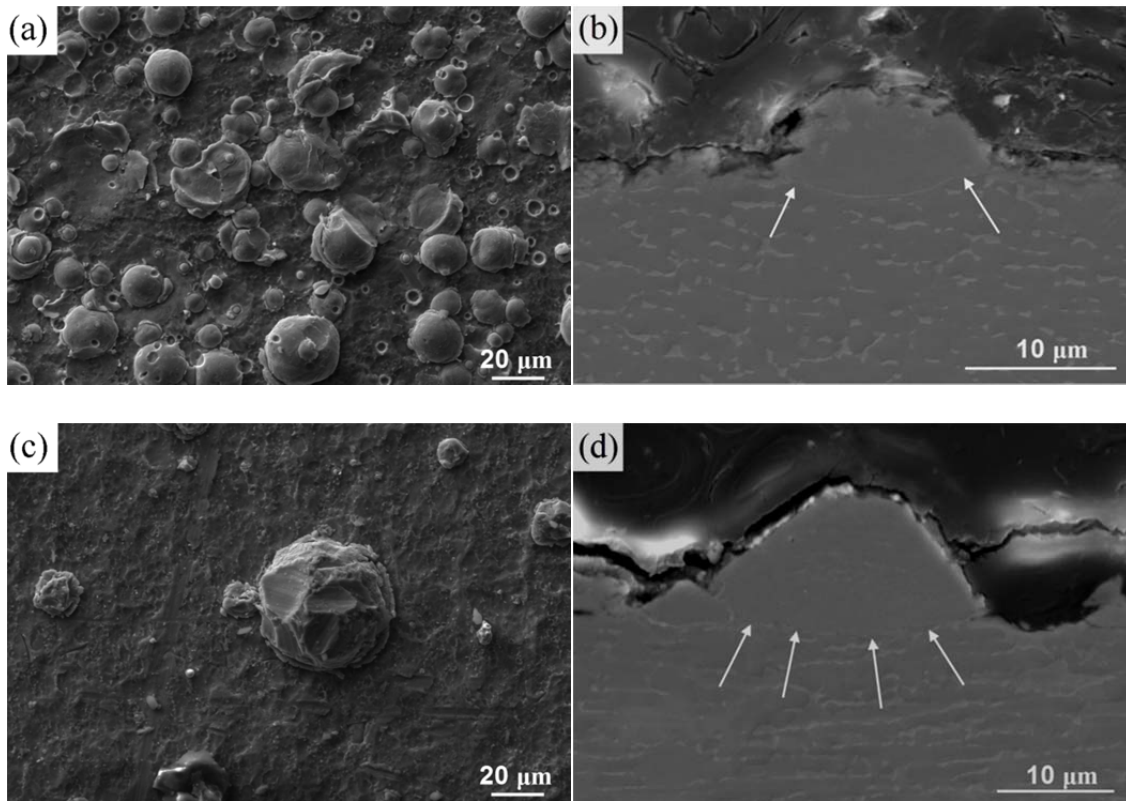


Figure 7.7 :Wipe Test SEM Micrographs of (a) Ti-6Al-4V LPCS top view, (b) Ti-6Al-4V LPCS cross-section view, (c) Ti-6Al-4V PGDS top view and (d) Ti-6Al-4V PGDS cross-section view where the arrow shows metallurgical bonding.

For Ti-6Al-4V feedstock powder, holes caused by the impact of small particles on the substrate are evident on the LPCS samples (Figure 7.7a). Small particles were accelerated to extreme velocities causing high deformation but did not adhere due to the high residual stresses. Figure 7.7a shows highly deformed particles with the presence of jetting marks at the edge of some LPCS splats. These were caused by the high pressures created on the particle's point of impact on the substrate that created high shear loads. These loads produced adiabatic shear instabilities, which induced local thermal softening due to the lack of heat transfer. This is causing a flow of material in the transverse direction, as can be observed in Figure 7.7b on each side of the deformed particle.

Figure 7.7c shows that PGDS splats presented smeared surface compared to the original smooth feedstock powder. These particles' sharp edges were hypothesized to be created during their travel in the spray device. In order to explain it, Figure 7.8 shows PGDS process at different states.

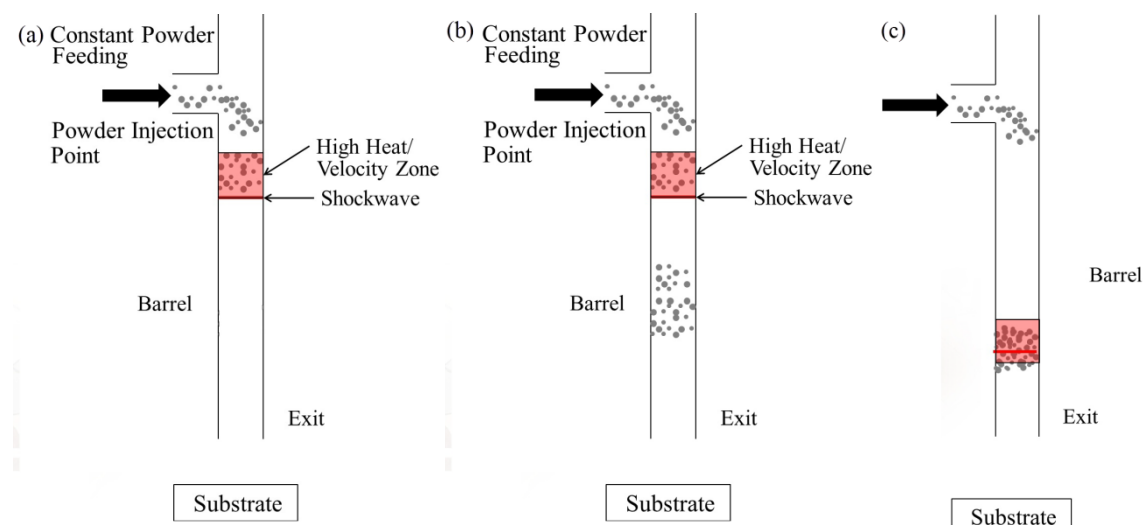


Figure 7.8 :PGDS schematic(a) at initial state, (b) after powder inside the barrel and (c) of the accelerated powder hitting the powder in the barrel.

The result could be explained by the acceleration of injected particles in the barrel with every shockwave. Since the powder particles were constantly fed while the driving gas was pulsed, a portion of them was injected between two shockwaves; in a zone that is not favourable to particle acceleration (Figure 7.8a and Figure 7.8b). These slow particles were hit by faster particles coming down the barrel from subsequent shockwaves (Figure 7.8c). With the contribution of the heat zone following the shockwave, particles' surfaces are easily broken into pieces during particle-particle impact thus creating debris that forms the high amount of micron size particles observed in Figure 7.2. This hypothesis was preferred over the particle-barrel interactions based on the spherical concave erosion sites found among the particles smeared surfaces (see Figure 7.7c). This brings evidence of a high temperature and enhanced particle ductility prior to impacting the substrate.

Furthermore, rough particles promote the formation of local metallurgical bonding since these regions present concentration of force at impact at the edges. These forces combine in those small points of impact leading to near melting regions from the energy produced. Figure 7.7b and d show moderate jetting sites in each etched cross-sections as well as some links between particles and substrate characterizing metallurgical bonding. This can be observed in both coatings produced with the LPCS and PGDS spray methods (pointed by arrows in Figure 7.7). A higher amount of metallurgical bonding could explain the increased adhesion strength of the PGDS coatings. Fracture surface analysis was carried out to further verify this hypothesis.

7.2.7 Fracture Surface Analysis

Fracture surface investigation of the adhesion tests samples were carried out to qualitatively characterize the possible metallurgical bonding mentioned in other studies [70,92,97]. Metallurgical bonding is identified by the presence of dimples and cup-cone regions [92,98]. Figure 7.9 shows the fracture surfaces for both spray processes. Circles identify regions of metallurgical bonding and arrows point to dimples. Higher concentration of these metallurgically bonded regions was observed on PGDS coatings compared to LPCS, which can explain the higher adhesion strength observed in coatings produced by the PGDS spray process. These larger metallurgical bonding areas were created with the PGDS process as a result of the higher powder temperature induced by the high-heat zone located behind the shockwave [96,99]. Low activation energy is required to form Titanium metallurgical bonds as indicated by Bae [92]. Furthermore, Titanium has a low thermal conductivity ($21.9 \text{ W m}^{-1}\text{K}^{-1}$) promoting highly localized temperature rise upon impact, thus enhancing metallurgical bonding. The high temperature, combined with low activation energy and sharp edges formed during the particle flight in the spray device, prior to particle impact on the substrate, contribute to the formation of metallurgical bonding. Therefore, it is concluded that the

results from the fracture surface analysis confirm the effect of metallurgical bonding in the adhesion strength results.

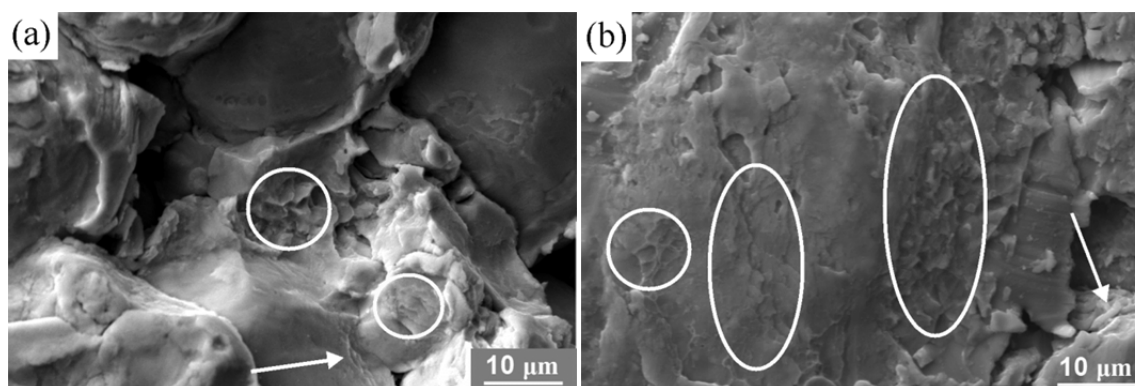


Figure 7.9: Surface fracture of bond plugs showing presence of dimples circled or pointed by arrows, (a) Ti-6Al-4V LPCS and (b) Ti-6Al-4V PGDS.

7.2.8 XRD and EDS Analysis

Titanium is usually subjected to oxidation or nitridation during thermal spray processes due to the high temperature involved and the exposition to oxygen/nitrogen. Oxides and nitrides phases are generally causing structural defects that can produce premature failure or corrosion of the coating. They can also produce decrease in the adhesion at the interface because they have a lower toughness compared to a metallic phase. Identification of such elements and related defects in the coating was therefore investigated. Figure 7.10 shows X-ray diffraction spectra of the feedstock powder and sprayed coatings for each spray process. The main crystal structure identified in the XRD spectrum of the as-received powders is hexagonal close packed (HCP) alpha phase Titanium. No traces of any phase of the possible typical contaminants such as chrome, iron, aluminum or copper were observed. From Figure 7.10 it can be observed that there was no formation of oxide phase or nitride phase crystal structure during spraying of Ti-6Al-4V feedstock powder with the LPCS process.

The XRD analysis of Ti-6Al-4V milled surface coating also indicates the absence of oxides phase and nitrides phase crystal structure in the coatings produced using the PGDS spray process.

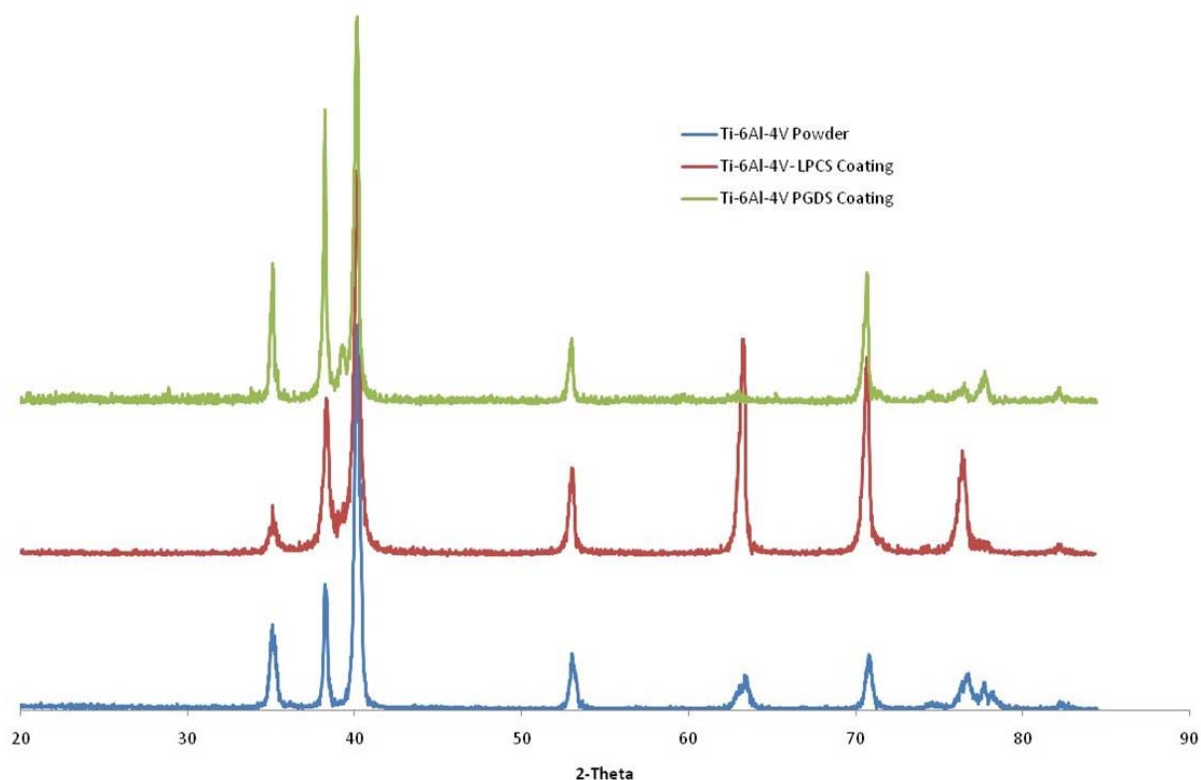


Figure 7.10 : XRD spectrum of feedstock powder Ti-6Al-4V, LPCS spray coating and PGDS coating in function of the intensity

An EDS scan inside the coating was done because the XRD evaluates only the surface of the coating. At each height in the coating, three mass percentages were performed to quantify elements in the coatings. A schematic of the procedure is shown in Figure 7.11. The quantitative values are presented in Table 7.5 for each spray process.

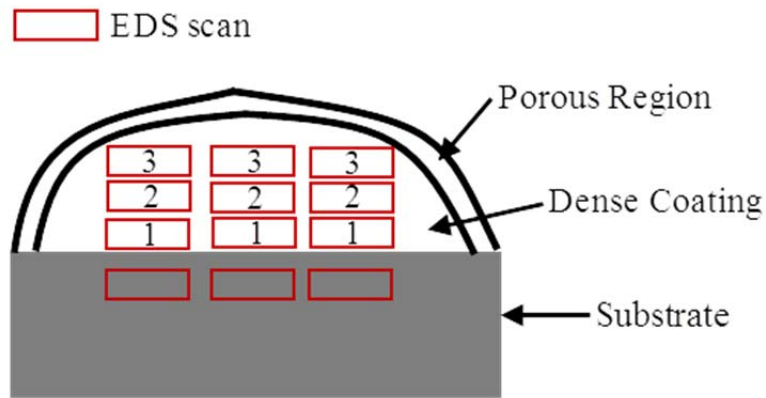


Figure 7.11 : Schematic of EDS regions on three different heights and near the coating on the substrate for element quantification throughout a cross-section.

Table 7.5 : Coatings' oxide and nitride levels in function of the process and the EDS regions

Process	Region	Oxide level (w%)	Nitride level (w%)
Substrate	Near the coating	0	0
LPCS	1	0	0
	2	0	0
	3	0	0
PGDS	1	0	0
	2	0	0
	3	0	0

It can be established that both processes did not produce oxidation or nitridation phases inside the coating. These results are in concordance with XRDs' analysis. A mapping of the elements was done using an SEM, and the results are shown in Figure 7.12 for LPCS and in Figure 7.13 PGDS.

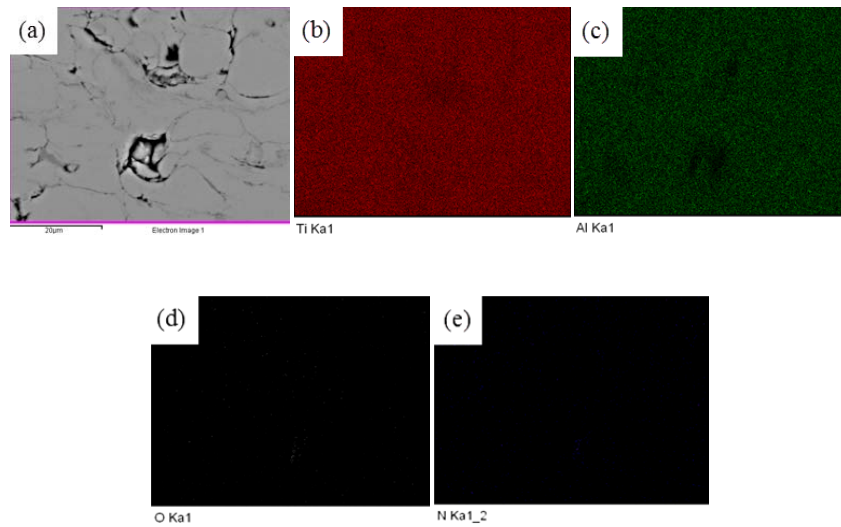


Figure 7.12 : SEM Element Mapping of LPCS coating (a) Ti-6Al-4V SEM image, (b) Titanium element in the coating, (c) Aluminum element in the coating, (d) Oxygen element in the coating, (e) Nitrogen element in the coating

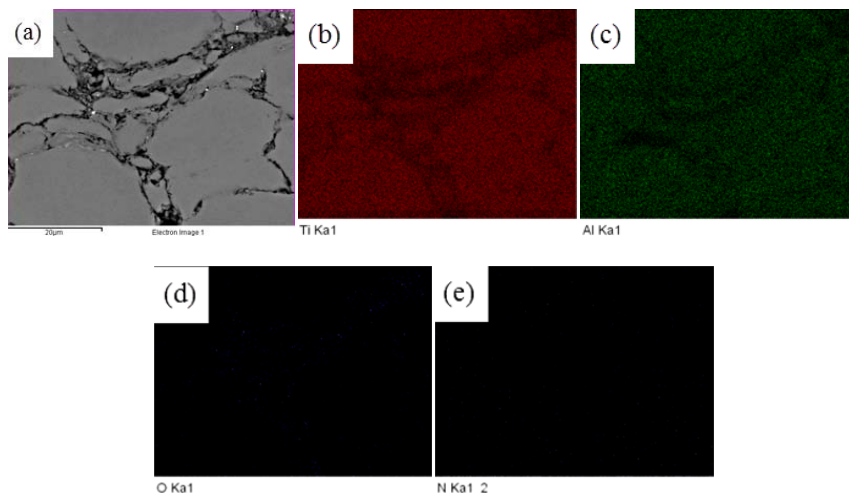


Figure 7.13 : Element Mapping of PGDSS coating (a) Ti-6Al-4V SEM image, (b) Titanium element in the coating, (c) Aluminum element in the coating, (d) Oxygen element in the coating, (e) Nitrogen element in the coating

The element mappings are in concordance with the EDS and the XRD's results. Titanium passive oxide layer around the particles and on the substrate were not detected because of their very small thickness. Investigation of the effects of micro-hardness difference during wear was then undertaken and will be discussed in the next section.

7.2.9 Sliding Wear Resistance

In this section, the coatings' mass loss after different oscillating sliding distances was computed and analyzed for each Ti-6Al-4V coatings and as received substrate. Results are presented in Figure 7.14 and Table 7.6.

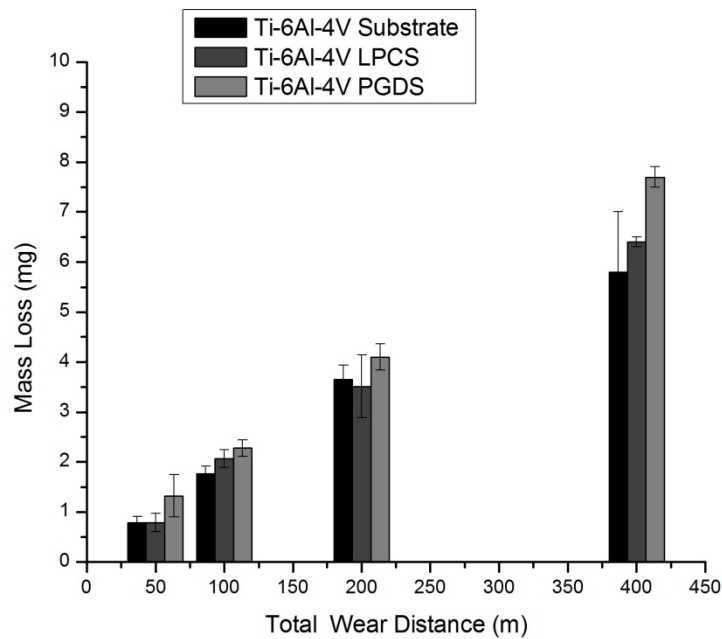


Figure 7.14 : Mass losses after wear test at different sliding distances on Ti-6Al-4V coatings and Ti-6Al-4V substrate.

Table 7.6 : Coatings mass loss after 50, 100, 200 and 400 meters sliding distance wear tests

Process	Mass loss after 50m (mg)	Mass loss after 100m (mg)	Mass loss after 200m (mg)	Mass loss after 400m (mg)
Substrate	0.8 ± 0.1	1.8 ± 0.2	3.7 ± 0.3	5.8 ± 1.2
LPCS	0.8 ± 0.2	2.1 ± 0.2	3.5 ± 0.6	6.4 ± 0.1
PGDS	1.3 ± 0.4	2.3 ± 0.2	4.1 ± 0.3	7.7 ± 0.2

A linear trend for the first 400m can be observed in Figure 7.14. Different mass losses were observed for Ti-6Al-4V coatings produced with LPCS and PGDS. Ti-6Al-4V coatings produced by LPCS spraying technique had a similar mass loss compared to the Ti-6Al-4V substrate. The wear behaviour of LPCS coatings is similar to the bulk material even though the coatings are made from agglomeration of thousands of individual deformed particles. This similar wear behaviour is explained by the higher hardness of LPCS coating to compensate the coating low ductility since it is composed of agglomerated particles instead of a solid block for the bulk material. The higher hardness of LPCS coating decreases the contact area between the ball and the coating [100]. For the two Ti-6Al-4V coatings, uniform tracks were formed, as seen in Figure 7.15.

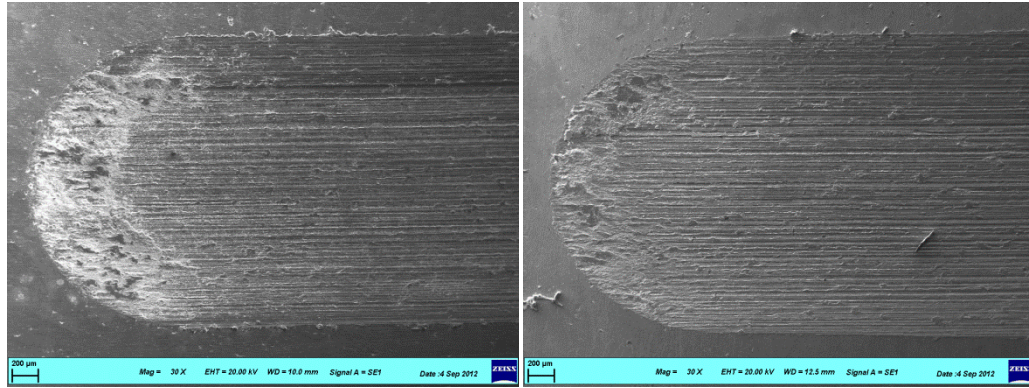


Figure 7.15 : Wear morphology of the track left by a silicon nitride ball with a force of 10 N at 5 mm s⁻¹ after 400m on Ti-6Al-4V LPCS coating (left) and Ti-6Al-4VPGDS coating (right).

Wear debris, created as a by-product of the multiple oscillations, were observed for each sample along the sliding direction of the silicon nitride ball. The higher amount of metallurgical bonding present in PGDS coating compared to LPCS coating is not improving the wear behaviour because the coatings are tested under the high local contact stress and high flash temperature. This could be explained by the small point of contact of the silicon nitride ball creating high pressures and temperatures changes to the morphology of the coating's surface [101–105].

7.2.10 Simulated Damage Repair Feasibility

Restoration of damaged Ti-6Al-4V parts were undertaken to analyze the microstructure of a repaired coatings. To simulate damage of the substrate, gauges of 1.5mm with a 10:1 slope were produced on a milling machine. These damages were then filled with Ti-6Al-4V coatings using both spray processes using the optimized parameters. Each sample was machined at the same level as

the substrate and polished. An example of the result is shown in Figure 7.16 and the coating characteristics are reported in Table 7.7.

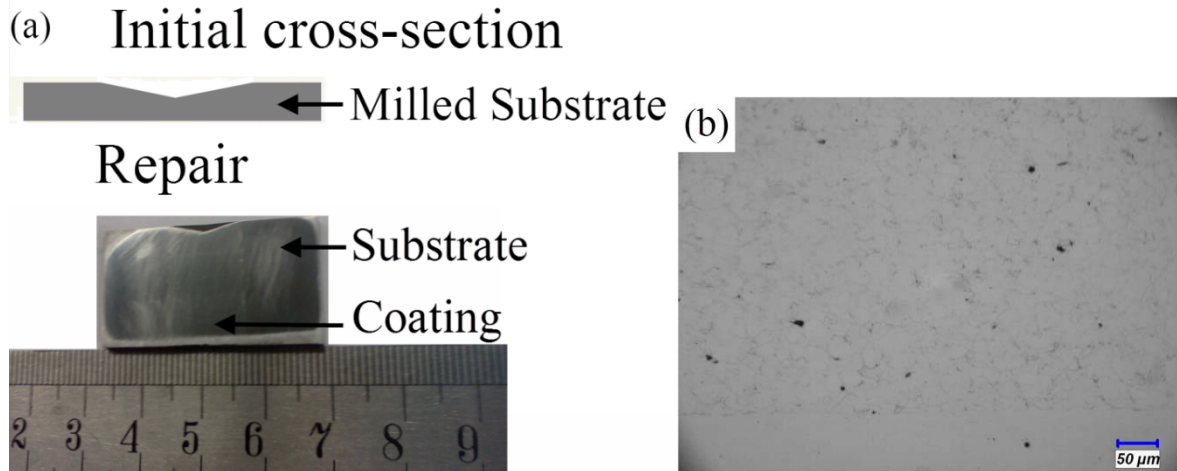


Figure 7.16 : Example of Simulated damage repair of Ti-6Al-4V with a (a) Ti-6Al-4V coating using LPCS and (b) Repair microstructure under optical microscope.

Table 7.7 : Simulated Damage Repair Results

Experiment	Porosity (%)	Micro-hardness (HV300)
Ti-6Al-4V LPCS	0.8 ± 0.3	375 ± 29
Ti-6Al-4V PGDS	1.5 ± 0.7	353 ± 12

In cold spray, the angle between the gas jet and the spray surface, known as the impact angle, should be perpendicular [61]. Studies involving Copper particles [61] and pure Titanium particles [106] have shown a detrimental effect in the deposition efficiency and coating microstructure when the spray angle is modified from perpendicular to parallel to the substrate. The milled angle of the substrate was 6 degrees. Even with this little angle, high quality Titanium coatings were achieved

resulting in a slight increase in Ti-6Al-4V coatings' porosity as can be observed in the cross-sections views in Figure 7.16. Micro-hardness values are similar for Ti-6Al-4V coatings with LPCS 400 ± 20 HV (flat) versus 375 ± 29 HV (repair) and PGDS 350 ± 20 HV (flat) versus 353 ± 12 HV (repair). In summary, Titanium alloy Ti-6Al-4V parts could be repaired efficiently by producing Ti-6Al-4V coating on a machined flat surface or with a 10 to 1 slope (6 degrees) or less. Also, even if the sprays were not perpendicular to the gas stream, the properties of Ti-6Al-4V coatings produced using either LPCS or PGDS were not significantly affected. Further studies would be required to assess the mechanical properties and behaviour of such repairs before applying either spraying techniques to commercial applications.

7.2.11 Ti-6Al-4V Coating Summary

Using the individual parameters values giving the best results presented in the previous chapter, coatings for both processes were analysed. The coating properties are summarized in Table 7.8.

Table 7.8 : Overall Results for LPCS and PGDS coatings

Characteristic	LPCS	PGDS
Porosity (%)	< 0.5	< 1
Deformation (L/D ₀)	1.4	1.4
Hardness (HV300)	400 ± 20	350 ± 20
Adhesion strength (MPa)	41 ± 4	63 ± 9
Wear Test for 400m (mg)	6.4 ± 0.1	7.7 ± 0.2
Oxide content (w%)	0	0
Nitride content (w%)	0	0

Coatings with low porosity were shown to provide higher hardness. Deformation analyzes were done and show that the deformation level is the same for both systems. Wipe tests were conducted and the etched cross-sections showed traces of metallurgical bonding. The fracture interfaces of the bond plugs were studied to view the amount of metallurgical bonding for each process. PGDS coatings presented higher level of metallurgical bonding than the LPCS; hence higher adhesion strength. Element identification was carried out. There was no formation of oxide phase or nitride phase crystal structure in the coating. The EDS experiments also confirmed the absence of oxides or nitrides throughout the coating. Wear tests were performed showing that the LPCS and PGDS coatings have slightly different behaviour in wear. Simulated damage repair was successfully performed on samples produced using both processes with no major effect of the coating quality at a small spray angle.

Chapter 8 – Conclusions

The general goal of this research work was to study the suitability of cold spray technology to produce Ti-6Al-4V coatings for industrial repair applications of parts. Two techniques were evaluated for this purpose: LPCS (Low Pressure Cold Spray) and PGDS (Pressurized Gas Dynamic Spray). The research work covered the technical application of the methods to produce the coating, including feasibility and experimental study of their individual parameters to obtain better results as well as evaluation of the properties of the LPCS and PGDS coatings obtained.

Deposition using LPCS and PGDS spray processes were successful to produce adequate coating using Ti-6Al-4V powder. At the onset of this study, various spray parameters of LPCS and PGDS used in this work were studied experimentally with helium as the propelling gas to select the values providing the best results. The values obtained for these individual parameters were used to achieve coatings with adequate density and hardness to be used for Titanium alloy repairs. The set of parameters for the LPCS process was achieved with a specific nozzle and limited to some parameters related to the available system.

Coatings were analyzed in order to characterize the mechanical and metallurgical properties. Ti-6Al-4V coatings with good densities (lower than 1% porosity) were obtained using both LPCS and PGDS processes. Higher coatings' micro-hardness was achieved with LPCS (400HV) process compared to PGDS (350HV). The micro-hardness gain obtained from the deposition of the feedstock powders was attributed to strain-hardening effect. Adhesion tests were performed for both processes coatings, and the PGDS coatings showed 35% higher bond strength (~63 MPa) compared to LPCS coatings (~41 MPa). This result was explained by the higher amount of metallurgical bonding in PGDS coating coming from a higher powder temperature at impact since the deformation level was equal for both systems. Presence of oxides and nitride in the coatings were verified with X-ray

diffraction (XRD) technique and the quantification level done by the energy-dispersive X-ray spectroscopy (EDS). These two equipments showed absence of formation of oxide and nitride crystal structure and phase in the two processes coatings. Wear resistance seemed to correlate with the micro-hardness obtained for the coatings. Mass losses of Ti-6Al-4V coatings were comparable to the mass losses measured for the bulk metal. Ti-6Al-4V restoration was achieved with minimal microstructural changes with both systems on Ti-6Al-4V samples with defects created by milling.

Chapter 9 –Future Work

Considering the results in this present research, further studies could be performed to continue the advancement of the work presented here.

1. The strategy to obtain the best values of the parameters for both processes of interest enabled to obtain values and understand the individual effect of each parameters but it would be good to develop a design of experiment (DOE) plan to obtain optimized values of the parameters considering possible interaction between them. Furthermore, the standard DOE method could provide models to help in defining optimal values. The data available from the studies presented here could be used to develop the level to be tested in the DOE.
2. During the research work for this thesis, coatings were evaluated using the best values from parameter obtained with a specific nozzle. The use of helium leads to higher particle velocities and therefore, higher deformations and adhesion. For an economic purpose, it might be interesting to study the use of spray using nitrogen gas as the main propellant gas on LPCS system.
3. Further improvement of LPCS's gas heater could be done to incorporate experiments at a temperature above 650°C using helium. Study of some parameters such as the nozzle stand-off distance and powder flow, morphology and distribution should be performed using this system to obtain the best working values an possibly optimal ones.
4. It should be considered that coatings' quality could be further improved with a different nozzle design.
5. As in the case of the LPCS work presented here, investigation of coating made with nitrogen main gas propellant could be developed for PGDS. This could include the improvement of

the valve material to be able to handle very high gas temperature in order to position this valve after the gas heater, hence enabling a loss reduction due to a shorter travel distance.

6. Study of the in flight particles' displacement in the barrel should be done. The barrel could be made of a transparent material, and a high velocity camera could track the particle travel path inside the barrel.
7. For industrial application of this technology, longer wear tests should be performed to compare the results with bulk material.
8. Further studies regarding restoration of Ti-6Al-4V actual parts should be performed and evaluated.

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